College of Chemistry and Biological Engineering

The College of Chemistry and Biological Engineering at Guilin University of Technology originated from the Geochemical Exploration Department in 1978. It was renamed the Department of Applied Chemistry in 1990, merged into the newly established Department of Materials Engineering in 1997, and renamed the Department of Materials and Chemical Engineering in 2001. In 2009, the College of Chemistry and Biological Engineering was established and is one of the key construction colleges at Guilin University of Technology. The college currently has 110 faculty members, including 41 professors, 37 associate professors, and 75 teachers with doctoral degrees. The college has 8 high-level talents, including experts receiving special allowances from the State Council of China, national young talents, specially appointed experts in Guangxi, and outstanding young talents in Guangxi.

The chemistry discipline at the college has entered the global top 1% according to ESI, and has the authority to grant Master's degrees in "Chemical Engineering and Technology" and "Chemistry." In addition, it has the authority to grant professional Master's degrees in "Materials and Chemical Engineering" and "Biotechnology and Medicine." The college offers four undergraduate majors, including "Chemical Engineering and Technology," "Energy Chemical Engineering," "Applied Chemistry," and "Biological Engineering." It has more than 1,600 full-time undergraduate students and over 500 graduate students.

The college has a "national-level virtual simulation laboratory for Chemical Engineering and Process," a provincial-level experimental teaching demonstration center. In addition, the college has a "provincial key laboratory for Electrochemical Functional Materials", as well as "Food Safety and Detection Guangxi key laboratories," and "Surface and Interfacial Electrochemistry Guangxi key laboratories." The college's instruments and equipment have a total value of over 81 million CNY. Furthermore, the college has two university-level modern industry colleges, namely the "Guangxi Featured Biomedical Industry College" and the "Guangxi New Energy Power Battery Modern Industry College."

In the past three years, the college has undertaken more than 30 national-level projects, including major projects funded by the National Natural Science Foundation, excellent young scientist projects, general/regional/young scientist projects, as well as over 50 provincial and ministerial-level projects and more than 30 commissioned projects from enterprises. The total research funding has exceeded 40 million CNY. The college has published over 380 SCI-indexed papers, obtained 6 provincial and ministerial-level scientific and technological achievements awards (including 1 Guangxi Youth Science and Technology Outstanding Contribution Award), and has been granted 148 national invention patents. In addition, the college has achieved a total technology transfer value with an amount of over 30.6 million CNY, including a single technology transfer worth 25 million CNY that set up a new record for the university.

Welcome Message

ISSSC Chair
Prof. Xianran Xing
FRSC

ISSSC Chair
Prof. J Paul Attfield
FRS

Dear Distinguished Scholars and Colleagues

It is our great honor and pleasure to invite you to join us with a contribution to the International Symposium on Solid State Chemistry (ISSSC) from 18th to 22nd October, 2023. ISSSC was planned three years ago but hold up owing to the COVID-19 pandemic.

ISSSC 2023 covers the following topics: (1) new directions of solid-state chemistry, (2) emerging materials on energy and environment, (3) advanced structural characterization, (4) local or defect structures.

Our 2023 symposium brings together innovators and contributors from the global solid-state chemistry community, and shares scientific breakthroughs, technological advances, and emerging opportunities and challenges. The symposium will include active discussions (posters and speeches) of solid state chemistry and related fields, discipline development, and technological innovation.

ISSSC 2023 has attracted ~100 delegates and collected ~ 70 paper abstracts in materials science and engineering. The conference will choose three Excellent Poster Awards to encourage young scientists.

Prof. Xianran Xing,   Prof. J. Paul. Attfield

Conference Organizations

Chairs

J. Paul Attfield, University of Edinburgh
Xianran Xing, University of Science and Technology Beijing

Advisory committee

Shouhua Feng, Jilin University
Jianhua Lin, Peking University
Atony R. West, University of Sheffield

Scientific committee

J. Paul Attfield
Xianran Xing
John S.O. Evans
Amparo Fuertes
Hiroshi Kageyama
Jun Chen
Junliang Sun
Changqing Jin
Susana García Martín
Li-Dong Zhao
Xueyuan Chen
Ling Chen
Qingzhen Huang
Valeriy Sidorov
Vladimir Cherepanov
Guocong Guo
Yuichi Shimakawa
Ling Huang
Ru-Shi Liu
Yang Ren
Jingtai Zhao

Conference Organizations

Organizers

University of Science and Technology Beijing
University of Edinburgh
Guilin University of Technology

Local organization committee

Chair: Fupei Liang

Secretary: Xiaojun Kuang, Youping Liu, Congling Yin, Xiangfei Kong

Members: Xiaoyan Yang, Yaoming Liu, Changzheng Hu, Bin Huang, Jinxiao Zhang, Jungu Xu

Local contact

Pick-up and Delivery: Changzheng Hu (+86 13297734950)
Registrations and Accommodation: Yaoming Liu (+86 13978340842)
Mediate and Technique: Bin Huang (+86 18276692561)
Communications after Conference: Xiaoyan Yang (+86 13978333736)

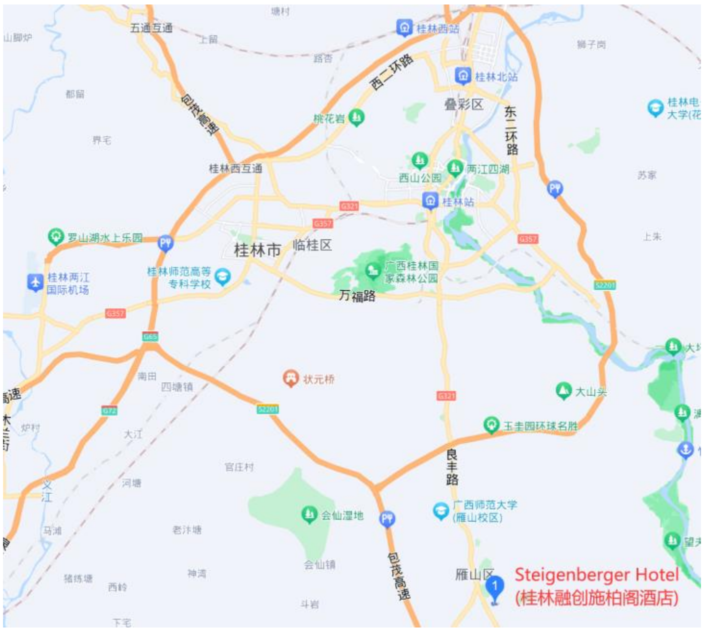
Conference Venue and Accommadations

Hotel: Steigenberger Hotel (桂林融创施柏阁酒店)

Address: No. 398 Dayan Road, Yanshan District, Guilin City, Guangxi, China（中国广西桂林市雁山区大雁路 398 号）

Tips：You can take a taxi to the hotel.

Map:



Agenda

Date	Time	Action	Place
Oct. 18th Wednesday	**9:00 - 22:00**	**Registration/Check-in**	**Steigenberger Hotel**
	18:30 - 20:30	**Welcome Reception**	**Steigenberger Hotel**
Oct. 19th Thursday	**9:00 - 18:00**	**Opening ceremony/Invited Lectures**	**Steigenberger Hotel, Ludi Hall, ground floor**
Oct. 20th Friday	**8:30 - 18:00**	**Invited Lectures/closing ceremony**	**Steigenberger Hotel, Ludi Hall, ground floor**
Oct. 21st-22nd Saturday-Sunday		**Departure/free exchange**	

Program, Thursday, Oct. 19th

Time	Event	Chair
9:00 - 9:25	**Opening Ceremony and Group Photo**	Xiaojun Kuang
	Session 1 Quantum Materials from High Pressures	
9:25 – 9:55	**Invited Lecture 1** J. Paul Attfield New Materials from High Pressure	Xianran Xing
9:55 - 10:25	**Invited Lecture 2** Changqing Jin Quantum Functional Materials: from Emergent Oxides to Polyhydrides	
10:25 - 10:40	**Tea Break**	
	Session 2 Design and Synthesis of (Meta) Stable Phase	
10:40 - 11:10	**Invited Lecture 3** Vladimir Cherepanov Perovskite-related Oxides in the Ln$_2$O$_3$-MO-TO$_x$ Systems: Phase Equilibria, Crystal Structure, and Oxygen Content	Yuichi Shimakawa
11:10 - 11:40	**Invited Lecture 4** Hiroshi Kageyama Strain Engineering of Properties in Mixed-Anion Compounds	
11:40 - 12:00	**Invited Lecture 5** Man-Rong Li Precise Synthesis of High-pressure Metastable State	
12:10 - 14:00	**Lunch/Break：** BelaBela Buffet Restaurant	
	Session 3 Advanced Structural Characterization	
14:00 - 14:30	**Invited Lecture 6** Junliang Sun 3D Electron Diffraction on Nano-crystals	J. Paul Attfield
14:30 - 15:00	**Invited Lecture 7** Susana García Martín	

	Long Range Ordering Structural Modulations in Layered-Perovskite Oxides Inducing 2D Properties	
15:00 - 15:20	**Invited Lecture 8** Lin Gu Insight into Energy Storage Materials from a Reductionist Perspective	Jun Chen
15:20 - 15:40	**Invited Lecture 9** Guocong Guo Electronic Structure Crystallography: from Crystal Structure to Electronic Structure	
15:40 - 16:00	**Invited Lecture 10** Qiang Li Local Structure in Nanocatalysts	
16:00 - 16:15	**Tea Break**	
Session 4 Structure-Property Relationship		
16:15 - 16:45	**Invited Lecture 11** Artem R. Oganov New Look at Old Things: Electronegativities, Chemical Hardnesses, and Stability of Molecules and Crystals	Valeriy Sidorov
16:45 - 17:05	**Invited Lecture 12** Minghui Yang Unleashing the Power of Metal Nitrides in Functional Materials	
17:05 - 17:25	**Invited Lecture 13** Kuo Li Diamond Nanothread	Minghua Zeng
17:25 - 17:45	**Invited Lecture 14** Mathieu Allix New Out-of-equilibrium Oxides Elaborated by Crystallisation from Glass or the Molten State	
17:45 - 18:05	**Invited Lecture 15** Zhihua Sun Exploring Molecule-Based Antiferroelectrics with Solid-State Energy Storage Properties	
18:30 - 20:00	**Banquet**：Guanyan Hall, Ground floor	

Program, Friday, Oct. 20th

Session 5 Electronic and Magnetic Materials		
Time	**Event**	**Chair**
8:30 - 9:00	**Invited Lecture 16** Yuichi Shimakawa Novel Functional Properties Induced by Charge Transitions in Oxides	Hiroshi Kageyama
9:00 - 9:30	**Invited Lecture 17** Jiawang Hong Flexoelectricity-induced Novel Effects in Suspended Films	
9:30 - 10:00	**Invited Lecture 18** Sergii Khmelevskyi Toward Predictive Theory of the Anomalous Volume Magnetostriction in Invar Alloys	Qingzhen Huang
10:00 - 10:20	**Invited Lecture 19** Kun Lin The New Structure of Terbium in Ferromagnetic State	
10:20 - 10:35	**Tea Break**	
Session 6 Optical Materials		
10:35 – 11:05	**Invited Lecture 20** Xueyuan Chen Luminescent All-Inorganic Perovskite Nanocrystals: Electronic Structure and Optical Properties	Ru-Shi Liu
11:05 - 11:25	**Invited Lecture 21** Ling Huang Frenkel Defect-modulated Anti-thermal Quenching Luminescence in $Sc_2(WO_4)_3$:Ln	
11:25 - 11:45	**Invited Lecture 22** Ling Chen Exploring and Property Enhancing of Inorganic Functional Compounds	Vladimir Cherepanov

11:45 - 12:05	**Invited Lecture 23** Xiaoming Wang Exploratory Synthesis of New Down-Conversion (Oxy)nitride Phosphors	
12:05 - 14:00	**Lunch + Break:** BelaBela Buffet Restaurant	
Session 7 Energy-Related Materials		
14:00 - 14:30	**Invited Lecture 24** Ru-Shi Liu Development of Solid-State Li-ion and Metal-Air batteries	Yaoqing Zhang
14:30 - 14:50	**Invited Lecture 25** Yang Ren Atomic Pinning Mitigates Voltage Decay in Li-Rich Mn-Based Layered Oxide Cathode	
14:50 - 15:10	**Invited Lecture 26** Ji-Jing Xu Construction of Materials and Devices for Metal-air Batteries	Yang Ren
15:10 - 15:30	**Invited Lecture 27** Ming Li Enhancing/Suppressing Electronic and Ionic Conductivity in Metal Oxides	
15:30 - 15:50	**Invited Lecture 28** Ying Tang Rattling Effect: A New Mechanism for Tuning Temperature Stability of Microwave Dielectric Ceramics	
15:50 - 16:30	**Tea Break + Posters**	
Session 8 Frontier and Multidiscipline		
16:30 - 16:50	**Invited Lecture 29** Takafumi Yamamoto Determination of the Reaction Pathways for Designing Solid-State Compounds	Jingtai Zhao
16:50 – 17:10	**Invited Lecture 30** Valeriy Sidorov Amorphous-Nanocrystalline Al-based Alloys with Improved Characteristics	

17:10 - 17:30	**Invited Lecture 31** Ping Miao Large Magnetovolume Effect in a Cobaltite Perovskite	Susana García Martín
17:30 - 17:50	**Invited Lecture 32** Alberto J. Fernández Carrión Oxide Ion-Conducting Materials Containing Tetrahedral Moieties: Structures & Conduction Mechanisms	
17:50 - 18:10	**Closing Ceremony** **ICF Poster Awards; Closing Remarks**	Xiaojun Kuang
18:30 - 20:00	**Dinner：** BelaBela Buffet Restaurant	

New Materials from High Pressure

J. Paul Attfield
Centre for Science at Extreme Conditions and School of Chemistry, University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, UK.
Corresponding author: j.p.attfield@ed.ac.uk

High pressure methods are important for synthesising new materials, and exploring changes of structure and property in dense matter. New oxide and nitride materials recently synthesized by our group and of interest for electronic and energy applications will be reviewed here. Examples are perovskites with Mn^{2+} at A-sites, such as $MnVO_3$ [1], the double perovskite Mn_2FeReO_6 [2] and double double perovskites $MnRMnSbO_6$ and $CaMnFeReO_6$ with order of A and B site cations [3,4,5]. A remarkable variety of new iron oxides has recently been reported at high pressures, and we have explored the substitutional chemistry of Fe_4O_5. Complex magnetic orders are observed in $MnFe_3O_5$ [6] and $CoFe_3O_5$ [7], while $CaFe_3O_5$ (prepared at ambient pressure) shows electronic phase separation driven by trimeron formation [8]. A new quantum phenomenon, quantised weak ferromagnetism, has recently been discovered in the perovskite $YRuO_3$ based on the unusual Ru^{3+} state [9]. A high pressure method using sodium azide has recently been developed to synthesise nitrides in high oxidation states giving the iron(IV) nitride, Ca_4FeN_4 [10], an electron-localised Ni^{2+} nitride, Ca_2NiN_2 [11], and a rare example of a nitride perovskite, $LaReN_3$ [12]. The latter material can be decomposed to give novel reduction products $LaReN_{2.5}$ and layered $LaReN_2$ demonstrating topotactic reduction chemistry analogous to that of perovskite oxides like $LaNiO_3$ and $SrFeO_3$.

References

[1] M. Markkula, A.M. Arevalo-Lopez, A. Kusmartseva, J.A. Rodgers, et al. *Phys. Rev. B* 84, 094450 (2011).
[2] Arévalo-López A.M., McNally G.M., Attfield J.P. *Angew. Chem.* 54, 12074 (2015).
[3] E. Solana-Madruga, Á. M. Arévalo-López, et al. *Angew. Chem.* 55, 9340 (2016).
[4] G. M. McNally, Á. M. Arévalo-López, P. Kearins, F. Orlandi, et al. *Chem. Mat.* 29, 8870 (2017).
[5] K. Ji, K. N. Alharbi, E. Solana-Madruga, et al., *Angew. Chem. Int. Ed.* **2021**, *60*, 22248.
[6] K. H. Hong, A. M Arevalo-Lopez, M. Coduri, et al. *J. Mater. Chem. C* **2018**, *6*, 3271–3275.
[7] K. H. Hong, E. Solana-Madruga, M. Coduri, J. P. Attfield *Inorg Chem.* **2018,** *57* (22), 14347-14352
[8] K. H. Hong, A. M. Arevalo-Lopez, J. Cumby, C. Ritter, J. P. Attfield *Nature Commun.* **2018,** *9*, 2975.
[9] K. Ji, A. Paul, E Solana-Madruga, A. M. Arevalo-Lopez, et al. *Phys. Rev. Mat.* **2020,** *4*, 091402(R).
[10] S. D. Kloß, A. Haffner, P. Manuel, M. Goto, Y. Shimakawa, J. P. Attfield, *Nat. Commun.* **2021**, *12*, 571.
[11] S. D. Kloß, J. P. Attfield, *Chem. Commun.* **2021**, *57*, 10427.
[12] S. D. Kloß, M. L. Weidemann, J. P. Attfield, *Angew. Chem. Int. Ed.* **2021**, *60*, 22260.

Quantum Functional Materials: from Emergent Oxides to Polyhydrides

Changqing Jin
Institute of Physics, Chinese Acdemy of Sciences, Beijing 100190, China
Corresponding author: Jin@iphy.ac.cn

With the advancement of synergetic high pressure techniques growing emergent quantum materials are synthesized by design. Those materials are seeds that might foster new generation technologies. Here we introduce some of our recent experimental discoveries of new quantum functional materials with unusual properties (I) the first orbital order reversed (Cu3dx^2-y^2 versus 3dz^2) cuprate superconductor (SC) showing surprisingly 80% *enhancement of transition temperature (Tc) than that with universal orbital order* [1]; (II) the electricalmagnet coupling compounds such as the first displacive type ferrolectric compound for A site ordered perovskite[2]; (III) the polyhydride SC including calcium hydride with Tc above 210K[3~8];

Acknowledgments: We are grateful to collaborators for the contributions.

For more details pls visit team Web at: **http://uhp.iphy.ac.cn**

References

[1] W. M. Li, J. F. Zhao, C. Q. Jin *et al.*, "Superconductivity in a unique type of copper oxide", **PNAS 116**, 12156(2019);

[2] J. F. Zhao, H. M. Weng, C. Q. Jin *et al*, "A combinatory ferroelectric compound bridging simple ABO3 and A-site-ordered quadruple perovskite", **Nature Communications 12,** 747(2021);

[3] Z. W. Li, X. He, C. Q. Jin *et al.*, "Superconductivity above 200K Observed in Superhydrides of Calcium", **Nature Communications 13**, 2863(2022);

[4] C. L. Zhang, X. He, C. Q. Jin *et al.*, "Superconductivity in Zirconium Polyhydrides with Tc above 70 K". **Science Bulletin 67**, 907(2022);

[5] C. L. Zhang, X. He, C. Q. Jin *et al.*, "Superconductivity above 80 K in polyhydrides of hafnium", **Materials Today Physics 27**, 100826(2022);

[6] X. He, C. L. Zhang, C. Q. Jin *et al.*, "Superconductivity Observed in Tantalum Polyhydride at High Pressure", **Chinese Physics. Letters 40**, 57404 (2023) (Express Letter)

[7] K. Lu, X. He, C. Q. Jin *et al.*, “Superconductivity with T_c 116K discovered in antimony polyhydrides”, **National Science Review**(DOI: 10.1093/nsr/nwad241)

[8] Z. W. Li, X. He, C. Q. Jin *et al.*, Superconductivity above 70 K observed in lutetium polyhydrides, **Science China: Physics Mechanics & Astronomy 66**, 267411(2023) (Editor focus)

Perovskite-related Oxides in the Ln_2O_3-MO-TO_x Systems (Ln = Rare Earth, M = Alkali Earth Elements, T=Co, Fe): Phase Equilibria, Crystal Structure, and Oxygen Content

V.A. Cherepanov,[1*] N.E. Volkova,[1] T.V. Aksenova,[1] A.S. Urusova,[1] I.A. Bastron,[1] M.V. Davydova,[1]
L.Ya. Gavrilova[1]

[1] *Institute of Natural Science and Mathematics, Ural Federal University, Mira str, 19, Yekaterinburg, 620002, Russia.*

Corresponding author: v.a.cherepanov@urfu.ru

A systematic study of phase equilibria of Ln_2O_3-MO-TO_x systems (Ln = rare earth, M = alkali earth elements, T=Co, Fe) reveals that depending of nature of Ln and T, ratio of Ln/M and Fe/Co different types of perovskite-related oxides are formed. Together with distorted perovskites a number of layered perovskite-type oxides or Ruddlesden-Popper type phases were isolated [1-10]. It is also shown that oxygen content plays an important role in the phase formation.

The homogeneity range of Sr-substituted oxides $(Ln_{1-x}Sr_x)TO_{3-\delta}$ shifts towards strontium enriched compositions with a decrease in the Ln radius. The cobaltites with Ln of medium radii (Sm, Gd) reveal ordering of Ln and Sr cations in the A-sublattice. An exchange of Sr by Ba leads to the formation of layered oxides of the "112" type $LnBaT_2O_{6-\delta}$, also called as double perovskites, in which Ln and Ba ions are located in successively alternating layers due to a large difference in radii. In systems with Ln of small radii layered phases of the "123" type, or so-called triple perovskites $LnBa_2Fe_3O_{8+\delta}$ are formed in the air, in which Ln layers sequentially alternate with two barium layers. In the systems with medium-sized Ln (Sm, Eu, Gd), the formation of a five-fold perovskite-like superstructure (quintuple perovskites) $Ln_2Ba_3(Fe,Co)_5O_{13+\delta}$ is detected by TEM. This type of superstructure contains pure Ln and Ba layers together with mixed Ln/Ba layers alternated along the *c*-axis.

Acknowledgements: The Ministry of Science and Higher Education of Russian Federation (project No 123031300049-8) is acknowledged for the financial support.

References

[1] T. V. Aksenova, N. E. Volkova, A. Maignan, V. A. Cherepanov, *J. Am. Ceram. Soc.* **2022**, *105*, 3601.
[2] L. V. Khvostova, N. E. Volkova, L. Ya. Gavrilova, A. Maignan, V. A. Cherepanov, *Mater. Today Comm.* **2021**, *29*, 102885.
[3] A. V. Maklakova, M. A. Vlasova, N. E. Volkova, L. Ya. Gavrilova, V. A. Cherepanov, *J. Alloys Compd.* **2021**, *883*, 160794.
[4] L. V. Khvostova, N. E. Volkova, L. Y. Gavrilova, A. Maignan, V. A. Cherepanov, *J. Europ. Ceram. Soc.* **2021**, *41*, 4199.
[5] N. E. Volkova, M. V. Bazueva, D. T. Aisarinova, A. D. Alkhamova, L. Ya. Gavrilova, V. A. Cherepanov, A. Maignan, *J. Alloys Compd.* **2021**, *860*, 158438.
[6] N. E. Volkova, K. S. Tolstov, L. Ya. Gavrilova, B. Raveau, A. Maignan, V. A. Cherepanov, *J. Am. Ceram. Soc.* **2021**, *104*, 2410.
[7] T. V. Aksenova, A. S. Urusova, V. A. Cherepanov, *Russ. J. Phys. Chem. A.* **2020**, *94*, 2495.
[8] A. S. Urusova, A. E. Vakhromeeva, T. V. Aksenova, A. V. Bryuzgina, V. A. Cherepanov, *Inorg. Mater.* **2020**, *56*, 42.
[9] A. S. Urusova, A. V. Bryuzgina, M. Yu. Mychinko, A. V. Dyakova, V. A. Cherepanov, *Inorg. Mater.* **2020**, *56*, 72.
[10] A. V. Maklakova, A. S. Baten'kova, M. A. Vlasova, N. E. Volkova, L. Ya. Gavrilova, V. A. Cherepanov, *Solid State Scien.* **2020**, *110*, 106453.

Strain Engineering of Properties in Mixed-anion Compounds

Hiroshi Kageyama,[1] *
[1] *Kyoto University, Kyoto, Japan*
Corresponding author: kage@scl.kyoto-u.ac.jp

Mixed-anion compounds are attracting attention because of novel functions that are not found in oxides [1]. In this presentation, I show several examples where strain can alter structures and properties of mixed-anion compounds. For example, in anion-vacancy ordered perovskite SrV(O,N) thin film, the period and orientation of anion-deficient layers can be altered by biaxial strain [2]. In $EuVO_2H$ or its-Sr substituted films, substrate strain induces electron transfer from Eu to V, resulting in a 4-fold enhancement of the ferromagnetic transition temperature and perpendicular magnetic anisotropy [3]. In a series of layered oxychalcogenides synthesized at high pressure, the giant tensile strain provided during decompression process from the chalcogen layer can add new functions to the oxide layer [4]. $Bi_{12}O_{17}Cl_2$ is the first example of six-layer fluorite structure, with a structural modulation due to inclusion of rock-salt-like rods, which can be removed by $O^{2-}/2F^-$ anion exchange, leading to the improved photocatalytic activity [5].

Acknowledgements: This work was supported by CREST (JPMJCR20R2), JSPS Core-to-Core Program (JPJSCCA20200004), JSPS KAKENHI (JP16H06438, JP17H04849, JP20H00384, JP21K05227, andJP22H04914).

References

[1] H. Kageyama, K. Hayashi, K. Maeda, J. P. Attfield, Z. Hiroi, J. M. Rondinelli, K. R. Poeppelmeier, *Nat. Commun*. **2018**, *9*, 772.

[2] T. Yamamoto, A. Chikamatsu, S. Kitagawa, N. Izumo, S. Yamashita, H. Takatsu, M. Ochi, T. Maruyama, M. Namba, W. Sun, T. Nakashima, F. Takeiri, K. Fujii, M. Yashima, Y. Sugisawa, M. Sano, Y. Hirose, D. Sekiba, C. M. Brown, T. Honda, K. Ikeda, T. Otomo, K. Kuroki, K. Ishida, T. Mori, K. Kimoto, T. Hasegawa, H. Kageyama, *Nat. Commun.* **2020**, *11*, 5923.

[3] M. Namba, H. Takatsu, R. Mikita, Y. Sijia, K. Murayama, H. Li, R. Terada, C. Tassel, H. Ubukata, M. Ochi, R. S. Puche, E. Palacios, N. Ishimatsu, D. Shiga, H. Kumigashira, K. Kinjo, S. Kitagawa, K. Ishida, T. Terashima, K. Fujita, T. Mashiko, K. Yanagisawa, K. Kimoto, H. Kageyama, *J. Am. Chem. Soc.* **2023**; DOI: 10.1021/jacs.3c04521.

[4] Y. Yang, T. Zhu, Y.Matsumoto, H. Kageyama, *Inorg. Chem.* **2022**, 61, 7026.

[5] D. Kato, O. Tomita, R. Nelson, M, A. Kirsanova, R. Dronskowski, H. Suzuki, C. Zhong, C. Tassel, K. Ishida, Y. Matsuzaki, C. M. Brown, K. Fujita, K. Fujii, M. Yashima, Y. Kobayashi, A. Saeki, I. Oikawa, H. Takamura, R. Abe, H. Kageyama, T. E. Gorelik, A. M. Abakumov, *Adv. Funct. Mater.* **2022**, 32, 2204112.

Precise Synthesis and Interception of High-pressure Metastable State

Mei-Huan Zhao,[1,2] Yifeng Han,[2] Martha Greenblatt,[3] David Walker,[4] Man-Rong Li,[1,2*]
[1] School of Chemistry and Chemical Engineering, Hainan University, Haikou 570228, Hainan, China.
[2] School of Chemistry, Sun Yat-sen University, Guangzhou 51006, Guangdong, China.
[3] School of Chemistry and Chemical Biology,Rutgers, the State University of Newjersey, Piscataway, 08854, New Jersey, USA.
[4] Lamont Doherty Earth Observatory, Columbia University, Palisades 10964, New York, USA.
Corresponding author: limanrong@hainanu.edu.cn

High-pressure solid-state synthesis advances boost discoveries of new materials and unusual phenomena, but endures stringent recipe conditions, poor yield, and high cost. A methodological approach for accelerated and precisely high-pressure synthesis is therefore highly desired. Here, we show a pipeline of data-mining, high-throughput calculations, experimental realization, and chemical interception of high-pressure metastable phases (**Fig. 1**), confined by thermodynamic formability (convex hull) and pressure-dependent relative enthalpy evolution, such as in the exotic $A_2BB'O_6$ perovskite family.[1-3] The developed methodology is expected to accelerate the big-data-driven discovery of generic chemical formula-based new materials beyond perovskite by high-pressure synthesis and shed light on the large-scale stabilization of metastable phases under mild conditions.

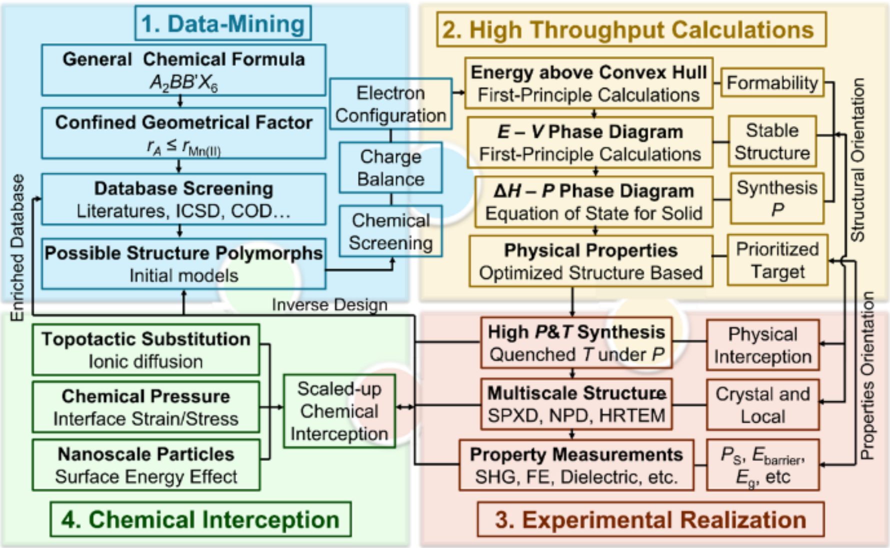


Figure 1 Schematic workflow of "precisely" high-pressure solid-state synthesis

Acknowledgements: The National Natural Science Foundation of China (No. 22090041) and the Guangdong Basic and Applied Basic Research Foundation (Grant No. 2022B1515120014) are acknowledged for the financial support.

References

[1] M. Zhao, C. Zhu, M.-R. Li, *et al. Chem. Mater.* **2022**, *34*, 186.
[2] M. Zhao, X. Zhou, M.-R. Li, *et al. Chem. Mater.* **2020**, *34*, 10153.
[3] X. Zhou, M. Zhao, X. Xing, M.-R. Li, *et al. Natl. Sci. Rev.* **2023**, *10*, nwad190.

3D Electron Diffraction on Nano-Crystals

Junliang Sun*
Peking University, 100871 Beijing, P. R. China.
Corresponding author: junliang.sun@pku.edu.cn

Knowing crystal structures is fundamentally important for wide fields (chemistry, physics, biology etc.) and various applications (catalysis, drug discovery etc.). When the crystal is too small for singe crystal X-ray diffraction, powder diffraction was the major method for their structure analysis. With the development of 3D electron diffraction techniques which can obtain single crystal diffraction data from nano-crystals, it become a powerful alternative choice.

Compared with traditional electron diffraction methods, this technique gives lower dynamical effects and much higher data completeness. Using the intensities abstracted from the data, complicated structures can be directly solved using similar methods as single-crystal X-ray diffraction. In this talk, the basic background and recent progress will be introduced and its application in a few fields will be also given as examples.

Acknowledgements: The National Natural Science Foundation of China (No. U21A20285, 22125102,) is acknowledged for the financial support.

References

[1] Wenjia Sun, Pohua Chen, Mingxuan Zhang, Jian-Xin Ma, and Junliang Sun *Angew. Chem. Int. Ed.* **2023**, e202305985.
[2] Zhipeng Zhou, Lei Zhang, Wei Liu, Junliang Sun, Zhikun Zheng et. al. *Nature Chem.* **2023**, 15, 841
[3] Yihan Shen, Wenjia Sun, Yang Liu, Zhengyang Zhou, Junliang Sun *Science China Materials*, **2022**, 65, 1417
[4] Jian Li, Cong Lin, Tianqiong Ma, Junliang Sun* *Nat. Commun.* **2022**, 13, 4016
[5] Jin-Hu Dou, Junliang Sun,* and Mircea Dinca* et. Al. *Nat. Mater.* **2021**,20, 222-228
[6] Jianyuan Li, Cong Lin, Mouyi Weng, Yi Qiu, Pohua Chen, Kai Yang, Weiyuan Huang, Yuexian Hong, Jian Li, Mingjian Zhang, Cheng Dong, Wenguang Zhao, Zhi Xu, Xi Wang, Kang Xu*, Junliang Sun, Feng Pan, *Nature Nanotech*, **2021**, 16, 599
[7] Jian Li#, Fengjuan Pan#, Shipeng Geng#, Cong Lin#, Lukas Palatinus, Mathiew Allix, Xiaojun Kuang*, Jianhua Lin, Junliang Sun* *Nat. Commun.* **2020**, 11, 4751.
[8] Xue Liu#, Yi Luo#, Wenting Mao, Jingang Jiang, Hao Xu*, Lu Han*, Junliang Sun* and Peng Wu* *Angew. Chem. Int. Ed.* **2020**, 59, 1166-1170.
[9] Chao Gao, Jian Li, Sheng Yin, Guiqing Lin, Tianqiong Ma, Yi Meng, Junliang Sun* and Cheng Wang* *Angew Chem. Int. Ed.* **2019**, 58, 9770-9775.
[10] Jian Li, Cong Lin, Yuxin Min, Youyou Yuan, Guobao Li, Sihai Yang, Pascal Manuel, Jianhua Lin, Junliang Sun* *J. Am. Chem. Soc.* **2019**, *141*,4990. DOI: 10.1021/jacs.9b00093
[11] Wei Hua, Hong Chen, Zheng-Bao Yu, Xiaodong Zou, Jianhua Lin*, Junliang Sun* *Angew. Chem. Int. Ed.* **2014,** *53* 5868-5871. DOI: 10.1002/anie.201309766

Long Range Ordering Structural Modulations in Layered-perovskite Oxides Inducing 2D Properties

Xabier Martínez de Irujo Labalde,[1,2] Rafael Marín Gamero,[1] Esteban Urones-Garrote,[1,3] Susana García-Martín[1*]

[1] *Complutense University of Madrid, Department of Inorganic Chemistry, Faculty of Chemistry, 28040-Madrid, Spain.*

[2] *University of Münster, Institute of Inorganic and Analytical Chemistry, 48149 Münster, Germany*

[3] *Complutense University of Madrid, National Center of Electronic Microscopy, 28040-Madrid, Spain*

Corresponding author: sgmartin@ucm.es

The variety of perovskite-related crystal structures and properties found in oxygen deficient $(A/A')_nB_nO_{3n-\delta}$ oxides are highly influenced by the nature of the B cations and also by the nature of the A/A' cations. The B atoms adopt different coordination polyhedra (octahedra, tetrahedra or squared pyramid) formed by the oxygen sublattice arranged in different manners that also depends on the types and ordering of the A and A' cations within the crystal structure. Layered perovskites $(A/A')_nB_nO_{3n-\delta}$ present ordering of the A cations in alternated (001)-planes. We have found that the complex combined ordering of the cation and anion sublattices in layered perovskites results in 2D-layers, interconnected in a 3D manner, that constrain the electric and magnetic properties of the compounds. We present in here the study of the crystal structure of oxides derived from the $GdBaCo_2O_{6-\delta}$ system, by means of STEM (Scanning-Transmission Electron Microscopy) with atomic resolution, in relation with their properties. Substitution of Co by Fe or Mn modifies the anion sublattice with implications in the properties of the oxides.[1-3] In addition, substitution of Gd and Ba by Ca in the $Gd_{0.8-x}Ba_{0.8}Ca_{0.4+x}Fe_2O_{6-\delta}$ series modifies the layered ordering of the A-sublattice and the Oxygen-environment of the Fe atoms, which highly impact on their electric and magnetic 2D-behaviour.[4-6]

Acknowledgements: The authors thank MCIN/AEI/10.13039/501100011033 for funding the Projects PID2019-106662RB-C44 and PID2022-139039OB-C22 and "NextGenerationEU"/PRTR for funding the Project TED2021-130452B-C2.

References

[1] D. Muñoz-Gil, D. Pérez-Coll, E. Urones-Garrote, U. Amador, S. García-Martín, *J. Mater. Chem. A*, **2017**, *5*, 12550.

[2] D. Ávila-Brande, G. King, E. Urones-Garrote, Subakti , A. Llobet, S. García-Martín, *Adv. Funct. Mater.* **2014**, *24*, 2510.

[3] D. Muñoz-Gil, E. Urones-Garrote, D. Perez-Coll, U. Amador, S. García-Martín, J. *Mater. Chem. A*, **2018**, *6*, 5452–5460

[4] X. Martínez de Irujo-Labalde, M. Goto, E. Urones-Garrote, U. Amador, C. Ritter, M. E. Amano Patino, A. Koedtruad, Z. Tan, Y. Shimakawa, S. García-Martín, *Chem. Mater*. **2019**, *31*, 5993.

[5] X. Martínez de Irujo-Labalde, Ul. Amador, C. Ritter, M. Goto, M. E. Amano Patino, Yu.. Shimakawa, S. García-Martín, *Inorg. Chem*. **2021**, *60*, 8027.

[6] R. Marín-Gamero, X. Martínez de Irujo-Labalde, E. Urones-Garrote, S. García-Martín, *Inorg. Chem*. **2020**, *59*, 5529.

Insight into Energy Storage Materials from a Reductionist Perspective

Lin Gu[1*]

[1] *Beijing National Center for Electron Microscopy and Laboratory of Advanced Materials, School of Materials Science and Engineering, Tsinghua University, Beijing, 100084, China.*

Corresponding author: lingu@tsinghua.edu.cn

Establishing a correlation between the structure and functionality of materials has been a long-standing challenge. Materials science based on reductionism greatly depends on one's knowledge of the elements. This understanding ranges from entirely solvable atomic energy levels to fundamentally solvable energy bands of phases under specific boundary conditions, and finally, to macroscopic material properties that may have only statistical solutions. Along this clue, here the macroscopic material is split into phase, until cell, atom, and electron step by step, exploring the material properties starting from the elementary particles. We mainly focus on band structure (electron) and dispersion relation (phonon) in reciprocal space, and the distribution of four fundamental degrees of freedom (lattice, charge, orbital, spin) in real space. As a powerful characterization method, spherical aberration corrected electron microscopy could acquire information about atomic-scale structure and electronic structure, which could get rid of the constraint condition of periodic potential field, single electron approximation, and adiabatic approximation theories to obtain the structure-activity relationship in solid materials. We focused on the atomic structure and electronic structure of energy storage materials from lattice and charge degrees of freedom. On this basis, the direct observation of electron occupied states is realized at orbital scale, which has a substantial impact on battery performance. This report will focus on physical mechanism of electrochemical energy storage materials to discuss the correlation between microstructure and electronic structure based on reductionism.

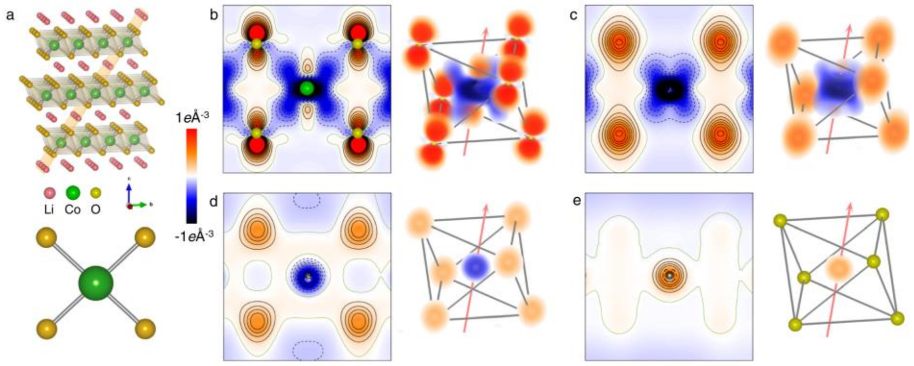


Figure 1. Experimentally probing electron density evolution of the Co–O and O–O interactions in Li$_x$CoO$_2$. **a** Structural model of LiCoO$_2$ with the indexed (01$\bar{4}$) plane near the [100] direction (top). CoO$_4$ (01$\bar{4}$) plane of the CoO$_6$ octahedra (bottom). **b–e** Static deformation density maps of the (01$\bar{4}$) CoO$_4$ plane and corresponding three-dimensional (3D) views of **b** LiCoO$_2$, **c** Li$_{0.6}$CoO$_2$, **d** Li$_{0.4}$CoO$_2$, and **e** Li$_{0.3}$CoO$_2$.

Acknowledgements: The National Natural Science Foundation of China (No. 52025025) is acknowledged for the financial support.

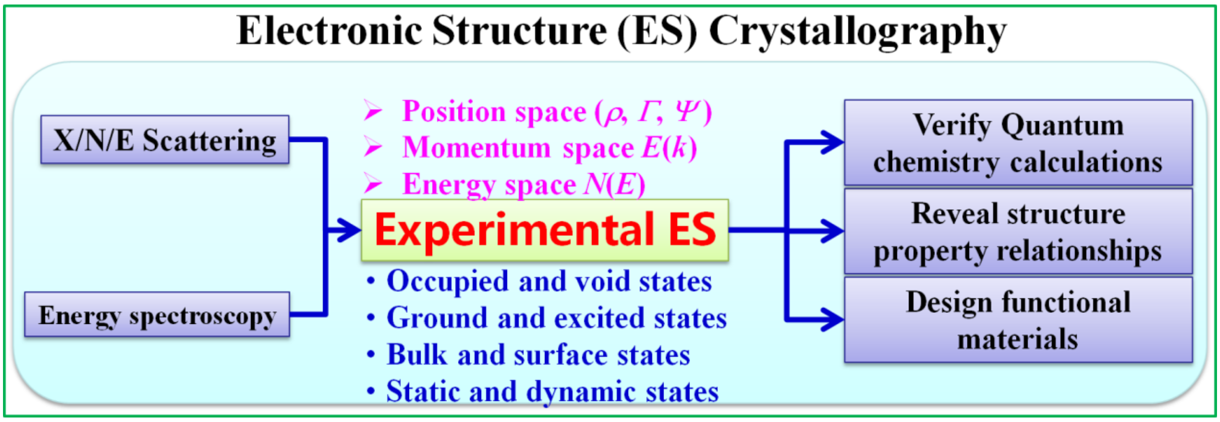
References

[1] T. Shang et al., *Nat. Comm.* **2022**, *13*, 5810.
[2] A. Gao et al., *Nat. Sustain.* **2022**, 5, 214.
[3] Z. Tang et al., *Angew. Chem. Int. Edit.* **2023**, 62, e202216898.

Electronic Structure Crystallography: from Crystal Structure to Electronic Structure

Guo-Cong Guo*, Xiao-Ming Jiang
Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, China, Fuzhou, 350002
Corresponding author: gcguo@fjirsm.ac.cn

The relationship between structure and performance is known as one of the four major challenges of 21st century chemistry. The material properties mainly depend on its electronic structure, which is usually obtained by first-principles approximation calculation. Obtaining the electronic structure through experimental methods was proposed by Nobel laureates Debye and Bragg in 1915 and 1922, respectively, but it has not been popularized for more than a hundred years. Electronic structure crystallography is an experimental crystallographic science that aims to study the electronic structures in real and momentum (or energy) space, combining experimental methods of X-ray/neutron/electron scattering and energy spectroscopy, consisting of an interdisciplinary discipline in the current frontier of crystallography. The intrinsic properties of a material are mainly determined by its electronic structure, which can be described in terms of electron density, electron wavefunction, or electron density matrix, where the Fourier transform (structure factor) of the electron density can be determined by scattering experiments. Therefore, a material's electron density can be obtained experimentally, and the electron density can be referred to as the experimental electron density. Moreover, by building a suitable theoretical model and using certain refinement techniques, the experimental electron wavefunction or experimental electron density matrix of a material can be further reconstructed to compute the material's physical and chemical properties.[1,2,3] In this paper, an electron structure *in-situ* testing instrument based on non-synchronous radiation light source was developed with the support of the national major scientific research instrument development project. The breakthrough of testing the electronic structure of real space 0-1 in China has been achieved, which has promoted the experimental research level of structural chemistry from the atomic level to the electronic level and laid a foundation for the study of structure-performance relationship and the popularization of electronic structure crystallography.



References

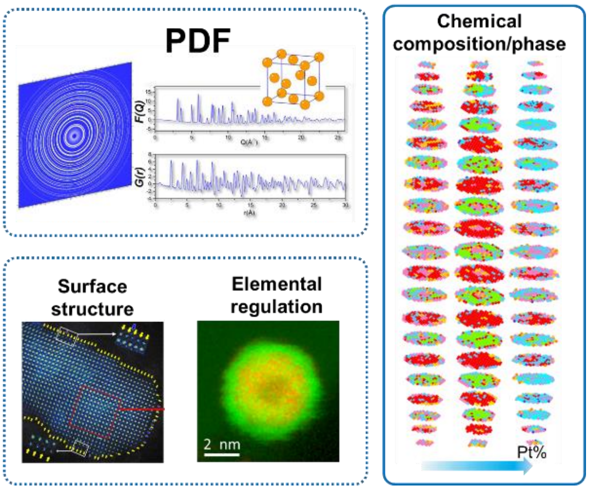
[1] Jiang, X.-M.; Guo, G.-C. Electronic structure crystallography (*in Chinese*), *Science Press, Beijing, 2022.*
[2] Jiang, X.-M.; Guo, G.-C; et al. *Angew. Chem. Int. Ed.* **2021**, *60*, 11799.
[3] Jiang, X.-M.; Guo, G.-C; et al. *Natl. Sci. Rev.* **2022**, *9*, nwac017.

Keywords: Electronic Structure Crystallography, X-ray diffraction technique

Local Structure in Nanocatalysts

Qiang Li,[1] Fan Xue,[1] Mingxin Lv[1], Xianran Xing[1]*
[1] *Institute of Solid State Chemistry, University of Science and Technology Beijing, Beijing 100083, China.*
Corresponding author: qiangli@ustb.edu.cn

Local structure in solid state catalysts, indicating the atomic arrangements from several anstroms to several nanometers, determines the phase distribution, ab/desorption process, and surficial electron transfer. However, the revelation of atomic 3D structure for nanocatalysts challenges the limitations of conventional methods. Notably, the identification of the cooperative relationship between the active sites and nearby coordination environment during catalytic reactions depends on the stereo distribution of local phases and chemical composition within a short range. Here, supported by the comprehensive method combining with Pair Distribution Functions (PDF) with Reverse Monte Carlo (RMC), we have achieved a local structural insight into the elemental distribution, phase segregation and anomalous structural transition in the nanosized catalysts. A segregation of local phase segments as disordered Pt-rich A1 and Pt_3Fe $L1_2$ phases were revealed to attribute to the marked improvement of HER activity and stability in $Pt_{56}Fe_{44}$. The high dispersity of active sites in the $Pd_{34}Cu_{66}$ alloy provided the excellent catalytic performance with 98% ethylene selectivity at complete acetylene conversion, which was surpassing than the most advanced catalysts available. Our study will provide an intuitionistic method to resolve the spatial structure of active sites and be essential to design nanocatalysts.



Acknowledgements: The National Key R&D Program of China (2020YFA0406202), The National Natural Science Foundation of China (22090042 and 22175018).

References

[1] Q. Li, H. Zhu, X. Chen, H. Liu, Y. Ren, Y. Chen, K. Ohara, L. Zhou, J. Chen, J. Deng, J., K. Lin, X. Kuang, X. Xing*, *J. Am. Chem. Soc.***2022**, *144*, 20298.
[2] H. Zhu, C. Yang, Q. Li, Y. Ren, J. C. Neuefeind, L. Gu, H. Liu, L. Fan, J. Chen, J. Deng, N. Wang, J. Hong*, X. Xing*, *Nat. Commun.* **2018**, *9*, 5063.

New Look at Old Things: Electronegativities, Chemical Hardnesses, and Stability of Molecules and Crystals.

Artem R. Oganov

Skolkovo Institute of Science and Technology, Skolkovo Innovation Center, Bolshoy Boulevard 30, Building 1, Moscow 121205, Russia

Corresponding author: A.Oganov@skoltech.ru

Chemical behavior of the elements can be rationalized and anticipated based on a few properties, such as electronegativity, radius (atomic, ionic, van der Waals radii), polarizability, valence state. Among these, electronegativity plays perhaps the most important role – chemical reactivity of the elements, bond energies, directions and heats of reactions, and many properties of molecules and solids are related to electronegativities of the elements. The oldest and the most widely used is Pauling's scale of electronegativity, developed in 1932 (see [1]) and based on bond energies. However, later it was found (e.g., [2]) that Pauling's formula, relating bond energies with electronegativity differences, is very inaccurate for significantly ionic bonds. We have proposed [3] another formula, which works well for bonds with any degree of ionicity, and obtained a new thermochemical scale of electronegativities for all elements. New electronegativities better follow chemical intuition than traditional Pauling's values (e.g. charge transfer in transition metal borides and hydrides is described qualitatively better, and so are oxyacids).

It is widely expected that electronegativities of the atoms depend on pressure. We have extended the concept of Mulliken electronegativities to high pressure [4] – which required modification of the definition and gave a new scale. The new electronegativity is defined as minus the chemical potential of the electron in an atom relative to homogeneous electron gas at the same pressure. We have tabulated electronegativities and chemical hardnesses of all elements up to Cm (#96) at pressures up to 500 GPa, and shown that they explain many unusual chemical phenomena known at high pressure [4]. Moreover, another important property, the chemical hardness, becomes particularly important at high pressure.

We have also studied another important concept – Mendeleev numbers, introduced in 1984 by Pettifor [5]. Pettifor showed that chemical behavior of the elements can be approximately characterized by just one number, which he called the Mendeleev number; he assigned these numbers to all elements, but the physical meaning of these remained unclear. We have shown [6] that Mendeleev number can be obtained by principal components analysis (PCA) or even a simple linear correlation applied to the set of points "atomic radius – electronegativity – polarizability" of all elements. This dimensionality reduction gives a single variable giving mathematically the best one-parameter description of the chemistry of the elements – the Mendeleev number. We have shown [6] that thus defined Mendeleev numbers perform better than those proposed by Pettifor [5]. Accurate representations of the chemical space require all key properties of the atoms to be explicitly used, but reduced-dimensionality representations (such as representation by Mendeleev numbers) allow easier visualization of big data.

References

[1] Pauling, L. *The Nature of the Chemical Bond* 3rd edn (Cornell University Press, 1960).

[2] Matcha, R. L. (1983). Theory of the chemical bond. 6. Accurate relationship between bond energies and electronegativity differences. *J. Am. Chem. Soc.* **105**, 4859–4862.

[3] Tantardini C., Oganov A.R. (2021). Thermochemical electronegativities of the elements. *Nature Communications* **12**, 2087.

[4] Dong X., Oganov A.R., Cui H., Zhou X.-F., Wang H.-T. (2022). Electronegativity and chemical hardness of the elements under pressure. *Proc. Natl. Acad. Sci.*, in press.

[5] Pettifor D.G. (1984). A chemical scale for crystal structure maps. *Solid State Commun.* **51**, 31-34.

[6] Allahyari Z., Oganov A.R. (2020). Nonempirical definition of Mendeleev numbers: organizing the chemical space. *J. Phys. Chem.* **C124**, 23867-23878.

Unleashing the Power of Metal Nitrides in Functional Materials

Minghui Yang
Dalian University of Technology, Dalian 116024, China
Corresponding author: myang@dlut.edu.cn

Metal nitrides are a type of interstitial compound with a unique crystal structure, exhibiting excellent electron conductivity, chemical stability, and corrosion resistance. In particular, certain metal nitrides demonstrate catalytic properties similar to noble metals due to the incorporation of nitrogen atoms, resulting in lattice expansion and electron structure resembling noble metals[1, 2]. The synthesis of metal nitrides with specific crystal structures and morphologies is challenging due to their material characteristics. In recent years, our team has successfully developed numerous novel metal nitrides and composite materials of significant theoretical and practical value. By employing systematic experiments along with synchrotron and in-situ facilities and theoretical calculations, we have elucidated the structure-property relationships of these materials. Noteworthy achievements include the discovery of zirconium nitride exhibits superior catalytic properties for the oxygen reduction reaction compared to platinum[1], the successful synthesis of Ni_2Mo_3N using soft urea methods, and the conceptual design of surface oxide-rich activation layer (SOAL) for oxygen evolution reaction[3]. Furthermore, we have recently developed the best-performing ultra-low platinum metal nitride material for hydrogen production from seawater[4]. Through detailed analysis of crystal and surface structures, we have not only identified outstanding performance of these materials in catalysis and sensing but also provided valuable insights for the design of high-performance materials in related areas.

Acknowledgements: The National Natural Science Foundation of China (No. 61971405) is acknowledged for the financial support.

References

[1] Yuan Y, Wang J, Adimi J, Shen H, Thomas T, Ma R, Attfield JP*, Yang M*, Zirconium nitride catalysts surpass platinum for oxygen reduction, *Nature Materials*, 2020, 19, 282.

[2] Liu J, Qi W, Xu M, Thomas T, Liu S*, and Yang M*, Piezo-catalytic techniques in environmental remediation. *Angewandte Chemie International Edition*, 2022. DOI:10.1002/anie.202213927

[3] Yuan Y, Adimi S, Guo X, Thomas T, Zhu Y, Guo H, Priyanga GS, Yoo P, Wang J, Chen J, Liao P*, Attfield JP*, Yang M*, Surface oxide-rich activation layer (SOAL) on Ni_2Mo_3N for rapid and durable oxygen evolution reaction, *Angewandte Chemie International Edition*, 2020, 59, 41, 18036.

[4] Hu H, Zhang Z, Zhang Y, Thomas T, Du H, Huang K, Attfield JP, Yang M*, An ultra-low Pt metal nitride electrocatalyst for sustainable seawater hydrogen production, *Energy & Environmental Science*, 2023, DOI: 10.1039/d3ee01541f

Diamond Nanothread

Kuo Li,[1*] Haiyan Zheng[1*]

[1] *Center for High Pressure Science and Technology Advanced Research, Beijing, China.*

Corresponding author: likuo@hpstar.ac.cn;zhenghy@hpstar.ac.cn

Diamond nanothread (DNTh) is the one-dimensional sp^3-C material with or without hetero atoms. Its intersection has a couple of carbon atoms and the repeating units are connected by two or more bonds. Therefore, it combines the mechanical properties of diamonds and polymers. Up to now, the DNTh can only be synthesized by pressure-induced polymerization of aromatics, typically at up to tens of GPa, and the quality, or the ordering in and between the DNThs is still a problem. Here we reviewed the progress in the synthesis of ordered or even crystalline DNThs. The strategy includes: 1) introduction of hetero(inert) atoms to limit the bonding route (poly-furan, poly-thiophene, poly-pyridazine, etc.); 2) introduction of strong intermolecular interactions, including hydrogen bonds (poly-aniline, etc.), quadrupole interaction (poly-arene-perfluoroarene); and 3) both (poly-triazine and poly-furandicarboxylic acid). It shows by introducing heteroatoms and strong intermolecular hydrogen bond will improve the crystallinity of the DNTh and thereby we can obtain 3D-crystalline DNTh.

Acknowledgements: The National Natural Science Foundation of China (No. 22022101) is acknowledged for the financial support.

References

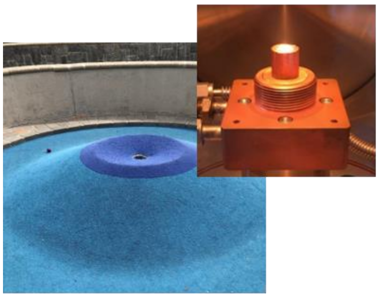
[1] X. Wang, X. Yang, Y. Wang, X. Tang, H. Zheng, P. Zhang, D. Gao, G. Che, Z. Wang, A. Guan, J. Xiang, M. Tang, X. Dong, K. Li, H. Mao, *J. Am. Chem. Soc.* **2022,** *144*, 21837

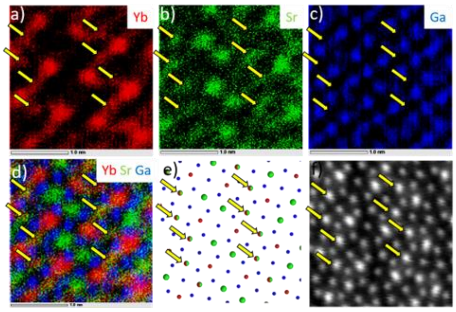
[2] D. Gao, X. Tang, J. Xu, X. Yang, P. Zhang, G. Che, Y. Wang, Y. Chen, X. Gao, X. Dong, H. Zheng, K. Li, H. Mao, *PNAS*, **2022,** *119*, e2201165119

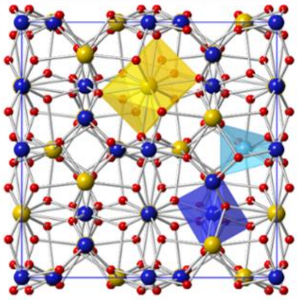
New Out-of-equilibrium Oxides Elaborated by Crystallisation from Glass or the Molten State

Mathieu Allix,[1*] Cécile Genevois,[1] Emmanuel Véron,[1] Victor Castaing,[2] Ana Becerro,[2] Alberto Fernandez,[2,3]
Xiaojun Kuang,[3] Franck Fayon,[1] Michael Pitcher[1]
[1] *CEMHTI CNRS UPR3079, Orléans, France;*
[2] *ICMS, Seville, Spain*
[3] *Guilin University of Technology, Guilin, China*
Corresponding author: mathieu.allix@cnrs-orleans.fr

In the context of new oxide materials discovery, glasses (and their parent under-cooled melts) can be considered as ideal precursors for exploratory synthesis: they can be crystallised at substantially lower temperatures that the equivalent ceramic reaction, which allows metastable crystalline solids with unusual and surprising features to be isolated. For example, we recently showed that the crystallisation of YAG glass or melt below 1000°C permits highly nonstoichiometric derivates such as $Y_{3.4}Al_{4.6}O_{12}$ to be isolated, which are totally inaccessible at the standard ceramic synthesis conditions of 1650°C [1]. When harnessed to apparatus such as laser-coupled aerodynamic levitation, a relatively wide range of compositions can be addressed that is not restricted to classic glass-forming systems. A few other examples will be presented, including non-stoichiometric gallate melilite oxides showing anionic conductivity [2,3] and strontium aluminates demonstrating persistent luminescence properties [4].







References

[1] W.Cao, A.I.Becerro, V.Castaing, X.Fang, P.Florian, F.Fayon, D.Zanghi, E.Veron, A.Zandoná, C.Genevois, M.J.Pitcher*, M.Allix*, 'Highly Nonstoichiometric YAG Ceramics with Modified Luminescence Properties', Adv. Funct. Mater., 33 2213418 (2023).

[2] M.Boyer, X.Yang, A.J.Fernandez Carrion, Q.Wang, E.Veron, C.Genevois, L.Hennet, G.Matzen, E.Suard, D.Thiaudière, C.Castro, D.Pelloquin, X.Kuang, M.Allix*, 'First transparent oxide ion conducting ceramics synthesized by full crystallization from glass', J. Mater. Chem. A, 6 5276-5289 (2018).

[3] J.Fan, V.Sarou-Kanian, X.Yang, M.Diaz-Lopez, F.Fayon, X.Kuang, M.J.Pitcher* and M.Allix*, 'La2Ga3O7.5: a metastable ternary melilite with a super-excess of interstitial oxide ions synthesized by direct crystallization of the melt', Chem. Mat., 32 9016-9025 (2020).

[4] V.Castaing, C.Monteiro, A.D.Sontakke, K.Asami, J.Xu, A.J.Fernández-Carrión, M.G.Brik, S.Tanabe, M.Allix, B.Viana, 'Hexagonal Sr1−x/2Al2−xSixO4:Eu2+,Dy3+ transparent ceramics with tuneable persistent luminescence properties', Dalton Trans., 49 16849 (2020).

Exploring Molecule-Based Antiferroelectrics with Solid-State Energy Storage Properties

Zhihua Sun（孙志华）*

Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

*E-mail: sunzhihua@fjirsm.ac.cn

Antiferroelectric (AFE) materials, characterized by the antiparallel arrangement of dipoles in adjacent sublattices, have recently emerged as the promising electroactive candidates for solid-state energy storage application. By applying a high electric field, the field-induced antipolar-polar transformation triggers superior physical properties, displaying a typical polarization *versus* electric field (*P*-*E*) double hysteresis loop. Currently, molecule-based AFE materials have attracted great interest due to their unique advantages of light weight, facile processability and structure flexibility. By optimizing the chemical compositions, we have effectively regulated intrinsic competitions between dipolar interaction and steric hindrance, and obtained a series of new molecule-based AFEs. The macroscopic physical properties of such AFE materials, including energy storage and electrocaloric (EC) effect, have been systematically studied. First principle density functional theory (DFT) methods were used to disclose the internal relationship between antiferroelectric orders and crystal structure of those materials. This study sheds light on the exploration of new molecule-based antiferroelectrics toward high efficiency energy storage capacitors and refrigeration devices.

Reference

[1] Yi Liu, Wuqian Guo, Lina Hua, Xi Zeng, Tian Yang, Qingshun Fan, Yu Ma, Changhao Gao, Zhihua Sun,* and Junhua Luo, **2023**, 145, 16193-16199.

[2] Haojie Xu,Wuqian Guo,Yu Ma,Yi Liu, Xinxin Hu, Lina Hua, Shiguo Han, Xitao Liu, Junhua Luo* and Zhihua Sun*, ***Nat. Commun.***, **2022,**13, 5329.

[3] Maofan Li, Shiguo Han, Yi Liu, Maochun Hong, Junhua Luo, and Zhihua Sun,* ***J. Am. Chem. Soc.***, **2020,** 142, 20744-20751.

[4] Haojie Xu, Wuqian Guo, Jiaqi Wang, Yu Ma, Shiguo Han, Yi Liu, Lei Lu, Xiong Pan, Junhua Luo,* and Zhihua Sun,* ***J. Am. Chem. Soc.*** **2021**, 143, 14379–14385.

[5] Shiguo Han, Xitao Liu, Yi Liu, Zhiyun Xu, Yaobin Li, Maochun Hong, Junhua Luo, and Zhihua Sun,* ***J. Am. Chem. Soc.***, **2019**, 141, 12470-12474.

Novel Functional Properties Induced by Charge Transitions in Oxides

Yuichi Shimakawa,[1*]
[1] *Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan.*
Corresponding author: shimak@scl.kyoto-u.ac.jp

In some transition-metal oxides synthesized under extreme conditions, unusually high valence states of the cations can be stabilized, and charge, spin, and lattice degrees of freedom are strongly correlated due to strong hybridization of low-lying *d* orbitals of the transition-metal ions with 2*p* orbitals of the coordinated oxygen ions. Such an oxide often exhibits a charge transition to relieve its electronic instability, leading to drastic changes in transport, magnetic, and structural properties. Some examples of such charge transitions inducing functional properties are presented.

$LaCu_3Fe_4O_{12}$ shows an intersite-charge-transfer transition of the unusually high valence $Fe^{3.75+}$ ions, accompanied by drastic changes in transport and magnetic properties. A concomitant significant structural change leads to a negative thermal expansion behavior [1,2]. A similar charge-transfer tansition in $NdCu_3Fe_4O_{12}$ is found to result in a large latent heat near room temperature. Importantly, the large latent heat can be utilized through the barocaloric effects. A charge disproportionation transition in $BiCu_3Cr_4O_{12}$ is also found to induce multiple caloric effects, in which thermal properties can be controlled by applying both pressure and magnetic fields. Such novel caloric effects can provide us with highly efficient and environmentally friendly energy systems [3-5]. Solid-state chemistry of the functional transition-metal oxides with novel functional properties is discussed.

Acknowledgements: The works were done in collaboration with many domestic and international collaborators. The works were supported by Grants-in-Aid for Scientific Research (Nos. 19H05823, 20K20547, 20H00397, and 23H05457) and Advanced International Collaborative Research Program (AdCORP) Grant No. 0MJKB2304 by Japan Science and Technology Agency (JST).

References

[1] Y.W. Long, YS, *et al.*, *Nature* **458**, 60 (2009).
[2] Y. Shimakawa (Review), *J. Phys. D: Appl. Phys.* **48**, 455106 (2015).
[3] Y. Kosugi, YS, *et al.*, *Adv. Func. Mater.* **31**, 2009476 (2021).
[4] Y. Kosugi, YS, *et al.*, *Sci. Rep.*, **11**, 12682 (2021).
[5] Y. Shimakawa and Y. Kosugi (Perspective review), *J. Mater. Chem. A*, **11**, 12695 (2023).

Flexoelectricity-induced novel effects in suspended films

Jiawang Hong,[1] Yingzhuo Lun,[1] Shaoqing Xu,[1] Tingjun Wang,[1] Xueyun Wang,[1]
[1] *School of Aerospace Engineering, Beijing Institute of Technology, Beijing 100081, China*
Corresponding author: hongjw@bit.edu.cn

Ferroelectric materials have been attracting wide interest due to their switchable polarization properties and fascinating applications in the areas of information storage, electronics and biology. The deliberate engineering of domain switching is critical for its applications. The flexoelectric field induced from the nano-tip indentation can switch the polarization in ferroelectric films. However, it usually occurs in a very localized area in ultrathin films, with possible permanent surface damage caused by a large tip-force. Here, we report a mechanical domain switching method based on the suspended films. Utilizing the large-scale bending deformation in suspended films subjected to nano-tip force, the transverse flexoelectric effect is significantly enhanced. Sizable-area domain switching under an ultralow tip-force can be realized in suspended van der Waals ferroelectrics with the surface intact. The film thickness range for domain switching is significantly improved by an order of magnitude to hundreds of nanometers, being far beyond the limited range of the substrate-supported ones. [1] Meanwhile, a nonreciprocal bending property driven by strong flexoelectricity is found in suspended films. The mechanisms underlying these novel effects are revealed by combining the theoretical model and phase-field simulations. [2,3] These findings provide new opportunities for the flexoelectricity-based domain controls in emerging low-dimensional ferroelectrics and related devices.

Acknowledgements: The National Key R&D Program of China (Grant No. 2021YFA1400300), the National Natural Science Foundation of China (Grant No. 12172047), are acknowledged for the financial support.

References

[1] Yingzhuo Lun, Xueyun Wang, Jiaqian Kang, Qi Ren, Tingjun Wang, Wuxiao Han, Ziyan Gao, Houbing Huang, Yabin Chen, Long-Qing Chen, Daining Fang，Jiawang Hong, *Adv. Mater.* **2023**, 35, 2302320.

[2] Songhua Cai, Yingzhuo Lun, Dianxiang Ji, Peng Lv, Lu Han, Changqing Guo, Yipeng Zang, Si Gao, Yifan Wei, Min Gu, Chunchen Zhang, Zhengbin Gu, Xueyun Wang, Christopher Addiego, Daining Fang, Yuefeng Nie, Jiawang Hong, Peng Wang, and Xiaoqing Pan, *Nat. Commun*. **2022**, 13, 5116.

[3] Yingzhuo Lun, Jiawang Hong and Daining Fang, *J. Mech. Phys. Solids*, **2022**, 164, 104891.

Toward Predictive Theory of the Anomalous Volume Magnetostriction in Invar Alloys

Sergii Khmelevskyi
[1] *Vienna Scientific Cluster Reserach Center, Technical University of Vienna, Wiedner Hauptrasse 8-10, Vienna 1040, Austria.*
Corresponding author: sk@cms.tuwien.ac.at

The Invar anomaly, a phenomenon observed in the canonical INVAR alloys Fe-Ni, has been investigated on a first-principles basis, incorporating longitudinal spin fluctuations in the paramagnetic region. We present an almost perfect quantitative description of the spontaneous volume magnetostrictions and their dependence on the alloy's chemical composition. We thus demonstrate on a first-principles basis that incorporating longitudinal spin fluctuations into the Disordered Local Moment framework based on the Coherent Potential Approximation leads to a truly predictive theory of the Invar anomaly in Fe-Ni alloys. Furthermore, our study facilitates a simple, chemically intuitive formulation of the Invar effect mechanism. This mechanism is rooted in the repopulation of anti-bonding states in the majority spin band and bonding states in the minority spin band at the Fermi level. This repopulation occurs due to thermal magnetic disorder effects that reduce the local atomic moments compare to their values in the ferromagnetic ground state due to itinerant character of the magnetism. We provide evidence that such repopulation of majority and minority spin states occurs with change of their bonding character in Fe-Ni alloys due to special position of the Fermi level in the metallic d-band. We visualize the bonding/anti-bonding character of electronic states in Fe-Ni alloy at the Fermi level using first-principle based Crystal Orbital Hamiltonian Population (COHP) analyses.

The New Structure of Terbium in Ferromagnetic State

Kun Lin,[1] Guodong Li,[1] Sergii Khmelevskyi,[2] Leonid V. Pourovskii,[3,4] Suihe Jiang,[1] Kenichi Kato,[5] Chengyi Yu,[1] Yili Cao,[1] Qiang Li,[1] Xiaojun Kuang,[6] Xianran Xing[1,*]

1 Beijing Advanced Innovation Center for Materials Genome Engineering, and Institute of Solid State Chemistry, University of Science and Technology Beijing, Beijing 100083, China

2 Research Center for Computational Materials Science and Engineering, Vienna University of Technology, Karlplatz 13, A-1040 Vienna, Austria

3 CPHT, CNRS, École polytechnique, Institut Polytechnique de Paris, 91120 Palaiseau, France

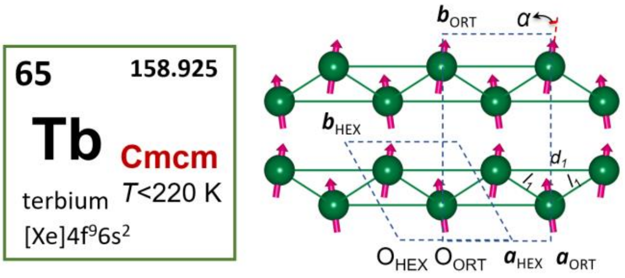
4 Collège de France, Université PSL, 11 place Marcelin Berthelot, 75005 Paris, France

5 RIKEN SPring-8 Center, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan

6 College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541006, China

*Corresponding author: xing@ustb.edu.cn

Metals typically crystallize in highly symmetric structures due to their non-directional and non-saturated metallic bonds. Here, we report that terbium metal in its ferromagnetic state adopts an unusual low-symmetry orthorhombic structure with the Cmcm space group. Similar structure has been previously observed only in few actinide metals with bonding 5f electrons at ambient pressure, such as uranium, neptunium and plutonium, but with different nearest coordination numbers and bond-length variations. Tb atom occupies the 4c site (0, ~0.1661, 1/4), building up −[Tb−Tb]− layers stacking along the *b*-axis. Our first-principles many-body calculations of the crystal field splitting in the correlated Tb 4f-shell demonstrate that the Cmcm structure for ferromagnetic terbium is stabilized by magneto-elastic forces due to a secondary order of quadrupolar moments in the ferromagnetic state. These findings are significant for further understanding the nature of terbium, including its electron structure, energy bands, phonons, and magnetism.



Acknowledgements: This research was supported by National Key R&D Program of China (2020YFA0406202), National Natural Science Foundation of China (22090042 and 21971009), Guangxi BaGui Scholars Special Funding (2019M660446), and the Fundamental Research Funds for the Central Universities, China (GJRC003, FRF-IDRY-GD21-03).

References

[1] Lin, K.; Li, G.; Khmelevskyi, S.; Pourovskii, L. V.; Jiang, S.; Kato, K.; Yu, C.; Cao, Y.; Li, Q.; Kuang, X.; Xing, X., The Structure of Terbium in the Ferromagnetic State. *J. Am. Chem. Soc.* **2023,** *145* (32), 17856-17862.

Luminescent All-inorganic Perovskite Nanocrystals: Electronic Structure and Optical Properties

Xueyuan Chen,[1,2,]* Wei Zheng,[1,2] Datao Tu,[1,2] and Jin Xu[1]
[1] CAS Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China
[2] Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou, Fujian 350108, China
* Corresponding author: xchen@fjirsm.ac.cn

All-inorganic perovskite nanocrystals (PeNCs) have shown great promise in optoelectronics and photovoltaics owing to their outstanding photophysical properties. In this talk, we shall focus on our recent efforts in the development of luminescent PeNCs from the controlled synthesis and electronic structure to their optoelectronic applications, with an emphasis on optical property tuning through cation incorporation and hetero-nanostructure design. For instance, we have devised a photoinduced method to synthesize $CsPbX_3$ (X = Cl, Br, I) PeNCs and nanocomposites with a high degree of control based on the light-triggered breakage of the covalent carbon-halogen bond of haloalkanes.[1] We have unveiled the anomalous excited-state dynamics of Mn^{2+} in spatially-confined 0D Cs_4PbCl_6 PeNCs and the unusual temperature dependence of bandgap in 2D $CsPbBr_3$ nanoplates.[2,3] Through the bandgap and surface structure engineering via Cd^{2+} doping, we have achieved efficient ultraviolet luminescence in $CsPbCl_3$ PeNCs.[4] Specifically, through sensitization by lanthanide-doped nanoparticles, we have realized full-spectrum upconversion and persistent luminescence tuning in $CsPbX_3$ PeNCs with a color gamut over 130% NTSC.[5,6] Furthermore, to address the lead toxicity and instability issues of $CsPbX_3$ PeNCs, we have developed a series of highly efficient lead-free luminescent metal halides based on the doping of lanthanide ions, transition metal ions, and/or main-group ns^2-metal ions (*e.g.*, Bi^{3+}, Te^{4+}, Sb^{3+}).[7-11] These findings provide fundamental insights into the structure-property relationship of PeNCs, thus laying a foundation for future design of luminescent PeNCs and their derivatives toward versatile applications.

References

[1] J. J. Wei, W. Zheng*, X. Y. Chen*, *et al.*, *Nano Today* **2021**, *39*, 101179.
[2] W. Zhang, W. Zheng*, X. Y. Chen*, *et al.*, *Adv. Sci.* **2020**, *7*, 2002210.
[3] S. H. Yu, J. Xu*, X. Y. Chen*, *et al.*, *Adv. Sci.* **2021**, *8*, 2100084.
[4] Y. Q. Zhang, D. T. Tu*, S. Q. Deng*, X. Y. Chen*, *et al*., *Angew. Chem. Int. Ed*. **2021**, *60*, 9693-9698.
[5] W. Zheng, X. Y. Chen*, *et al*., *Nat. Commun.* **20**18, *9*, 3462.
[6] Z. L. Gong, W. Zheng*, X. Y. Chen*, *et al.*, *Angew. Chem. Int. Ed*. **2019**, *58*, 6943-6947.
[7] Z. L. Gong, W. Zheng*, X. Y. Chen*, *et al.*, *Nano Today* **2022**, *44*, 101460.
[8] X. W. Cheng, W. Zheng*, X. Y. Chen*, *et al.*, *Adv. Sci.* **2022**, *9*, 2103724.
[9] W. Zhang, W. Zheng*, L. Y. Li*, X. Y. Chen*, *et al.*, *Angew. Chem. Int. Ed*. **2022**, *61*, e202116085.
[10] J. Y. Sun, W. Zheng*, X. Y. Chen*, *et al.*, *Angew. Chem. Int. Ed*. **2022**, *61*, e202201993.
[11] Y. F. Pei, D. T. Tu*, X. Y. Chen*, *et al.*, *Angew. Chem. Int. Ed*. **2022**, *61*, e202205276.

Frenkel Defect-modulated Anti-thermal Quenching Luminescence in $Sc_2(WO_4)_3$:Ln

Yang Wei,[1] Ling Huang[1*]
[1] *Institute of Advanced Materials, Nanjing Tech University*
[2] *College of Chemistry, Xinjiang University*
Corresponding author: iamlhuang@njtech.edu.cn

The solid-state chemistry of $ScWO_4$ has been a prevalent topic due to its fascinating functionalities in luminescent materials, solid state electrolyte, negative thermal expansion, and infrared transmitting ceramics. However, the genuine role of WO_4^{2-} in luminescence has been puzzled for several decades. Herein, we have unambiguously disclosed the formation of singlet and triplet energy reservoirs through partial overlap of the energy levels between intrinsic and extrinsic WO_4^{2-} groups generated during sample annealing treatment.
Upon heating, the excitation energy stored in energy reservoirs will be acceleratedly released and resonantly transferred to matched energy levels of codoped lanthanide ions (Ln^{3+}), which leads to thermally enhanced 415-fold downshifting and 405-fold upconversion luminescence (**Figure 1**).

This study has enriched the luminescence mechanism studies, updated the solid-state chemical principles of the old yet charming SWO, and pointed out a new direction to material design for reliable generation of high-temperature luminescence, which possesses great potentials in high-power lighting, high-power lasing, fracture probing in engine blades, thermophotovoltaics, photothermal catalysis, and so on.

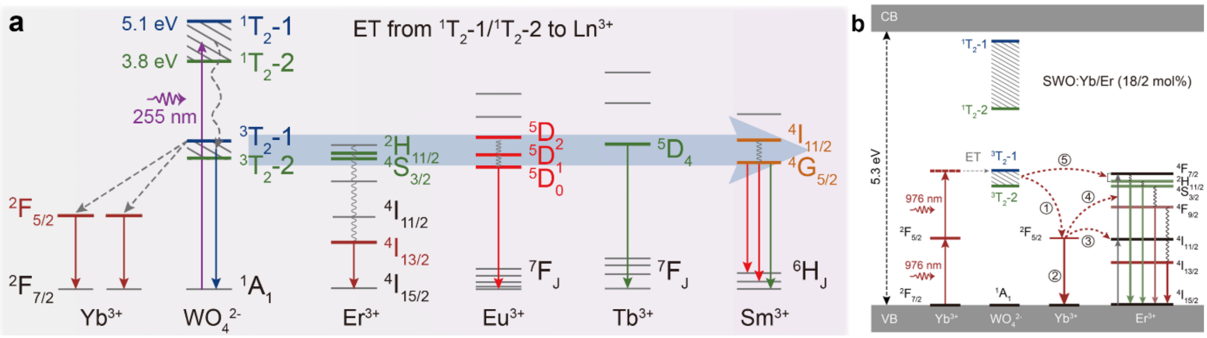


Figure 1. Host-activator energy transfer pathways for (a) downshifting and (b) upconversion luminescence.

Acknowledgements: The National Natural Science Foundation of China (No. 21871137 and 91956107) is acknowledged for the financial support.

References

[1] H. J. Borchardt, *J. Chem. Phys.* **1963**, *39*, 504.
[2] Y. Wei, Yue Pan, Enlong Zhou, Ze Yuan, Hao Song, Yilin Wang, Jie Zhou, Jiahui Rui, Mengjiao Xu, Lixin Ning, Zhanning Liu, Hongyu Wang, Xiaoji Xie, Xiaobin Tang, Haiquan Su, Xianran Xing, Ling Huang, *Angew. Chem. Int. Ed.* **2023**, *62*, e202303482.

Exploring and Property Enhancing of Inorganic Functional Compounds

Ling Chen*
College of Chemistry, Beijing Normal University, Beijing 100875, People's Republic of China
E-mail: chenl@bnu.edu.cn

Our research primarily focuses on the exploratory syntheses of inorganic solid functional compounds, aiming to unravel the intricate relationships between crystallographic structures and their corresponding macroscopic properties, notably second-order nonlinear optical properties [1-5] or thermoelectric properties [6-10]. The examples are the first monofluorophosphates exhibiting excellent second-harmonic generation, [1, 2] and an inorganic solid state NLO switch material with a linearly tunable T_c. [3] Additionally, we have proposed a novel design theory based on *π conjugation confinement* structures for achieving deep ultraviolet second-harmonic generation compounds [4]. Furthermore, our investigations into chalcogenides have uncovered the band structure bucket effect that may offer a guideline for exploratory synthesis of novel chalcogenide with a desired band gap. [5]

We have also explored various thermoelectric compounds, such as $CsCu_5Se_3$, KCu_5Se_3, Ag_9GaSe_6, among others. Their complex crystallographic structures containing soft- and rigid-sublattices, or multiple coordination spheres of Cu^+, or the mixed valence states of selenium, ultimately lead to reduced lattice thermal conductivity. The interlayer π-bond interactions in Bi_8Se_7 have demonstrated a substantial increase in carrier mobility along the direction of structure stacking. [6-10].

References

[1] Lu, J.; Yue, J. N.; Xiong, L.; Zhang, W. K.; Chen, L.; Wu, L. M. Uniform Alignment of Non-π-Conjugated Species Enhances Deep Ultraviolet Optical Nonlinearity. *J. Am. Chem. Soc.* 2019, *141*, 8093−8097.

[2] Pan, C. Y.; Yang, X. R.; Xiong, L.; Lu, Z. W.; Zhen, B. Y.; Sui, X.; Deng, X. B.; Wu, L. M.; Chen, L. Solid-State Nonlinear Optical Switch with the Widest Switching Temperature Range Owing to Its Continuously Tunable Tc. *J. Am. Chem. Soc.* 2020, *142*, 6423−6431.

[3] Yang, Y. C.; Liu, X.; Zhu, C. F.; Zhu, L.; Wu, L. M.; Chen, L. Inorganic Solid-State Nonlinear Optical Switch with a Linearly Tunable *Tc* Spanning a Wide Temperature Range. *Angew. Chem. Int. Ed.* 2023, *62*, e202301404.

[4] Xiong, L.; Wu, L. M.; Chen, L. A General Principle for DUV NLO Materials: *π*-Conjugated Confinement Enlarges Band Gap. *Angew. Chem. Int. Ed.* 2021, *60*, 25063–25067.

[5] Liu, Q. Q.; Liu X.; Wu, L. M.; Chen, L. $SrZnGeS_4$: A Dual-Waveband Nonlinear Optical Material with A Transparency Spanning UV–Vis and Far-IR Spectral Regions. *Angew. Chem. Int. Ed.* 2022, *61*, e202205587.

[6] Jia, F.; Liu, Y. Y.; Zhang, Y. F.; Shu, X.; Chen, L.; Wu, L. M. Bi_8Se_7: Delocalized Interlayer π Bond Interactions Enhancing Carrier Mobility and Thermoelectric Performance Near Room Temperature. *J. Am. Chem. Soc.* 2020, 142, 12536−12543.

[7] Ma, N.; Li, Y. Y.; Chen, L.; Wu, L. M. α-$CsCu_5Se_3$: Discovery of a Low-Cost Bulk Selenide with High Thermoelectric Performance. *J. Am. Chem. Soc.* 2020, 142, 11, 5293-5303.

[8] Ma, N.; Li, F.; Li, J. G.; Liu, X.; Zhang, D. B.; Li, Y. Y.; Chen, L.; Wu, L. M. Mixed-Valence $CsCu_4Se_3$: Large Phonon Anharmonicity Driven by the Hierarchy of the Rigid $[(Cu^+)_4(Se^{2-})_2](Se^-)$ Double Anti-CaF_2 Layer and the Soft Cs^+ Sublattice. *J. Am. Chem. Soc*. 2021, 143, 18490−18501.

[9] Li, F.; Liu, X.; Ma, N.; Yang, Y. C.; Yin, J. P.; Chen, L.; Wu, L. M. Overdamped Phonon Diffusion and Nontrivial Electronic Structure Leading to a High Thermoelectric Figure of Merit in KCu_5Se_3. *J. Am. Chem. Soc.* 2023, *145*, 14981−14993.

[10] Liu, J. Y.; Chen. L.; Wu, L. M. Ag_9GaSe_6: High-Pressure-Induced Ag Migration Causes Thermoelectric Performance Irreproducibility and Elimination of Such Instability. *Nat. Commun.* 2022, 13, 2966.

Exploratory Synthesis of New Down-Conversion (Oxy)nitride Phosphors

Xiao-Ming Wang*

[1] *Shaanxi Normal University, School of Chemistry & Chemical Engineering, Xi'an 710062, P. R. China.*

Corresponding author: xmwang@snnu.edu.cn

(Oxo)nitridosilicates are famous for their broad diversity of structure, excellent physics and chemical stability, as well as red-shifted emission in phosphor-converted light emitting diodes (pc-LEDs). For example, the mainstream red phosphors Eu^{2+}-doped $M_2Si_5N_8$ (M = Ca, Sr, Ba) and CaAlSiN3. From a structural perspective, compared to oxosilicates, which primarily consist of SiO_4 tetrahedra featuring either terminal $O^{[1]}$ or bridging $O^{[2]}$ atoms, (oxo)nitridosilicates are predominantly composed of $Si(O/N)_4$ tetrahedra, with $N^{[1]}$, $N^{[2]}$, $N^{[3]}$, and $N^{[4]}$ atoms bridging as many as four adjacent tetrahedral centers. This variability allows for a wide range of additional structural possibilities. However, the number of (oxo)nitridosilicate is still relatively small compared to the oxosilicates. One reason is the challenging synthesis conditions for nitride compounds, and another reason is the lack of deep understanding of (oxo)nitridosilicate structural traits.

Predicting the outcome of a solid-state reaction is difficult, but elucidating (oxo)nitridosilicate structure feature can help us think logically about where to look for new compounds. In this report, we used **Chemical Unit Substitution** and **Anionic Condensation** strategies to explore some new oxonitridosilicates phosphors. The chemical unit substitution strategy lies in the fact that the structural building blocks are replaced, but the structure framework remains unchanged. For example, taking $Ba_3Al_2O_6$ as the template, replacing the $[AlO]^+$ with $[SiN]^+$, $Ba_3Al_2O_6$ could be transformed into $M_3Si_2O_4N_2$ (M = Ca, Sr). The anionic condensation strategy means substituting $3O^{2-}$ with $2N^{3-}$ in oxonitridosilicate and keeping the compound charge balance during the process. As a result, the number of anions in the final structure decreases, forcing the framework to rearrange and form a new structure, as shown in Fig. 1. The luminescent properties of these new types of oxonitridosilicates phosphors have also been studied accordingly.

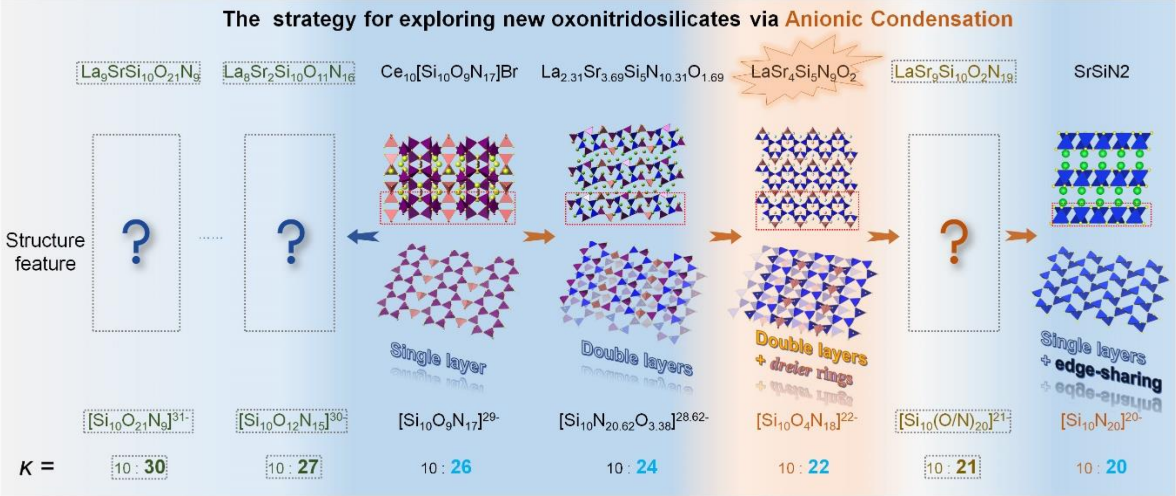


Fig 1. The strategy for exploring new oxonitridosilicates via anionic condensation.

Acknowledgements: This project is funded by the National Natural Science Foundation of China (22271180，51972203 and 201371015)

References

[1] R.X. Li, X.M. Wang, S.R. Zhang, X. Gu, Z.P. Yang, H. Jiao, *Chem. Commun.*, **2022**, 58, 4739-4742.

[2] H.W. Zheng, X.M. Wang, H.W. Wei, Y. Zheng, C.L. Yin, Z.P. Yang, H. Jiao, *Chem. Commun.*, **2021**, 57, 3761-3764.

Development of Solid-State Li-ion and Metal-Air Batteries

Ru-Shi Liu*

Department of Chemistry, National Taiwan University, Taipei, Taiwan

Corresponding author: rsliu@ntu.edu.tw

To reach carbon neutrality before 2050, 80% of fossil fuels will be replaced by renewable energy to decrease CO_2 emissions. In energy substitution, energy storage devices, such as Li-ion batteries, are widely used in the smart grid and electric cars. After 30 years of development, the energy density of Li-ion batteries reaches 300 mAh kg^{-1}. Solid-state Li-ion batteries are studied intensively for a high energy density of 500 mAh kg^{-1} before 2030. In a solid-state battery, solid-state electrolyte is essential in improving electrochemical performance. In this report, an development on solid-state electrolytes will be introduced.[1-4] Different rechargeable metal-Air batteries have caught much attention as one of the most intriguing methods that could simultaneously address carbon dioxide-related environmental concerns and ever-increasing sustainable energy storage demands. We will also introduce these types of batteries and give prospects compared to solid-state Li-ion batteries.[5-7]

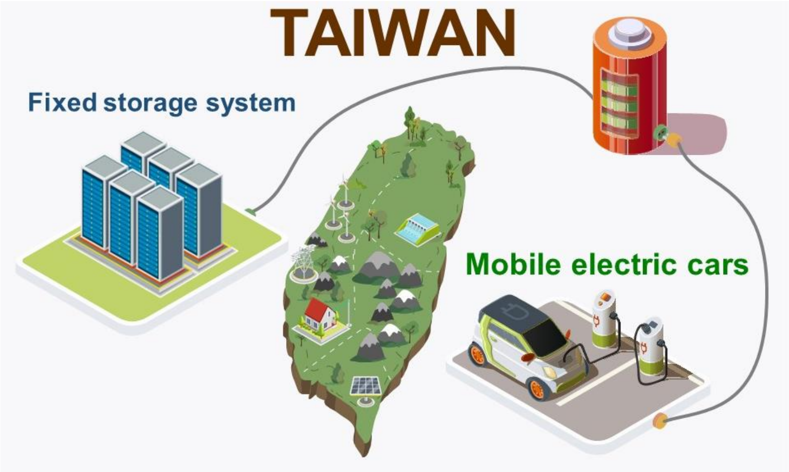


Figure. The strategy of Taiwan to development of batteries.

Acknowledgments: This work was financially supported by the National Science and Technology Council in Taiwan with the contrast number NSTC 109-2113-M-002-020-MY3.

References

[1] Z. Z.Tong, B. Bazri, S. F. Hu, R. S. Liu, *J. Mater. Chem. A* **2021**, *9*, 7396.

[2] Y. Meesala, Y. K. Liao, A. Jena, N. H. Yang, W. K. Pang, S. F. Hu, H. Chang, C. E. Liu, S. C. Liao, J. M. Chen, X. Guo, R. S. Liu, *J. Mater. Chem. A* **2019**, 7, 8589.

[3] A. Jena, Y. Meesala, S. F. Hu, H. Chang, and R. S. Liu, *ACS Energy Lett.* **2018**, 3, 2775.

[4] Y. Meesala, A. Jena, H. Chang, and R. S. Liu, *ACS Energy Lett.* **201**7, 2, 2734.

[5] K. Iputera, J. Y. Huang, S. C. Haw, J. M. Chen, S. F. Hu, R. S. Liu, *J. Mater. Chem. A* **2022**, 10, 3460.

[6] Z. Tong, S. B. Wang, M. H. Fang, Y. T. Lin, K. T. Tsai, S. Y. Tsai, L. C. Yin, S. F. Hu, R. S. Liu, *Nano Energy* **2021**, *85*, 105972.

[7] S.Thoka, Z.Tong, A. Jena, T. F. Hung, C. C. Wu, W. S. Chang, F. M. Wang, X. C. Wang, L. C. Yin, H. Chang, S. F. Hu, and R. S. Liu, *J. Mater. Chem. A* **2020**, 8, 23974.

Atomic Pinning Mitigates Voltage Decay in Li-Rich Mn-Based Layered Oxide Cathode

Yang Ren,[1*] Qi Liu[1*]
[1] *Department of Physics, City University of Hong Kong, Hong Kong, China.*
Corresponding author: yangren@cityu.edu.hk, qiliu63@cityu.edu.hk

Li- and Mn-rich (LMR) layered cathodes have higher capacities than those of existing commercial cathodes for Li-ion batteries (LIBs)[1]. However, LMR cathodes suffer from voltage decay, which hinders their commercialization. During battery operation, the discharge voltage of LMR cathodes decreases, leading to a rapid decrease in the energy density and causing problems for battery management systems. Researchers have used various strategies to tackle this problem, such as surface coating, doping, and defect or interfacial engineering. But the issue of voltage decay remains unsolved[2].

Here we report a Co-free LMR Li-ion battery cathode with negligible voltage decay. The material has a composite structure consisting of layered $LiTMO_2$ and various stacked Li_2MnO_3 components, where transition metal (TM) ions that reside in the Li layers of Li_2MnO_3 form caps to strengthen the stability of the honeycomb structure. This capped-honeycomb structure is persistent after high-voltage cycling and prevents TM migration and oxygen loss as shown by experimental and computational results. This work demonstrates that the long-standing voltage decay problem in LMRs can be effectively mitigated by internally pinning the honeycomb structure, which opens an avenue to developing next-generation high-energy cathode materials.

Acknowledgements: National Key R&D Program of China (2020YFA0406203), the Shenzhen Science and Technology Program (Project No. JCYJ20220818101016034, SGDX2019081623240948), the General Research Fund (GRF) scheme (CityU 11220322), CityU 9610533 and the Shenzhen Research Institute, City University of Hong Kong are acknowledged for the financial support.

References

[1] Zheng, J. et al. *Adv. Energy Mater.* **2017**, **7**, 1601284.
[2] Liu, T. et al. *Nature* **2022**, 606, 305–312.
[3] Luo, D., Zhu, H., Xia, Y. et al. *Nat Energy* **2023**. https://doi.org/10.1038/s41560-023-01289-6.

Construction of Materials and Devices for Metal-air Batteries

Ji-Jing Xu*

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China

Metal-air batteries owning 2-10 times the energy density of lithium-ion batteries, combining with the advantages of both rechargeable batteries and fuel cells, are considered to be the preferred scheme to solve the increasingly serious energy and environmental issues at present. However, a series of challenges including the slow reaction kinetics of cathode, electrolyte decomposition, lithium dendrites on anode still exist in the battery system, which restricts its practical performance and industrial application. As for these problems, our group have focused on the following researches: (1)We have proposed the new concept of "porous material-based solid-state electrolyte", and constructed a series of novel porous materials-based solid-state electrolytes to improve the stability of solid electrolytes, further revealed the "molecular channel transport" mechanism of lithium-ion, and solved the problem of electrolyte volatilization/decomposition in liquid metal-air batteries and poor electrolyte stability in solid-state batteries to achieve the solid metal-air battery device with high safety and stability; (2) We have proposed a novel outfield-assisted strategy to improve the reaction kinetics of metal-air batteries in the worldwide, and developed a variety of "external field assisted" cathode materials, revealed the enhanced mechanism of outfields on the reaction kinetics for cathode, and further built the high-performance outfield-assisted metal-air battery devices.

Acknowledgements: The National Natural Science Foundation of China (No. 51972141, 21835002, 21621001) is acknowledged for the financial support.

References

[1] Xiwen Chi, Malin Li, Jiancheng Di, Pu Bai, Lina Song, Xiaoxue Wang, Fei Li, Shuang Liang, Jijing Xu*, and Jihong Yu*, *Nature* **2021**, *592*, 551–557.

[2] Xiao-Xue Wang, Li-Na Song, Li-Jun Zheng, De-Hui Guan, Cheng-Lin Miao, Jia-Xin Li, Jian-You Li, Ji-Jing Xu*, *J. Am. Chem. Soc.* **2023**, *145*, 5718–5729.

[3] Xiao-Xue Wang, De-Hui Guan, Cheng-Lin Miao, De-Chen Kong, Li-Jun Zheng, and Ji-Jing Xu*, *Angew. Chem. Int. Ed.* **2023**, *62(37)*, e202308837.

[4] Li-Jun Zheng, Li-Na Song, Xiao-Xue Wang, Shuang Liang, Huan-Feng Wang, Xing-Yuan Du, and Ji-Jing Xu*, *Angew. Chem. Int. Ed.* **2023**, DOI:10.1002/anie.202311739.

[5] Fei Li, Ma-Lin Li, Huan-Feng Wang, Xiao-Xue Wang, Li-Jun Zheng, De-Hui Guan, Li-Min Chang, Ji-Jing Xu*, and Yu Wang, *Adv. Mater.* **2022**, *34*, 2107826.

[6] Xiao-Xue Wang, De-Hui Guan, Fei Li, Ma-Lin Li, Li-Jun Zheng, and Ji-Jing Xu*, *Adv. Mater.* **2022**, *34*, 2104792.

[7] Guan-Yu Qiao, Dehui Guan, Shuai Yuan, Heng Rao, Xiao Chen, Jia-Ao Wang, Jun-Sheng Qin*, Ji-Jing Xu*, and Jihong Yu*, *J. Am. Chem. Soc.* **2021**, *143*, 14253-14260.

[8] Li-Na Song, Wei Zhang, Ying Wang Xin Ge, Lian-Chun Zou, Huan-Feng Wang, Xiao-Xue Wang, Qing-Chao Liu, Fei Li, and Ji-Jing Xu*, *Nat. Commun.* **2020**, *11*, 2191.

[9] De-Hui Guan, Xiao-Xue Wang, Ma-Lin Li, Fei Li, Li-Jun Zheng, Xiao-Lei Huang, and Ji-Jing Xu*, *Angew. Chem. Int. Ed.* 2020, 59, 19518-19524.

[10] Ma-Lin Li, Xiao-Xue Wang, Fei Li, Li-Jun Zheng, Ji-Jing Xu*, and Ji-Hong Yu*, *Adv. Mater.* **2020**, *32*, 1907098.

Enhancing/Suppressing Electronic and Ionic Conductivity in Metal Oxides

Ming Li*
Advanced Materials Research Group, Faculty of Engineering, University of Nottingham
University Park, Nottingham, NG7 2RD, United Kingdom.
Corresponding author: ming.li@nottingham.ac.uk

The electrical conductivity and conduction mechanisms of metal oxides are often very sensitive to low levels of nonstoichiometry (typically <1 at%) that is associated with either impurities in raw materials or deliberate chemical doping or 'accidental' element loss/gain during sample processing. As such metal oxides often exhibit complex electrical behaviours involving different types of charge carriers (e.g., electrons, holes, ions) and inhomogeneity in different regions (e.g., grains, grain boundaries, surface layers). Understanding the electrical conduction mechanisms and defect chemistry is crucial to design new materials and improve the performance of existing materials for a variety of electronic and electrochemical applications. In this presentation two examples will be discussed:

1) How to suppress both oxide ion conductivity and electronic conductivity in perovskite oxide $BaTiO_3$ for high-temperature, high-voltage dielectric applications (e.g., multilayer ceramic capacitors)

2) How to achieve extremely high electronic conductivity (~10,000 S/cm at room temperature) in perovskite oxides.

Rattling Effect: A New Mechanisms for Tuning Temperature Stability of Microwave Dielectric Ceramics

Ying Tang[1], Liang Fang[2, *], Huaicheng Xiang[1], Jie Li[2]
1 College of Science, Guilin University of Technology, Guilin 541004, China
2 College of Materials Science and Engineering, Guilin University of Technology, Guilin, 541004, China
Email: tangyinggl001@aliyun.com

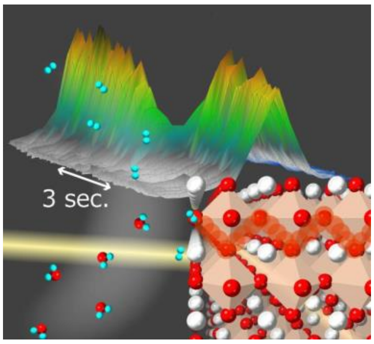
Microwave dielectric ceramics (MWDCs) play a key role in wireless communication devices with a wide range of applications from resonators, filters, GPS to WLAN and so on. There are three prime requirements to judge microwave properties: the suitable dielectric constant ε_r, the high quality factor Q, and the stable temperature coefficient of resonant frequency (τ_f). With the rapid development of 5G communications, low-ε_r materials could be minimized cross coupling with conductors and shorten the time for electronic signal transition. However, most low-ε_r dielectric materials have larger negative τ_f, which results in the temperature instability of the corresponding microwave devices and therefore unacceptable for practical application. Recently, the τ_f values changed from negative to positive value were found in the normal-inverse garnet ceramics with no phase-transition, and the dominant mechanisms responsible for tuning τ_f (phase transition and dilution of ionic polarizability) could not be explained. Based on structure refinements, bond valence and Raman spectrum, we firstly revealed and proposed that the rattling effect might be a new mechanism for tuning τ_f value in dielectric materials, which also have been confirmed in some dielectric materials systems. This finding would be provided a new idea for developing solid solution ceramics with excellent temperature stability, and the precise control of τf is still challenging, and this mechanism needs to be further studied.

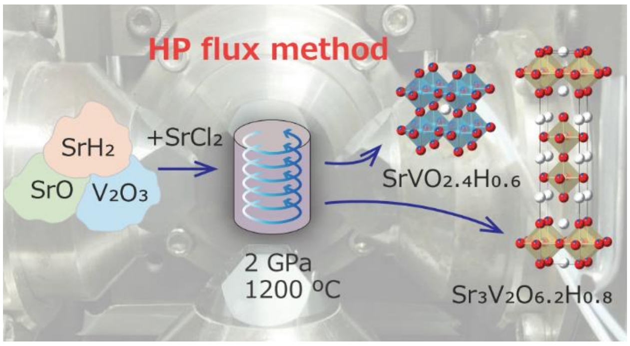
Determination of the Reaction Pathways for Designing Solid-State Compounds

Takafumi Yamamoto [1*]
[1] *Laboratory for Materials and Structures, Institute of Innovative Research, Tokyo Institute of Technology,*
Yokohama, Kanagawa 226-8503, Japan.
Corresponding author: yama@msl.titech.ac.jp

Understanding the mechanisms behind chemical reactions is one of the biggest issues in materials chemistry since this makes it possible to create compounds with the desired structures or to optimize reactions toward functional uses. However, reactions in solid-state crystalline compounds are rather poorly understood compared with molecular reactions whose steps have been well analyzed.

Here, I show the recent progress in revealing the reaction pathways for designing solid-state compounds. One example is time-resolved synchrotron X-ray techniques that reveal the fast topochemical solid-gas reduction mechanisms in layered perovskite $Sr_3Fe_2O_{7-\delta}$ (from $\delta \sim 0.4$ to $\delta = 1.0$) [1]: We found that the reaction process can indeed be manipulated by using a surface treatment to control the rate-determining step in the crystalline material. This indicates that metastable phases, which cannot be reached from a pristine sample, will be synthesized by the reduction of the surface-modified sample with appropriate temperature control. The other example is in-situ synchrotron XRD measurements that reveal the reaction pathways of oxyhydrides synthesized under high-pressure and high temperature [2]: We found that the addition of the $SrCl_2$ flux promotes diffusion during high-pressure and high-temperature reactions and can be used as a selective synthesis of the oxyhydride phases. We believe that our approaches are effective in designing new solid-state compounds.





Acknowledgments: The Grant-in-Aid for Transformative Research Areas (A) “Supra-ceramics” (JSPS KAKENHI Grant Numbers JP22H05147) and JSPS KAKENHI Grant Numbers JP22H01767 is acknowledged for the financial support.

References

[1] T. Yamamoto, et al, *Adv. Sci*. **2023**, 10, 2301876.
[2] J. Suzuki, T. Yamamoto et al, *J. Am. Chem. Soc*., accepted (https://doi.org/10.1021/jacs.3c02240)

Amorphous-nanocrystalline Al-based Alloys with Improved Characteristics

Valerii Sidorov[1*], Boris Rusanov[1], Anastasija Rusanova[2],
Alexander Sabirzyanov[3], Valentin Perevishin[4]
[1]*Ural State Pedagogical University, Ekaterinburg, Russia,*
[2]*Institute of Metallurgy UB RAS, Ekaterinburg, Russia,*
[3]*Ural State University of Railway Transport, Ekaterinburg, Russia,*
[4]*Ural Federal University, Ekaterinburg, Russia.*
Corresponding author: sidorov@uspu.ru

Amorphous Al-TM-REM alloys are becoming more and more popular nowadays due to their low specific gravity, ultrahigh strength and corrosion resistance. At the first stage of crystallization of these alloys, aluminum nanoparticles appear in amorphous matrix, and if this state is "stabilized", the alloys exhibit unique mechanical properties. It turned out that this can be done by applying special heat treatment of the melt before quenching. The regime of such treatment can be proposed on the basis of measuring physical and chemical properties of the alloys in liquid state.

This report presents the results of measuring density, viscosity, electrical resistivity and magnetic susceptibility of Al-Ni-Co-REM alloys with tendency to amorphization in crystalline and liquid states. Density was determined by gamma-penetration method; viscosity - by torsion oscillation method; electrical resistivity - by contactless method in rotating magnetic field, and magnetic susceptibility - by the Faraday's method.

It has been found that the alloys remain microheterogeneous in liquid state, as evidenced by nonlinear form of properties temperature dependences, and only at temperatures above $T = 1300–1350$ K the polytherms can be fitted by linear functions. Upon subsequent cooling, density and viscosity hysteresis below 1300 K were recorded. However, no hysteresis was found in resistivity and susceptibility polytherms.

According to the results obtained, a regime of melts heat treatment before quenching was proposed, and high-quality amorphous ribbons were prepared by spinning method. Structure and crystallization kinetics of amorphous ribbons were studied using X-ray diffraction, high-resolution transmission electron microscopy, differential scanning calorimetry, and electrical resistivity measurements using the four-probe AC method.

It is shown that Al-Ni-Co-REM alloys are characterized by 3–4 crystallization stages and have a higher thermal stability of the amorphous state compared to Al-Ni-REM and Al-Co-REM ternary compositions. At the first stage of crystallization, regardless of nickel/cobalt ratio in the composition, fcc-Al nanoparticles are separated. Further heating of the alloys and transition to the second stage of crystallization is associated with the continued growth of these nanoparticles. However, a detailed analysis of the alloys structure using high-resolution transmission electron microscopy made it possible to associate the second stage of crystallization with the appearance of ternary intermetallic compounds $Al_{19}Ni_5REM_3$ ($Al_{23}Ni_6REM_4$) (see, for example, [1]). These compounds are formed along the boundaries of aluminum nanoparticles, inhibiting their further growth. Thus, it becomes possible to "stabilize" the nano-structured state of Al-Ni-Co-REM alloys by applying a special heat treatment of the melts before quenching.

Acknowledgements: Russian Science Foundation (No. 22–23–00177) is acknowledged for the financial support.

References

[1] P. Svec, B. Rusanov, A. Moroz et al. *JALCOM*, **2021**, *876*, 160109.

Large Magnetovolume Effect in a Cobaltite Perovskite

Ping Miao
[1]*Institute of High Energy Physics, Chinese Academy of Sciences, China*
[2]*Spallation Neutron Source Science Center, China*
Corresponding author: miaoping@ihep.ac.cn

Materials that show negative thermal expansion (NTE) have significant industrial merit because they can be used to fabricate composites whose dimensions remain invariant upon heating. In some materials, NTE is concomitant with the spontaneous magnetization due to the magnetovolume effect (MVE). Here we report a new class of MVE material; namely, an A-site ordered perovskite $PrBaCo_2O_{5.5+x}$ ($0 \leq x \leq 0.41$), in which strong NTE is induced by hole doping [1]. Through a comprehensive study with multiple probes, in particular neutron diffraction under variant temperatures, hydrostatic pressures and magnetic fields, we found the MVE originates from an magnetoelectric transition from an antiferromagnetic insulating large-volume (AFILV) phase to a ferromagnetic less-insulating small-volume (FLISV) phase (see Figure 1) [2, 3]. Based on the mechanism, we further modified the thermal expansion properties in the A-site disordered $La_{0.5}Ba_{0.5}CoO_{3-x}$, which crystallizes into a cubic structure and features the isotropic thermal expansion. Room-temperature zero thermal expansion has been finally achieved in this simple cubic perovskite, which holds high potential for practical applications [4, 5].

References

[1] P. Miao, X. Lin, A. Koda, S. Lee, Y. Ishikawa, S. Torii1, M. Yonemura, T. Mochiku, H. Sagayama, S. Itoh, Y. Wang, R. Kadono and T. Kamiyama, (2017). *Adv. Mater.* **29**, 1605991

[2] Z. Tan, P. Miao, X. Lin, S. Lee, Y. Ishikawa, M. Hagihala, S. Torii, Y. Wang, M. Yonemura and T. Kamiyama, (2018). *Physica B*, **551**, 111

[3] P. Miao, Z. Tan, S. Lee, Y. Ishikawa, S. Torii, M. Yonemura, A. Koda, K. Komatsu, S. Machida, A. Sano-Furukawa, T. Hattori, X. Lin, K. Li, T. Mochiku, R. Kikuchi, C. Kawashima, H. Takahashi, Q. Huang, S. Itoh, R. Kadono, Y. Wang, F. Pan and T. Kamiyama, (2021). *Phys. Rev. B* **103**, 094302

[4] Z. Tan, P. Miao, Y. Ishikawa, M. Hagihala, S. Lee, S. Torii, M. Yonemura, T. Moyoshi and T. Kamiyama, (2018). *Atom Indonesia* **44**, 49

[5] Z. Tan, P. Miao*, Y. Ishikawa, M. Hagihala, S. Lee, S. Torii, M. Yonemura, T. Moyoshi and T. Kamiyama, (2020). *J. Phys. Chem. Lett.* **11**, 6785

Oxide Ion-Conducting Materials Containing Tetrahedral Moieties: Structures & Conduction Mechanisms

Alberto J. Fernández Carrión,[1,2] Xiaoyan Yang,[1] , Xiaojun Kuang[1*]
[1] *College of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, P. R. China.*
[2] *Departamento de Química Inórganica. Universidad de Sevilla, Spain*
Corresponding author: kuangxj@glut.edu.cn

Solid-state oxide ion conductors are key for technology applications, particularly in solid oxide fuel cells (SOFCs) where they enable efficient conversion of chemical energy into electricity. To achieve high current densities and oxide ion conductivity for SOFCs, materials featuring oxide ion conductivities above 10^{-2} S cm^{-1} at intermediate temperatures (500-600 °C) are required. High oxide ion mobility depends on specific crystal structural features, with oxide ion conduction occurring through defects like vacancies or interstitials in crystalline materials. Thus, understanding the stabilization of these defects and the underlying mechanisms of oxide ion conduction is crucial for designing new materials that can operate at lower temperatures.

In this contribution, a set of ion-conducting compounds containing tetrahedral moieties in their crystal structure will be presented. The interest in these compounds lies in the flexibility of tetrahedral units, which promotes oxide ion migration. Emphasis will be devoted to examining these materials and gaining a comprehensive understanding of the role of tetrahedral units in oxide ion migration. This understanding is essential for revealing potential advancements in electrolytes for Solid Oxide Fuel Cells (SOFCs) and related devices.

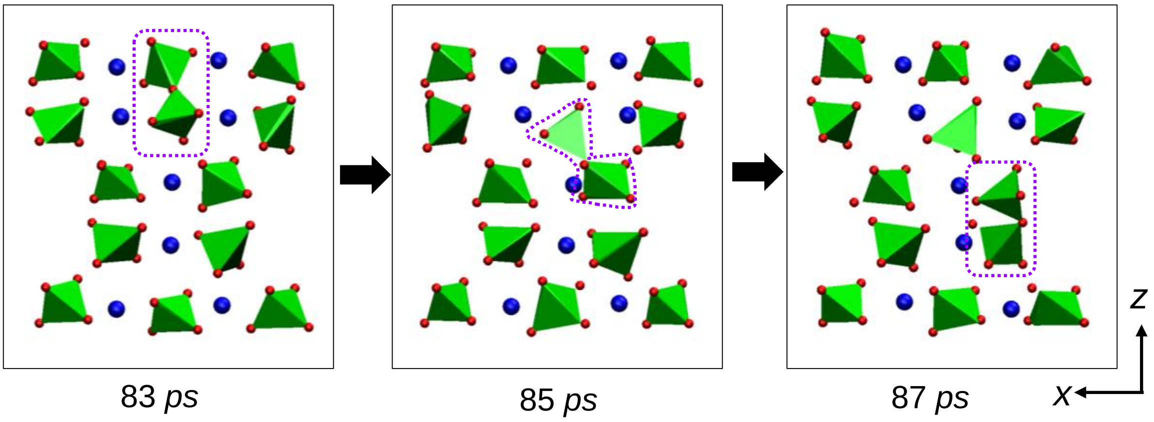


Figure 1. Oxide vacancy migration in the scheelite structure, representing a case of a solid-state electrolyte demonstrating the stabilization and transportation of oxygen vacancies throughout the structure

Acknowledgements: The National Natural Science Foundation of China (No. 22090043, 21622101, 21850410458, 22005073) and Guangxi Natural Science Foundation (no. 2019GXNSFGA245006, 2019GXNSFBA245010, 2020GXNSFAA297050) are acknowledged for the financial support.

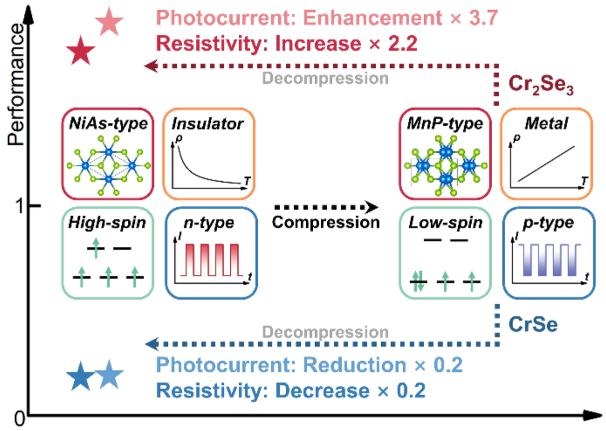
References

[1] X. Yang, A.J. Fernández Carrión, X. Kuang. *Chem. Rev.* **2023**, 123, 9356-9396.

Pressure-Driven Multistate Switching in NiAs-Type Transition Metal Chalcogenides

Chen Li,[1,2] Yonggang Wang[1,2*]
[1] *School of Materials Science and Engineering, Peking University, Beijing 100871, China*.
[2] *Center for High Pressure Science and Technology Advanced Research (HPSTAR), Beijing 100193, China*.
Corresponding author: ygw@pku.edu.cn

NiAs-type compounds tend to undergo phase transitions to MnP-type structures under external stimuli such as temperature and pressure, which accompanied by numerous changes in physical properties.[1] Among them, a class of NiAs-type defective compounds with periodic metal vacancies, represented by $Cr_{1-x}Te$, have different physical properties due to the various vacancy concentrations.[2] Herein, we summarize the structural and physical property transformations of three types of transition metal chalcogenides under pressure. Concomitant with the typical NiAs-to-MnP phase transition, the materials undergo pressure-driven multiple switching in physical properties, including insulator-metal transition, spin-crossover, and *n*-*p* conduction-type switching. In addition, due to the structural discrepancy between NiAs-type and NiAs-type defective compounds, pressure treatment has opposite effects on their optoelectronic properties. Such NiAs-type transition metal chalcogenides capable of multistate switching shed light on designing novel multifunctional responsive devices.



Acknowledgements: This work was supported by the Major Program of the National Natural Science Foundation of China (22090041), the National Natural Science Foundation of China (52073003), and the National Key R&D Program of China (2018YFA0305900).

References

[1] K. Selte, A. Kjekshus, A. F. Andresen, Å. Pilotti, S. Svensson, C.-G. Swahn, *Acta Chem. Scand., Ser. A*, **1973**, *27*, 3195.
[2] H. Ipser, K. L. Komarek, K. O. Klepp, *J. Less-Common Met.*, **1983**, *92*, 265.

Crystal Structure Determination from Weak/Extra Reflections in Powder Diffraction Pattern

Chun-Hai Wang[1*]

[1] *The School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, China.*

Corresponding author: chwang81@gmail.com

Crystal structure refinements and crystal structure determinations from powder diffraction data are widely used in the research of solid-state chemistry. Sometimes, weak/extra reflections (e.g., $I/I_{max} < 3\%$) are observed in the pattern that deviates from the calculated curve based on the proposed structure model. These reflections are often considered as "impurity" reflections. With careful experimental control during sample synthesis and high-quality diffraction measurements (e.g., synchrotron X-ray diffraction, neutron diffraction, diffraction with high-brightness X-ray source and/or high-sensitivity detector), the "intrinsic" weak/extra reflections can be identified. These reflections generally arise from long-range structure distortion/ordering, which can be described using a large "supercell" structure model. However, solving the additional structure parameters in the supercell through random refinements can be challenging. The crystal structure distortion can be determined using the DISTORTION method based on group theory [1,2], which effectively avoids overparameterization and improves reliability. For example, in the case of $SrUO_{4-x}$, we successfully solved the structure distortion (ordering of deficient oxygen) from reflections as weak as $I/I_{max} < 0.1\%$ [3]. On the other hands, the high intensity microbeam single crystal diffraction technique enables a way to determine the crystal structures with weak reflections from selected micro particles in well crystallized powder samples [4,5].

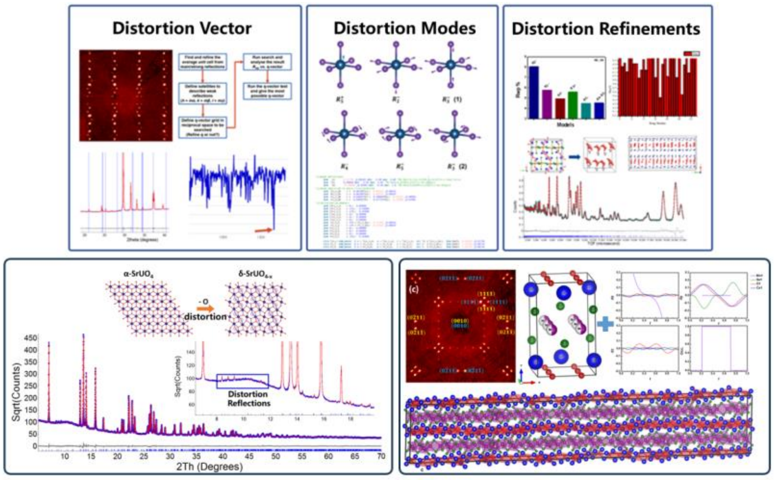


Fig.1 Distortion analysis and examples of crystal structure determination from weak reflections

Acknowledgements: The National Natural Science Foundation of China (No. 22075229) is acknowledged for the financial support.

References

[1] S. Kerman, B. J. Campbell, K. K. Satyavarapu, H. T. Stokes, F. Perselli, J. S. O. Evans, *Acta Crystallogr. A* **2012**, 68: 222.

[2] D. Orobengoa, C. Capillas, M. I. Aroyo, J. M. Perez-Mato, *J. Appl. Crystallogr.* **2009**, 42: 820.

[3] G. L. Murphy, C.-H. Wang, G. Beridze, Z. Zhang, J. A. Kimpton, M. Avdeev, P. M. Kowalski, B. J. Kennedy, Inorg. Chem. **2018**, 57(10): 5948.

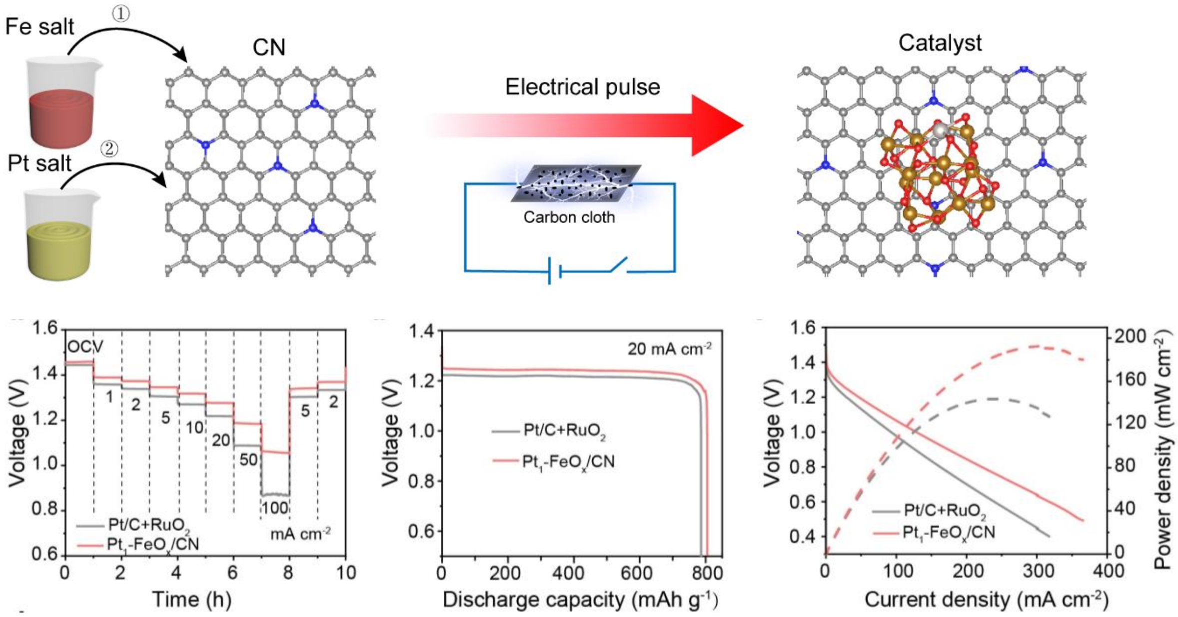
[4] C.-H. Wang, C. M. Ainsworth, D.-Y. Gui, E. E. McCabe, M. G. Tucker, I. R. Evans, J. S. O. Evans, *Chem. Mater.* **2015**, 27(8): 3121.

[5] X.-Y. Feng, C.-H. Wang, H. Pan, Z. Ji, X.-M. Wang, L. Fang, and F. Luo, *J. Phys. Chem. C*, **2022**, 126: 18466.

Electrical Pulse Induced One-step Formation of Atomically Dispersed Pt on Oxide Clusters for Ultra-Low-Temperature Zinc-Air Battery

Chenliang Ye,[1] Meng Zheng,[2] Zhiming Li, Jin Wang [1*]， Yadong Li [2*]
[1] *College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China.*
[2] *Department of Chemistry, Tsinghua University, Beijing, 100084, China.*
Corresponding author: wangjin19@szu.edu.cn, ydli@mail.tsinghua.edu.cn

Atomic sites anchored on small oxide clusters is an attractive new catalytic material. Herein, we report an electrical pulse approach to synthesize atomically dispersed Pt on various oxide clusters in one step within ~1 s with nitrogen-doped carbon as the support (Pt_1-MO_x/CN). As a proof-of-concept application, Pt_1-FeO_x/CN is shown to exhibit high activity for oxygen reduction reaction (ORR) with a half-wave potential of 0.94 V vs RHE, in contrast to the poor catalytic performance of atomically dispersed Pt on large Fe_2O_3 nanoparticles. Our work has revealed that, by tuning the size of the iron oxide down to the cluster regime, an optimal OH* adsorption strength for ORR is achieved on Pt_1-FeO_x/CN due to the regulation of Pt-O bonds. The unique structure and high catalytic performance of Pt_1-FeO_x/CN enable the Zinc-Air batteries an excellent performance at ultralow temperature of －40 °C with a high peak power density of 45.1 mW cm^{-2} and remarkable cycling stability up to 120 h



Schematic illustration of synthesis of Pt_1-FeO_x/CN and its electrochemical performance in ZABs

Acknowledgements: This work was supported by National Key R&D Program of China (2021YFA1600800) and National Natural Science Foundation of China (22022508).

References

[1] Ye Chenliang, Zheng Meng, Li Zhiming, Fan Qikui, Ma Haiqing, Fu Xianzhu, Wang Dingsheng, Wang Jin*, Li Yadong*, *Angew Chem Int Ed*. **2022**, *61(51), e202213366*.

Chemical Regulation of Functional Composite Solids

Qian Zhu,[1] Zhiyu Shao,[1] Xiaofeng Wu,[1] Keke Huang[1*],Shouhua Feng[1]
[1] *Jilin University, Changchun, Jilin, 130012.*
E-mail: kkhuang@jlu.edu.cn

Chemical composites can break through the performance bottleneck of a single material, which is an important strategy in the current search for efficient functional solids. Changes such as charge transfer and orbital coupling occur after the composite of solids, which can realize the enhancement of the original function of the material or even generate new functions. Optimization of the electronic state of the composite phase is considered to be the fundamental reason for enhancing the performance of functional materials. However, the precise synthesis of composite solids to establish well-defined conformational relationships remains a central issue in the current research field of solid state chemistry.

In terms of synthesis, functionally enhanced perovskite composite solids with different compositions, such as $RuO_2/La_{0.9}Fe_{0.92}Ru_{0.08-x}O_{3-\delta}$ and $CoFe/La_{0.9}FeO_3$, have been successively constructed by constructing defects and doping [1][2]. Further, $CoFe/La_{0.8}Fe_{0.9}Co_{0.1}O_{3-\delta}$ functional composite solids were synthesized by modulating the defects and exsolution temperature of perovskite oxides[3]. In the study of $FeNi/NiFe_2O_4$ exsolution, the mechanism of preferential breaking of octahedral metal-oxygen bonds during spinel exsolution was found [4]. In addition, the α-FeOOH/NiOOH composite structure was constructed by building a composite phase to change the overall electronic state, which induced a change in the electronic state of NiOOH for high-efficiency UOR and OER [5], and $NiS/NiFe_2O_4$ composites were prepared by utilizing a plasma-induced phase reconstruction method, which resulted in the formation of a short-range ordered NiS structure, which changed the overall electronic state of the composite [6]. For orbital modulation, we synthesized Cu/TiO_2 using hydrothermal-photodeposition method, and achieved highly selective CO_2 photoreduction reaction by adjusting the composite degree for the modulation of Ti-t_{2g} orbital occupation in TiO_2 [7]. Regarding the modulation of charge transfer, by constructing Cu/Cu_2O in situ, we explored the linear relationship between the composite degree of the two phases on the charge transfer between them and on the catalytic activity [8].

In the next step, we will continue to develop innovative synthetic methods to achieve a quantitative description of the complexity of inorganic functional composite solids. With the help of large scientific devices and advanced characterization means, such as high-energy synchrotron X-ray, neutron diffraction/scattering, and density-functional theory simulations, we will explore the effect of the complexity on the overall electronic state and its relationship with the catalytic activity, discover the essential structure-function relationship of functional composite solids and promote the further development of inorganic solid chemistry.

Keywords: solid functional materials; composites; exsolution

References

[1] Jiang, Y.; Huang, K.; Feng, S. *et al. ACS Sustainable Chem. Eng.*, 2018, 6, 11999-12005.
[2] Jiang, Y.; Huang, K.; Feng, S. *et al. ACS Sustainable Chem. Eng.*, 2020, 8, 302-310.
[3] Cong, Y.; Geng, Z.; Huang, K.; Feng, S. *et al. Angew. Chem. Int. Ed.*, 2021, 60, 23380.
[4] Guo, X.; Yao, L.; Huang, K.; Feng, S. *et al. Chem. Sci.*, 2022, 13, 9440.
[5] Cai, M.; Zhu, Q.; Huang, K.; Feng, S. *et al. Adv. Mater.* 2023, 35, 2209338.
[6] Shao, Z.; Zhu, Q.; Huang, K.; Feng, S. *et al. Adv. Mater.* 2022, 34, 2110172.
[7] Zhu, K.; Zhu, Q.; Huang, K.; Feng, S. *et al. Angew. Chem. Int. Ed.* 2022, e202207600.
[8] Zhu, Q.; Zhu, K.; Huang, K.; Feng, S. *et al. Nano. Res.* 2022, 7099–7106.

Spin Dependent Electronic Transport Properties of Mn-Based Antiperovskites

Sihao Deng,[1, 2, *] Hongde Wang,[1, 4] Qingzhen Huang,[1] Cong Wang,[4, *], Lunhua He[1, 3, *]
[1] *Spallation Neutron Source Science Center, Dongguan 523803, China.*
[2] *Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China*
[3] *Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*
[4] *School of Integrated Circuit Science and Engineering, Beihang University, Beijing 100191, China.*
Corresponding author: dengsh@ihep.ac.cn; congwang@buaa.edu.cn; lhhe@iphy.ac.cn

Mn-based antiperovskite compounds with triangular magnetic lattice show a variety of magnetic structures accompanied by some fascinating physical properties, including a large magnetocaloric effect, giant magnetoresistance, giant barocaloric effect, baromagnetic effect, negative thermal expansion, and anomalous hall effect etc. Among them, face-centered magnetic atoms (such as Mn) and body-centered N (C) atoms can form NMn_6 or CMn_6 octahedra, and six magnetic atoms Mn are located at the six corners of the octahedron, which is prone to magnetic frustration. Thereby it generates the abounding magnetic structures. Here, we investigate the chiral spin states and their associated electronic transport properties in antiperovskite materials. For $Mn_{3.33}Ni_{0.67}N$, in addition to the Γ^{5g} triangular antiferromagnetic configuration, there is also a weaker ferromagnetic component perpendicular to the Γ^{5g} plane, which in turn shows non-zero scalar spin chirality values. By cooling with an external magnetic field, the ferromagnetic component is frozen, thereby realizing the manipulation of the chirality of the magnetic structure. Experimentally, we have discovered a vertical shift of the magnetization curve and to an asymmetrical magnetoresistance, and observed the chiral Hall effect. Our findings open interesting prospects for tailoring specific materials properties for the development of future chiral spintronic devices.

Acknowledgements: The National Natural Science Foundation of China (Grant Nos. 52371190, U2032167, 12041202, U2032220, U1832219, and 52272264) is acknowledged for the financial support.

References

[1] S. Deng, et al. Controlling Chiral Spin States of a Triangular-Lattice Magnet by Cooling in a Magnetic Field. Adv. Funct. Mater. 1900947 (2019).

Peeking the Glass Phase in the Grain Boundary of $Na_3Zr_2Si_2PO_{12}$ by Solid-State NMR

Chenjie Lou,[1] Wenda Zhang,[1,2] Jipeng Fu,[3] Xiaojun Kuang,[2] Mingxue Tang[1,4*]
[1] *Center for High Pressure Science and Technology Advanced Research, Beijing 100193, China.*
[2] *College of Materials Science and Engineering, Guilin University of Technology,Guilin 541004, China.*
[3] *Institute of Optoelectronic Materials and Devices China Jiliang University, Hangzhou 310018, China.*
[4] *University of Science and Technology Beijing, Beijing 100083, China.*
Corresponding author: mingxue.tang@hpstar.ac.cn

$Na_3Zr_2SiPO_{12}$ was proven as a promising electrolyte in solid-state sodium batteries. However, its poor conductivity precludes application because of the large ionic resistance caused by grain boundary. Herein we proposed an additional glass phase to connect the grain boundary via Ga_2O_3 introduction, resulting in enhanced sodium-ion conduction and electrochemical performance. The optimized $Na_3Zr_2SiPO_{12}$-0.15Ga electrolyte exhibits Na^+ conductivity of 1.65 mS cm^{-1} at room temperature and a low activation energy of 0.16 eV, with 20% glass phase filled in grain boundary (Fig. 1). Atomic level sensitive NMR[1,2] is employed to determine and quantify the amount of glass phase. Temperature-dependent NMR line shapes and spin-lattice relaxation were used to demonstrate the estimation of Na self-diffusion and Na ion hopping. The strategy of design dense glass-ceramic electrolyte and the structure-dynamics-property correlation from NMR can be extended to wider optimization in material community.

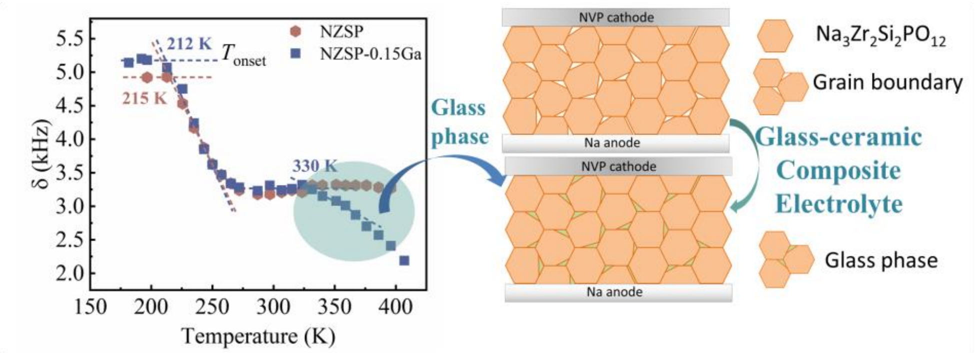


Fig. 1. The composite electrolyte filled with glass phase in grain boundary was constructed by introducing Ga_2O_3 into the traditional $Na_3Zr_2SiPO_{12}$ electrolyte. An additional glass phase is determined and quantified by analyzing the linewidth and integral of ^{23}Na and ^{31}P NMR signal, to correlate the optimized ion conduction.

Acknowledgements: The National Natural Science Foundation of China (No. 21974007 and 22090043) is acknowledged for the financial support.

References

[1] J. Zheng, M. Tang, Y. Hu, *Angew. Chem. Int. Ed.* **2016**, *55*, 12538.
[2] P. Ding, L. Wu, Z. Lin, C. Lou, M. Tang, X. Guo, H. Guo, Y. Wang, H. Yu, *J. Am. Chem. Soc.* **2023**, *145*, 1548.

Unraveling the Dominance of Structural Vacancies in Sodium Ion Conductivity in Na_3SO_4F

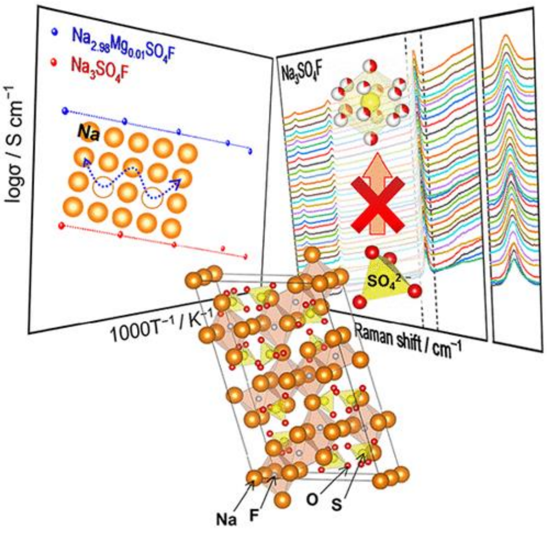
Yuxiang Li,[1] Ting He,[1] Guowei Zhao,[2] Jiujun Zhang,[1] and Ya Tang[1]*

[1] *Department of Chemistry, College of Sciences, Shanghai University, Shanghai 200444, People's Republic of China.*

[2] *College of Chemistry and Chemical Engineering, Huanggang Normal University, Huanggang, Hubei 438000, People's Republic of China.*

Corresponding author: tangya0709@shu.edu.cn

Solid electrolytes are important materials for energy storage and conversion applications, and the coexistence of the paddle-wheel effect and vacancy diffusion mechanism is commonly observed in many solid electrolytes. However, the mechanism that significantly contributes to this remains unknown. To address this issue, we assess the phase stability and conduction properties of Na_3SO_4F (NSOF) and magnesium-doped NSOF ($Na_{2.98}Mg_{0.01}SO_4F$, NMSOF). Our results reveal that incorporating Na vacancies in NSOF (i.e., NMSOF) leads to a significant increase in ionic conductivity, with a 2 order of magnitude difference compared to NSOF. The phase transition temperature of NMSOF is also significantly lower than that of NSOF, demonstrating the role of vacancies in enhancing the mobility of Na cations. Furthermore, Raman spectroscopy confirms that the polyanion SO_4^{2-} rotation has a minor effect on the sodium conduction mechanism. Our study provides a fundamental understanding of the sodium conduction mechanism of polyanion-based sodium superionic conductors, including the impact of vacancies on Na conductivity.



Acknowledgements: The National Natural Science Foundation of China (22002086 and 51803116), the Shanghai Overseas High-Level Talents (58-D305-23-201) is acknowledged for the financial support.

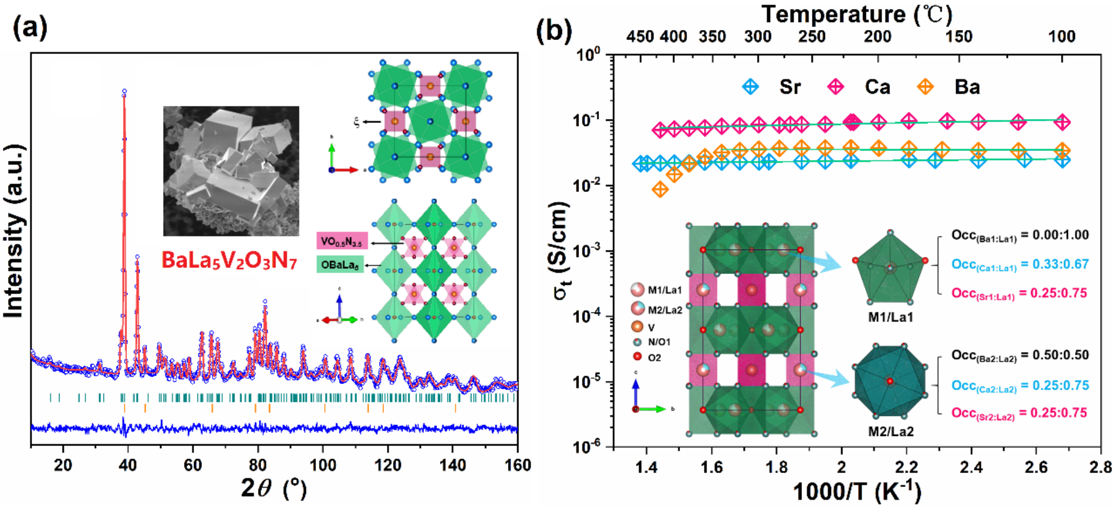
References

[1] Yuxiang Li, Xue Wang, Heng Wang, Ting He, Daixin Ye, Hongbin Zhao, Guowei Zhao, Jiujun Zhang, and Ya Tang*, *J. Phys. Chem. Lett.* ***2023**, 14, 6832−6839*.

M-La-V-O-N (M = Ba, Sr, Ca): a Novel Anti-perovskite Oxynitride for Electrode Applications

Shi-Rui Zhang,[1] Xiao-Ming Wang,[1*] Xiao-Jun Kuang,[2*] Huan Jiao [1*]
[1] *Shaanxi Normal University, School of Chemistry & Chemical Engineering, Xi'an 710062, Shaanxi Province, P. R. China.*
[2] *Guilin University of Technology, College of Chemistry and Bioengineering, Guilin 541004, P. R. China.*
Corresponding author: xmwang@snnu.edu.cn; kuangxj@glut.edu.cn; jiaohuan@snnu.edu.cn

The exploration of transition metal oxynitrides has garnered significant interest due to their intriguing property diversity. Herein, we present a series of promising new transition metal oxynitrides M-La-V-O-N (M = Ba, Sr, Ca), which features an anti-perovskite structure type. The existence of oxygen vacancy leads to the coexistence of V^{4+}/V^{5+} in the process of $BaLa_5V_2O_3N_7$ powder preparation. This unique structural configuration endows the material with remarkable conductivity, particularly at low temperatures. The substitution of elements with smaller atomic radii results in a rearrangement of cation positions to maintain structural stability. In terms of performance, $Ca_4La_8V_4O_8N_{12}$ powder still maintains good crystallinity at 450°C, and the electronic conductivity of $Sr_3La_9V_4O_7N_{13}$ ceramic sheet is also 2 times higher than that of $BaLa_5V_2O_3N_7$. Both the thermal stability and electronic conductivity of the fully substituted sample are improved, which is a positive effect due to the adjustment of the oxygen vacancy. Considering the difference in the diverse progress of oxides and oxynitrides in the field of electronics, transition metal oxynitrides still show great potential in terms of electrical properties. The study of the electrical properties of M-La-V-O-N (M = Ba, Sr, Ca) system paves the way for the wide technical application of transition metal oxynitrides materials.



Acknowledgements: This project is funded by the National Natural Science Foundation of China (51972203, 22271180 and 21875049), the Guangxi Natural Science Foundation (No. 2018GXNSFDA281015 and 2019GXNSFGA245006) and Guangxi BaGui Scholars Special Funding.

References

[1] S.R. Zhang, X.M Wang, L.M. Fang, J.C. Li, Y.Y. Xu, Z.H. Ren, Z.P. Yang, X.J. Kuang, H. Jiao, *Chem. Commun*. **2023**, *59*, 10612.

Multimodal Structure Solution with ^{19}F NMR Crystallography of Spin Singlet Molybdenum Oxyfluorides

Fenghua Ding, Kent J. Griffith, and Kenneth R. Poeppelmeier*
Department of Chemistry, Northwestern University, Evanston, Illinois 60208, USA.
Corresponding author: krp@northwestern.edu

Complex crystal structures with subtle atomic scale details are now routinely solved using complementary tools such as X-ray and/or neutron scattering combined with electron diffraction and imaging. Identifying unambiguous atomic models for oxyfluorides, needed for materials design and structure–property control, is often still a considerable challenge. In this work, NMR crystallography and single-crystal X-ray diffraction are combined for the complete structure solution of three new compounds featuring a rare triangular early transition metal oxyfluoride cluster $[Mo_3O_4F_9]^{5-}$. After framework identification by single-crystal X-ray diffraction, 1D and 2D solid-state ^{19}F NMR spectroscopy supported by *ab initio* calculations are used to solve the structures of **(1)** $K_5[Mo_3O_4F_9]\cdot 3H_2O$, **(2)** $K_5[Mo_3O_4F_9]\cdot 2H_2O$, and **(3)** $K_{16}[Mo_3O_4F_9]_2[TiF_6]_3\cdot 2H_2O$ and to assign the nine distinct fluorine sites in the oxyfluoride clusters. Furthermore, ^{19}F NMR identifies selective fluorine dynamics in $K_{16}[Mo_3O_4F_9]_2[TiF_6]_3\cdot 2H_2O$. These dual scattering and spectroscopy methods are used to demonstrate the generality and sensitivity of ^{19}F shielding to small changes in bond length—on the order of 0.01 Å or less—even in the presence of hydrogen-bonding, metal–metal bonding, and electrostatic interactions. Starting from the structure models, the nature of chemical bonding in the molybdates is explained from molecular orbital theory and electronic structure calculations. The average Mo–Mo distance of 2.505 Å and diamagnetism in **(1)**, **(2)** and **(3)** are attributed to a metal–metal bond order of unity along with a $1a^2 1e^4$ electronic ground state configuration for the $[Mo_3O_4F_9]$ cluster, leading to a rare trimeric spin singlet involving d^2 Mo^{4+} ions. The approach to structure solution and bonding analysis is a powerful strategy for understanding the structures and chemical properties of complex fluorides and oxyfluorides.

References

[1] Ding, F., Griffith, K. J., P. Koçer, C., Saballos, R. J., Wang, Y., Zhang, C., Nisbet, N. L., Morris, A. J., Rondinelli, J. M., and Poeppelmeier, K. R. Multimodal Structure Solution with ^{19}F NMR Crystallography of Spin Singlet Molybdenum Oxyfluorides. *J. Am. Chem. Soc.* **2020**, 142, 12288-12298.

Rational Design and Controlled Synthesis of Antimony-Based Ultraviolet Nonlinear Optical Materials

Xuehua Dong,[1] Guohong Zou[1*]
College of Chemistry, Sichuan University, Chengdu 610065, P. R. China
Corresponding author: zough@scu.edu.cn

Nonlinear optical crystal materials have greatly expanded the tunable range of lasers through frequency conversion, promoting the rapid development of laser technology. Due to the existing physical and chemical defects in crystal materials or difficulties in growth, as well as higher demands for the comprehensive performance of crystals in practical applications, nonlinear optical crystals that can achieve high conversion efficiency under high-intensity lasers are extremely rare. Therefore, the exploration of new material systems is particularly urgent.

Sb^{3+} readily forms asymmetric coordination environments and possesses a rich variety of coordination modes. Antimony-based oxysalts have been found to exhibit large nonlinear optical coefficients, suitable birefringence, a wide transparent wavelength range, and high laser damage thresholds, making them suitable for nonlinear optical crystal applications. By conducting in-depth research on the relationship between the structure and properties of antimony-based oxysalt compounds, a series of compounds have been synthesized, achieving the structural design and controlled preparation of antimony-based oxysalt compounds. Additionally, new methods for the controlled preparation and crystal growth of such compounds, especially hydrolizable antimony-based oxysalts, have been developed. Excellent multifunctional frequency-doubling crystals have been screened and identified from this class of compounds."

Acknowledgements: This work was supported by the National Natural Science Foundation of China (Grant Nos. 22122106, 22071158), the Fundamental Research Funds from Sichuan University (2021SCUNL101).

References

[1] Deng, Y.; Huang , L.; Dong, X.; Wang, L.; OK, K.; Lin, Z.; Zou, G. *Angew. Chem. Int. Ed.* **2020,** *59,* 21151.
[2] Dong, X.; Huang , L.; Zeng, H.; Lin, Z.; Wang, X.; OK, K.; Zou, G. *Angew. Chem. Int. Ed.* **2019,** *58,* 6528.

Structural Mechanism and Performance Regulation Of BNT-Based Lead-Free Piezoelectric Ceramics

Huajie Luo[1], Hui Liu[1], Mingxue Tang[1], Jun Chen[1*]

[1] *Beijing Advanced Innovation Center for Materials Genome Engineering, University of Science and Technology Beijing, Beijing 100083, China*

*Corresponding Author: junchen@ustb.edu.cn

We proposed a general chemical substitution method to simultaneously improve d_{33} and T_d of $Bi_{0.5}Na_{0.5}TiO_3$-$BaTiO_3$ (BNT-BT) via introducing oxygen-defect perovskite. This has been demonstrated by introducing $BaAlO_{2.5}$ into BNT-BT perovskite crystal lattice and forming solid-solutions, in which a series of ceramics with *P*4*mm* phase after electrical poling can be achieved. Not only its d_{33} but also T_d can be much improved, which goes far beyond the performance boundary limit of d_{33} vs. T_d for all BNT-BT based systems. Based on the proposed strategy of oxygen-defect perovskite, a defect engineered morphotropic phase boundary (MPB) and giant strain of 1.12% was achieved in lead-free $Bi_{0.5}Na_{0.5}TiO_3$ (BNT)-based ceramics. The incorporation of the perovskite $BaAlO_{2.5}$ with nominal oxygen defect into BNT will form strongly polarized directional defect dipoles, leading to a strong pinning effect after aging. The large asymmetrical strain is mainly attributed to two factors: the defect dipoles along crystallographic [001] direction destroys the long-range ordering of the ferroelectric activating a reversible phase transition, while the defect dipoles promote polarization rotation when the dipoles are aligned along the same direction of the applied electric field.

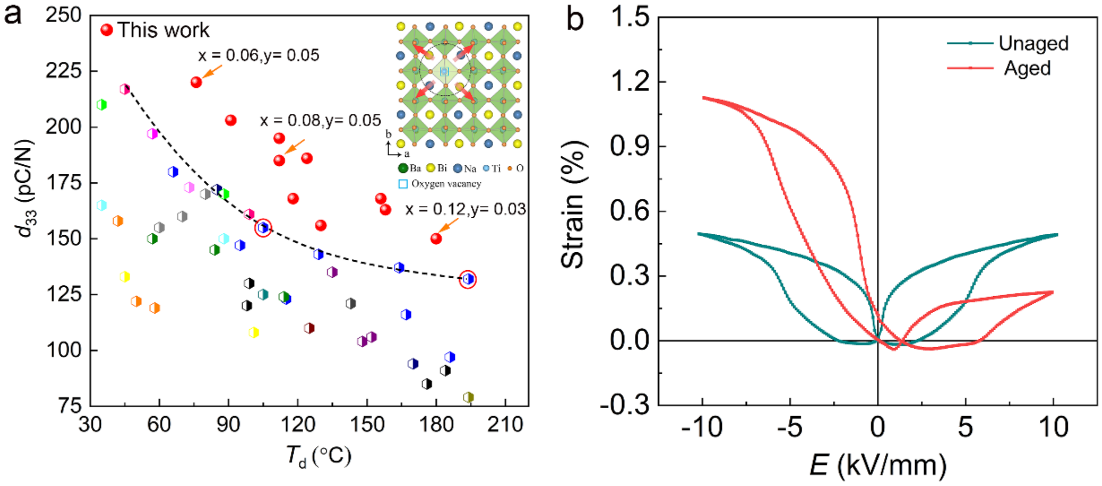


Fig. 1. (a) Comparison of d_{33} vs. T_d for the BNT-BT-based compositions, (b) bipolar *S*-*E* curves measured for the BNT–6BA before aging and after aging.

References:

[1] H. Luo, H. Liu, J. Chen*, et al. *Acta. Mater.* **2021**, 208, 116711.
[2] H. Luo, S. Deng, J. Chen*, et al. *Acta. Mater.* **2021**, 218, 117202.
[3] H. Luo, S. Tang, J. Chen*, et al. *Acta. Mater.* **2023**, 254, 119024.
[4] H. Luo, H. Liu, J. Chen*, etal. *Sci. Adv.* **2023**, 9, eade7078.

Topochemical Synthesis of Ca_3CrN_3H Involving a Rotational Structural Transformation for Catalytic Ammonia Synthesis

Yu Cao,[1] Yoji Kobayashi,[2] Hiroshi Kageyama[1*]

[1] *Graduate School of Engineering, Kyoto University, Kyoto University-Katsura Campus, Nishikyo-ku, Japan.*

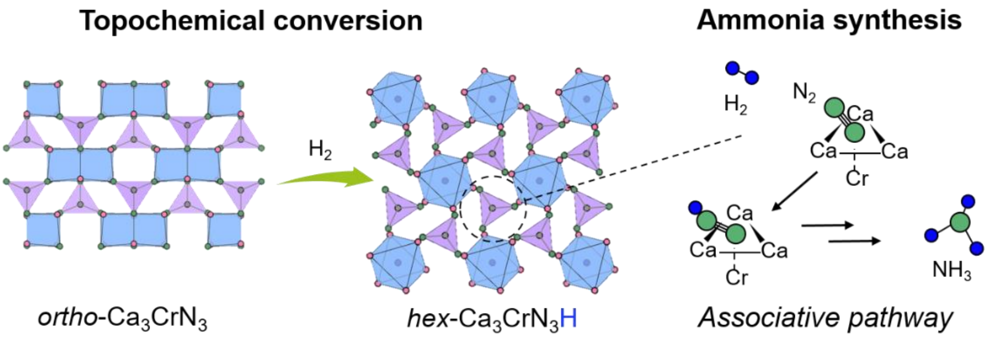
[2] *Chemical Science Program, KAUST Catalysis Center, Division of Physical Science and Engineering, King Abdullah University of Science and Technology.*

Corresponding author: kage@scl.kyoto-u.ac.jp

Topochemical reactions have led to great progress in the discovery of new metastable compounds with novel chemical and physical properties.[1] With these reactions, the overall crystal structure of the host material is generally maintained. Here we report a topochemical synthesis of a hexagonal nitride hydride, *h*-Ca_3CrN_3H, by heating an orthorhombic nitride, *o*-Ca_3CrN_3, under hydrogen at 673 K, accompanied by a rotational structural transformation.[2] The hydrogen intercalation modifies the Ca-N rock-salt-like atomic packing in *o*-Ca_3CrN_3 to a face-sharing octahedral chain in *h*-Ca_3CrN_3H, mimicking a "hinged tessellation" movement.

In addition, the *h*-Ca_3CrN_3H exhibited stable ammonia synthesis activity via an associative N_2 reduction pathway when used as a catalyst. The activity of *h*-Ca_3CrN_3H (3800 $\mu molg^{-1}h^{-1}$) is better than that of our previous reported non-Ru/Fe catalysts, such as TiH_2 (2800 $\mu molg^{-1}h^{-1}$),[3] $BaTiO_{2.5}H_{0.5}$ (1400 $\mu molg^{-1}h^{-1}$),[3] and $VH_{0.39}$ (3200 $\mu molg^{-1}h^{-1}$)[4] at 5 MPa and 673 K. Typically, transition metals are considered as the centers for the activation of dinitrogen. Here we demonstrate that Ca_3CrN_3H can activate dinitrogen through active sites where calcium provides the primary coordination environment.[5] DFT calculations reveal that an associative mechanism is favorable, distinct from the dissociative mechanism found in traditional Ru or Fe catalysts.

The topochemical synthesis of *h*-Ca_3CrN_3H and the following catalytic application encourage the expansion and exploration of a large group of A_3MN_3H hexagonal antiperovskite nitride-hydride materials and even other structural types as promising ammonia synthesis catalysts.



References

[1] H. Kageyama, K. Hayashi, K. Maeda, J. P. Attfield, Z. Hiroi, J. M. Rondinelli, K. R. Poeppelmeier, *Nat. Commun*. **2018**, *9*, 772.

[2] Y. Cao, M. A. Kirsanova, M. Ochi, W. Al Maksoud, T. Zhu, R. Rai, S. Gao, T. Tsumori, S. Kobayashi, S. Kawaguchi, E. Abou-Hamad, K. Kuroki, C. Tassel, A. M. Abakumov, Y. Kobayashi, and H, Kageyama, *Angew. Chem. Int. Ed.* **2022**, *61*, e202209187.

[3] Y. Kobayashi, Y. Tang, T. Kageyama, H. Yamashita, N. Masuda, S. Hosokawa, H. Kageyama, *J. Am. Chem. Soc.* **2017**, *139*, 18240.

[4] Y. Cao, A. Saito, Y. Kobayashi, H. Ubukata, Y. Tang, H. Kageyama, *ChemCatChem* **2021**, *13*, 191.

[5] Y. Cao, E. Toshcheva, W. Almaksoud, R. Ahmad, T. Tsumori, R. Rai, Y. Tang, L. Cavallo, H. Kageyama, and Y. Kobayashi, *ChemSusChem*, **2023**, e202300234.

Modulated Structure Determination Of Oxide-Ion Conductor $CeNbO_{4+\delta}$ by Combining 3DED, Synchrotron X-ray Powder Diffraction, and Neutron Powder Diffraction

Jian Li,[1,#,*] Xiaojun Kuang, [2*] Junliang Sun,[1*]
[1] *College of Chemistry and Molecular Engineering, Peking University, 100871, Beijing, P. R. China.*
[2] *Guangxi Key Laboratory of Optical and Electronic Materials and Devices, College of Materials Science and Engineering, Guilin University of Technology, 541004, Guilin, P. R. China.*
[#] *Current address: State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210023, China*
Corresponding author: jian.li@nju.edu.cn; kuangxj@glut.edu.cn; junliang.sun@pku.edu.cn

$CeNbO_{4+\delta}$, a family of oxygen hyperstoichiometry materials with varying oxygen content ($CeNbO_4$, $CeNbO_{4.08}$, $CeNbO_{4.25}$, $CeNbO_{4.33}$) that shows mixed electronic and oxide ionic conduction, has been known for four decades. However, the oxide ionic transport mechanism has remained unclear due to the unknown atomic structures of $CeNbO_{4.08}$ and $CeNbO_{4.33}$. We determine the incommensurately modulated structure of $CeNbO_{4.08}$ and the superstructure of $CeNbO_{4.33}$ by combining 3D ED, synchrotron X-ray powder diffraction (SPD), and neutron powder diffraction (NPD). Using the same methods, the superstructure of $CeNbO_{4.25}$ was also re-determined. The structure models are sufficiently accurate to reveal the interstitial oxygen sites and allow to elucidate how the extra oxygen atoms change the structural connectivity. With the accurate structure in hand, two oxide ion migration events are able to identify in $CeNbO_{4.08}$ and $CeNbO_{4.25}$ by molecular dynamics simulations, which was a synergic-cooperation knock-on mechanism involving continuous breaking and reformation of Nb_2O_9 units. However, the excess oxygen in $CeNbO_{4.33}$ hardly migrates because of the high concentration and the ordered distribution of the excess oxide ions. The relationship between the structure and oxide ion migration for the whole series of $CeNbO_{4+\delta}$ compounds elucidated here provides a direction for the performance optimization of these compounds.

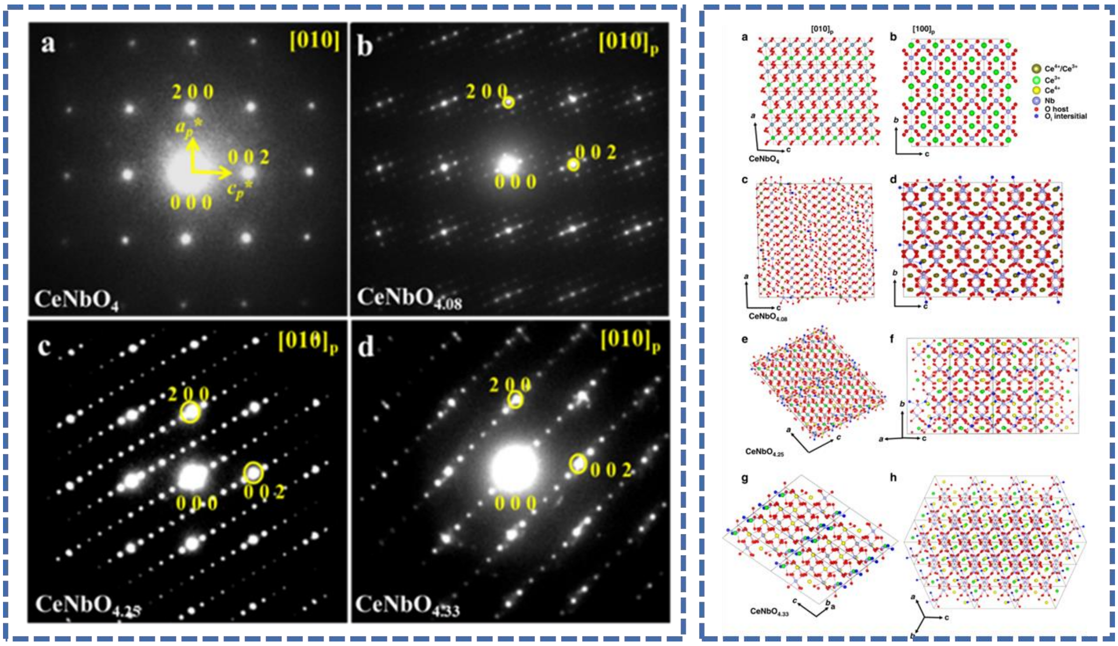


Figure 1 Modulated structure determination of oxide-ion conductor $CeNbO_{4+\delta}$ by Combining 3DED, SPD and NPD. (left a-d, [010]p zone axis SAED of $CeNbO_{4+\delta}$, right a-h, structure model of $CeNbO_{4+\delta}$)

References

[1] Jian Li, Fengjuan Pan, Shipeng Gen. Cong Lin, Lukas Palatinus, Mathieu Allix, Xiaojun Kuang, Jianhua Lin Junliang Sun. Modulated structure determination and ion transport mechanism of oxide-ion conductor $CeNbO_{4+\delta}$. *Nat Commun* 11, 4751 (2020). https://doi.org/10.1038/s41467-020-18481-x

Understanding the Doping Behavior of In^{3+} into SrGa$_{12}$O$_{19}$ by Rietveld Refinements on High Resolution Powder XRD and its Correlation to Bandgap Engineering

Weihua Li,[1] Guangxiang Lu,[1] Pengfei Jiang,[1] Tao Yang[1*]
[1] *College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 401331, People's Republic of China*
Corresponding author: taoyang@cqu.edu.cn

The hexagallate SrGa$_{12}$O$_{19}$ is a special host with five independent Ga^{3+} sites, including one tetrahedral, one trigonal biyramidal, and three octahedral coordination environments (see **Fig. 1**). From the fundamental aspect, this is a particularly interesting case to study the selective doping behavior of In^{3+} and its correlation to the bandgap engineering. The average structures with different In^{3+} doping concentrations (SrGa$_{12-x}$In$_x$O$_9$, $x \leq 2$) can be determined by Rietveld refinements on high resolution powder XRD, and the detailed analyses on the selective site occupancy, respective movements of metal and oxygen atoms, changes of all bond distances of Ga-O polyhedra give a reliable and logical scheme of the structural evolution. More interestingly, the site preferential occupation can be understood by structural chemistry analyses as well as the DFT calculations, and the band structure evolution can be proved by optical absorption spectra, consequently, the narrowing of the bandgap can be utilized to improve the photocatalytic water splitting activity of In^{3+}-doped SrGa$_{12}$O$_{19}$, which was indeed performed experimentally.

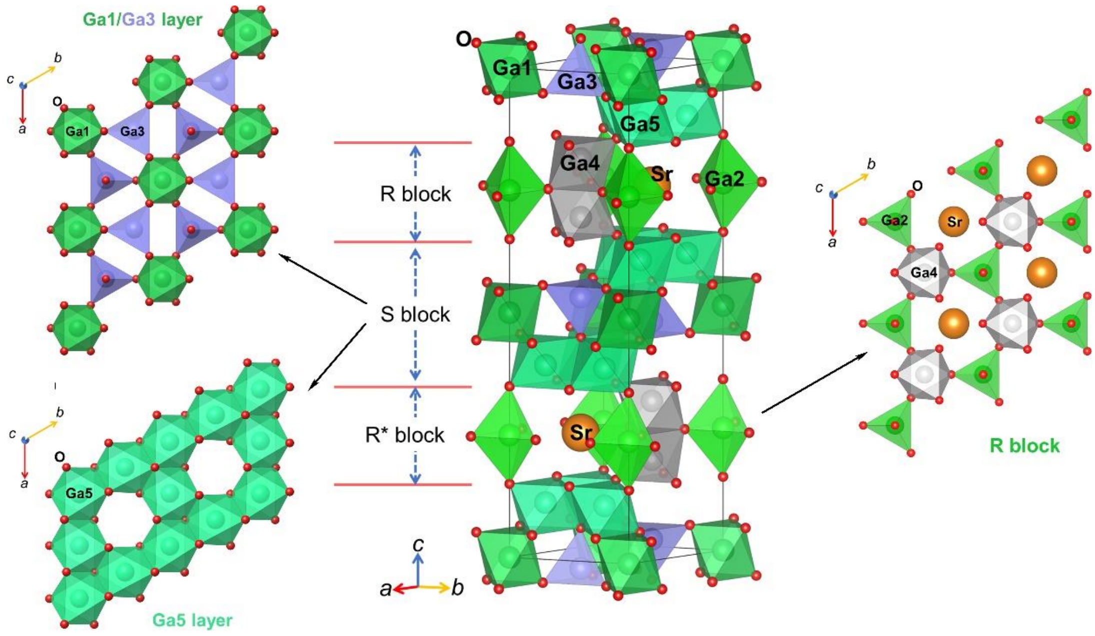


Fig. 1. Structure overview for SrGa$_{12}$O$_{19}$ and the interconnections between Ga-O polyhedra within each layer.

Acknowledgements: This work was financially supported by the National Natural Science Foundation of China (22171032 and 22271030).

Pressure-modulated Magnetism and Negative Thermal Expansion in the Ho_2Fe_{17} Intermetallic Compound

Yili Cao, Xianran Xing *
Beijing Advanced Innovation Center for Materials Genome Engineering, Institute of Solid State Chemistry, University of Science and Technology Beijing, Beijing, 100083, China
Corresponding author: xing@ustb.edu.cn

Hydrostatic and chemical pressure are efficient stimuli to alter crystal structure and are commonly used for tuning electronic and magnetic properties in materials science. However, chemical pressure is difficult to quantify and clear correspondence between these two types of pressure is still lacking. Here, we study intermetallic candidates for permanent magnet with negative thermal expansion (NTE). Based on in situ synchrotron X-ray diffraction, negative chemical pressure is revealed in Ho_2Fe_{17} on Al doping and quantitatively evaluated by using temperature and pressure dependence of unit cell volume. Combination of magnetization and neutron diffraction measurements also allowed to com-pare the effect of chemical pressure on magnetic ordering with that of hydrostatic pressure. Intriguingly, pressure can be used to control suppression and enhancement of NTE. Electronic structure calculations indicate that pressure affected the top of the majority band with respect to Fermi level (EF), which has implication for the magnetic stability, which in turn plays critical role in modulating magnetism and NTE. This work presents a good example of understanding the effect of pressure and utilizing it to control properties of functional materials.

Acknowledgements: The National Key R&D Program of China (2020YFA0406202), National Natural Science Foundation of China (22090042, 22275015, 21731001 and 21971009) is acknowledged for the financial support.

References

[1] Y. Cao *et al.*, *Chem. Mater.* 2023, **35**, 3249-3255.
[2] Y. Cao *et al.*, *Phys. Rev. Lett.* 2021, **127**, 055501.

Controlling Magnetization (and Spin) by Electric Field

Junling Wang
Department of Physics
Southern University of Science and Technology (SUSTech)
Shenzhen, China
Corresponding author: jwang@sustech.edu.cn

Multiferroic materials, such as $BiFeO_3$, allow for the electric-field control of magnetization because of their magnetoelectric coupling effect. They have been studied extensively for the rich underlying physics and potential applications in spintronic devices. However, research on conventional multiferroic materials have encountered serious obstacles, e.g., small coupling coefficients of Type-I multiferroics and low temperature/high conductivity of Type-II multiferroics.

Recent developments on 2D ferroelectric materials open a new paradigm in the field. After a brief review of our previous work on $BiFeO_3$, I will talk about the unique properties of 2D ferroelectric materials and the opportunities they brought in term of electric-field control of electron spin and magnetization.

References

[1] "Room-temperature ferroelectricity in $CuInP_2S_6$ ultrathin flakes", Fucai Liu, Lu You, Kyle L. Seyler, Xiaobao Li, Peng Yu, Junhao Lin, Xuewen Wang, Jiadong Zhou, Hong Wang, Haiyong He, Sokrates T. Pantelides, Wu Zhou, Pradeep Sharma, Xiaodong Xu, Pulickel M. Ajayan, Junling Wang*, Zheng Liu*, ***Nature Communications***, doi: 10.1038/ncomms12357 (2016).

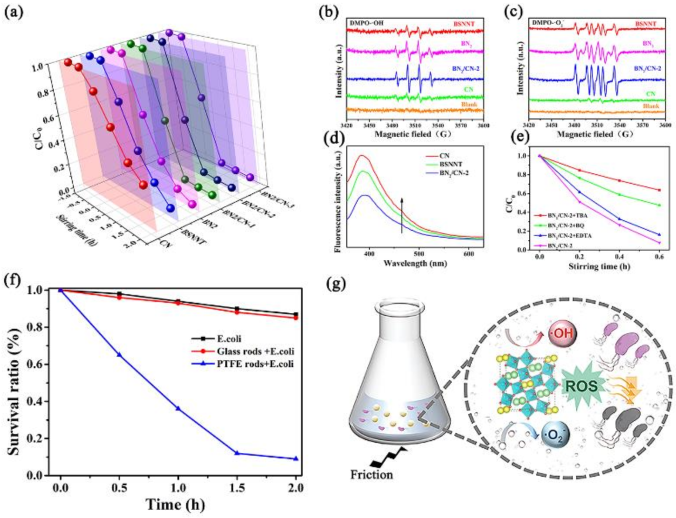
[2] "Origin of giant negative piezoelectricity in a layered van der Waals ferroelectrics", Lu You, Yang Zhang, Shuang Zhou, Apoorva Chaturvedi, Samuel A. Morris, Fucai Liu, Lei Chang, Daichi Ichinose, Hiroshi Funakubo, Weijin Hu, Tom Wu, Zheng Liu, Shuai Dong*, Junling Wang*, ***Science Advances***, 4, eaav3780 (2019).

[3] “Towards two-dimensional van der Waals ferroelectrics“, Chuanshou Wang, Lu You*, David Cobden, Junling Wang*, ***Nature Materials*** **22**, 542 (2023).

Tribocatalyzed Degradation and Sterilization by Regulating Oxygen Vacancies and Constructing Heterojunctions

Zuheng Jin, Zhihong Zhu, Changzheng Hu
College of Materials and Engineering, Guilin University of Technology, Guilin 541004,China
Corresponding author: huchzh@foxmail.com

In contrast to conventional oxidation techniques, tribocatalysis degradation of organics has gained much attention in recent years due to its mild requirement and low amount of energy needed. Therefore, we prepared $Ba_{1.4}Sr_{3.6}NdNb_7Ti_3O_{30}$ (BSNNT) ferroelectric nanopowder by a solid-phase synthesis method and further investigated the effects of oxygen vacancies and heterojunctions on the tribocatalysis effect. The results showed that the introduction of oxygen vacancies not only reduced the valence electron potential required for the reaction but also greatly reduced the combination of electrons and holes. The BSNNT-N_2/CN-2 (BN_2/CN-2) Z-type heterojunction achieves a tribocatalytic enhancement with 98.2% RhB degradation in 2 h. Besides, the BN_2/CN-2 Z-type heterojunction also showed good inhibition of bacteria under tribocatalyzed conditions. Ultimately, it was demonstrated that the hydroxyl radicals and superoxide radicals generated during tribocatalysis degraded the dyes and inhibited the growth of bacteria by ESR. A friction-energy efficient degradation of dyes and sterilization of strongly polarized ferroelectric materials is provided.



Acknowledgements: The authors at the Guilin University of Technology thank the National Natural Science Foundation of China (12164012), Science and Technology Major Project of Guangxi (AA21077012), for financial support.

References

[1] X. L. Liu, H. W. Pang, X. W. Liu, Q. Li, N. Zhang, L. Mao, M. Q. Qiu, B. W. Hu, H. Yang, X. K. Wang, The Innovation. 2021, 2, 29.
[2] M. J. Hao, M. Q. Qiu, H. Yang, B. W. Hu, X. X. Wang, Sci. Total Environ. 2021, 760, 26.
[3] Z. Jin, X. Zheng, Z. Zhu, C. Hu, L. Liu, L. Fang, Z. Cheng, Appl. Surf. Sci. 2023, 625, 157228.

Structural Design and Synthesis of New Nonlinear Optical and/or Birefringent Crystals

Sangen Zhao[1*]

[1] *Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, 350002, China*

Corresponding author: zhaosangen@fjirsm.ac.cn

Second-order nonlinear optical (NLO) crystals and birefringent crystals have important applications in modern optoelectric sciences and technics. We have proposed the so-called “local polarity induced assembling” strategy[1] to rationally design and synthesize new NLO crystals. Based on this strategy, we have successfully constructed multiple new functional groups with local polarity, and then discovered a series of UV NLO crystals with high performances. Furthermore, we have explored new systems of NLO crystals and revealed their microscopic mechanisms on the structure-property relationships.[2-3] On the other hand, we designed and synthesized a variety of birefringent crystals,[4-7] and revealed the microscopic relationships between structure and birefringence, which would shed useful insights on the structural design and synthesis of birefringent crystals.

Acknowledgements: The National Natural Science Foundation of China (No. 22122507, 22193042) is acknowledged for the financial support.

References

[1] Yanqiang Li, Junhua Luo, Sangen Zhao, ***Acc. Chem. Res.***, 55， 3460-3469, **2022**.

[2] Yanqiang Li, Weiqi Huang, Yang Zhou, Xianyu Song, Jieyu Zheng, Han Wang, Yipeng Song, Minjuan Li, Junhua Luo, Sangen Zhao, ***Angew. Chem. Int. Ed.***, 61, e202215145, **2023**.

[3] Li, Yanqiang**;** Zhang, Xu**;** Zheng, Jieyu**;** Zhou, Yang**;** Huang, Weiqi**;** Song, Yipeng**;** Wang, Han**;** Song, Xianyu**;** Luo, Junhua**;** Zhao, Sangen, ***Angew. Chem. Int. Ed.***, e202304498, **2023.**

[4] Minjuan Li, Xu Zhang, Zheyao Xiong, Yanqiang Li, Yang Zhou, Xin Chen, Yipeng Song, Maochun Hong, Junhua Luo, Sangen Zhao, ***Angew. Chem. Int. Ed.*** 61, e202211151, **2022**.

[5] Weiqi Huang, Xu Zhang, Yanqiang Li, Yang Zhou, Xin Chen, Xiaoqi Li, Fafa Wu, Maochun Hong, Junhua Luo, Sangen Zhao, ***Angew. Chem. Int. Ed.*** 61, e202202746, **2022**.

[6] Yanqiang Li, Xu Zhang, Yang Zhou, Weiqi Huang, Yipeng Song, Han Wang, Minjuan Li, Maochun Hong, Junhua Luo, Sangen Zhao, ***Angew. Chem. Int. Ed.***, 61, e202208811, **2022**.

[7] Yang Zhou, Xu Zhang, Maochun Hong, Junhua Luo, Sangen Zhao, ***Sci. Bull.***, 67, 2276-2279, **2022**.

Anti-thermal Quenching Upconversion Luminescence in Positive/negative Thermal Expansion Core/shell $NaYF_4@ScF_3$ Nanoparticles

Yilin Wang,[1] Jiahui Rui,[1] Xianran Xing,[2] Ling Huang[3*]

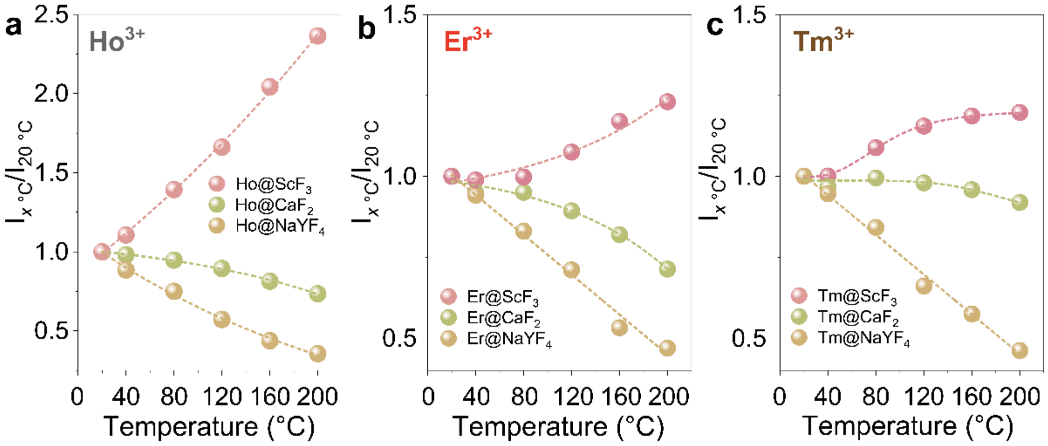
[1] *College of Materials Science and Engineering, Nanjing Tech University, Nanjing 211816, China.*

[2] *Institute of Solid State Chemistry, University of Science and Technology Beijing, Beijing 100083, China.*

[3] *State Kay Laboratory of Chemistry and Utilization of Carbon-Based Energy Resources, College of Chemistry, Xinjiang University, Urumqi 830046, China.*

Corresponding author: lhuang@xju.edu.cn

Thermal quenching, or photoluminescence loss at high temperature, is an inherent principal obstacle to many practical applications of luminescent materials. Various strategies have been designed to overcome this stubborn issue, such as water desorption, energy compensation from certain defects, et al.[1, 2] However, these strategies inevitably lead to compromised photoluminescent intensity at room temperature, which is also not favorable for practical applications. Recently, thermally enhanced upconversion photoluminescence (UCL) was reported in lanthanide-doped negative thermal expansion (NTE) materials, such as $Yb_2W_3O_{12}$, ScF_3.[3, 4] These NTE materials, however, are not suitable for luminescence due to their low quantum efficiency. Herein, cubic $NaYF_4$:Yb/Ln@ScF_3 (Ln = Ho, Er and Tm) core/shell upconversion nanoparticles (UCNPs) were constructed. The UCL of $NaYF_4$:Yb/Ln@ScF_3 at room temperature is comparable to $NaYF_4$:Yb/Ln@$NaYF_4$ but the thermal stability is much reinforced. The mismatch of the thermal expansion coefficients of $NaYF_4$ core and ScF_3 shell consistently imposes a thermal-stimulated pressure at elevating temperature, which facilitates the thermal stability. This thermal-stimulated pressure strategy could be universal and feasible to develop various excellent high-temperature luminescent materials.



Acknowledgements: The National Natural Science Foundation of China (Grant No. 22205103), the Natural Science Foundation of Jiangsu Province (Grant No. BK20220329), are acknowledged for the financial support.

References

[1] J. Zhou, S. Wen, J. Liao, C. Clarke, S. A. Tawfik, W. Ren, C. Mi, F. Wang, D. Jin, *Nat. Photonics* **2018**, *12*, 154.

[2] Y. H. Kim, P. Arunkumar, B. Y. Kim, S. Unithrattil, E. Kim, S. -H. Moon, J. Y. Hyun, K. H. Kim, D. Lee, J. -S. Lee, W. B. Im, *Nat. Mater.*, **2017**, *16*, 543.

[3] H. Zou, X. Yang, B. Chen, Y. Du, B. Ren, X. Sun, X. Qiao, Q. Zhang, F. Wang, *Angew. Chem. Int. Ed.*, **2019**, *58*, 17255.

[4] B. Ren, B. Chen, J. Zhao, Y. Guo, X. Zhang, X. Chen, Y. Du, Z. Deng, G. Zhu, F. Wang, *Chem. Mater.*, **2021**, *33*, 158.

Phase Formation and Ionic Conduction in Na-Doped $Sr_2MgSi_2O_7$ Melilite-type Silicate

Wenda Zhang[1], Jie Feng[1], Fengqi Lu[1], Alberto J. Fernández-Carrión[1], Hui Fu[2,*], and Xiaojun Kuang[1, 3,*]

[1] *Guangxi Key Laboratory of Optic and Electronic Materials and Devices, MOE Key Laboratory of New Processing Technology for Nonferrous Metals and Materials, College of Materials Science and Engineering, Guilin University of Technology, Guilin 541004 P. R. China*

[2] *Beijing National Laboratory for Molecular Sciences, Analytical Instrumentation Center, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China.*

[3] *Guangxi Key Laboratory of Electrochemical and Magnetochemical Function Materials, College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, P. R. China*

Corresponding author: *E-mail: kuangxj@glut.edu.cn
*E-mail: fuhui@pku.edu.cn

Please submit your abstract in Word or portable document format (i.e. only .doc, .docx, or .pdf files will be accepted). The abstract must be prepared in English with **one-page** limitation, including figures, tables and references. Please follow the formatting style described below. We strongly recommend that you directly type this abstract template.

The Na-doped melilite-type silicate $Sr_2MgSi_2O_7$ was reported to display high oxide ion conductivity. In this work, through multiple complementary techniques including X-ray diffraction, scanning electron microscopy, transmission electron microscopy, solid state ^{29}Si and ^{23}Na nuclear magnetic resonance spectroscopy, as well as DFT calculation of defect formation energies, we found that it is hard to replace Sr by Na in $Sr_2MgSi_2O_7$ and the $Sr_{2-x}Na_xMgSi_2O_{7-0.5x}$ compositions formed mixed crystalline $Sr_2MgSi_2O_7$ and Na-containing glassy phases. AC impedance spectroscopy measurements indicated that the ionic conduction in $Sr_{2-x}Na_xMgSi_2O_{7-0.5x}$ could be from Na^+ ions in the glassy phase, instead of the oxide ions.

Acknowledgements: National Natural Science Foundation of China (No. 22090043, 21622101), Guangxi Natural Science Foundation (No. 2019GXNSFGA245006) are acknowledged for the financial support. The authors acknowledge Prof. Dr. Mingxue Tang for fitting the the correction of ^{23}Na NMR spectrum.

References

[1] Kovalevskiy, C.L. Yin, J. Nuss, U. Wedig, M. Jansen, *Chem. Sci*., **2020**, *11*, 962.

[2] X. Kuang, M. A. Green, H. Niu, P. Zajdel, C, Dickinson, J. B. Claridge, L. Jantsky, and M. J. Rosseinsky, *Nat. Mater.*, **2008**, *6*, 498-504.

[3] J. Fan, V. Sarou-Kanian, X. Yang, M. Diaz-Lopez, F. Fayon, X. Kuang, M. J. Pitcher and M. Allix, *Chem. Mater.*, **2020**, *32*, 9016-9025.

[4] C. Tealdi, G. Chiodelli, S. Pin, L. Malavasi and G. Flor, *J. Mater. Chem. A*, **2014**, *2*, 907-910.

Correlating O-deficiency and luminescence property of Tb^{3+} doped SrO

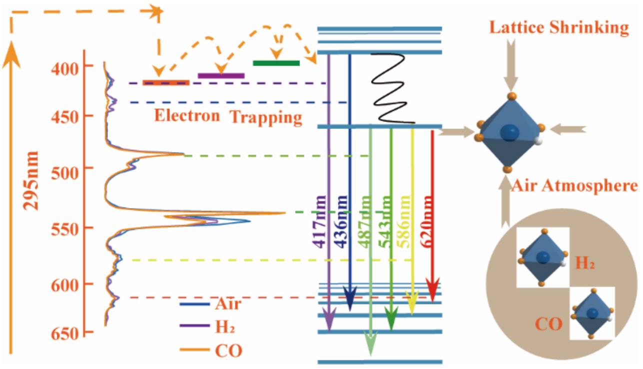
Kaina Wang,[1] Jipeng Fu,[1]* Mingxue Tang,[2]**

[1] Key Laboratory of Rare Earth Optoelectronic Materials and Devices of Zhejiang Province, Institute of Optoelectronic Materials and Devices, China Jiliang University, Hangzhou 310018, China.

[2] Center for High Pressure Science and Technology Advanced Research, Beijing 100094, China.

Corresponding author: fujipeng@cjlu.edu.cn, mingxue.tang@hpstar.ac.cn.

Accurate characterization of defects in solid luminescent materials and how they affect the luminescent properties of rare earths is an important scientific issue in the field of rare earth luminescence research, the elaboration of the crystal field constitutive relations will contribute to the design and synthesis of new rare earth luminescent materials, and can promote the exploration of high efficiency luminescence of low-excitation cross-section rare earth ions, which is scientifically important for the enhancement of the rare earth luminescence efficiency and the color rendering index. Cubic rock salts have large deformation and rotational flexibility to lower or destroy the rare-earth transition barrier through interstitial or vacancy defects. Oxygen vacancies and heteroatoms in the cubic structure of SrO are designed by introducing H_2 or CO reducing atmosphere, which leads to deformation of adjacent oxygen octahedral structures, resulting in crystal field distortion and energy trapping. Trivalent terbium (Tb^{3+}) ions with typical $^5D_4 \rightarrow {}^7F_J$ (J = 3, 4, 5, and 6) multiple transitions have been shown to be excellent activators for the production of green-emitting phosphors. However, Tb^{3+} ions have parity prohibiting 4f → 4f absorption leaps in symmetric matrix lattices. Usually, doping additional ions as sensitizers overcomes this problem by an energy transfer (ET) strategy. Furthermore, lattice defects in phosphors have been shown to not only act as photon absorption centers, but also modulate the crystal field around the luminescent centers. Thermally assisted tunneling of Tb^{3+} from the defects to the $^5D_4$ state and a reduction of the electron population in the $^5D_3$ state were observed. Finally, the prepared SrO: $0.01Tb^{3+}$ phosphor was encapsulated with commercial phosphors, and the CCT of the encapsulated LEDs were 3850 K, 4136 K, and 4741 K, with color rendering indices of 90.3, 90.8, and 92.1, respectively. These insights will advance the fundamentals of cubic rock salt crystal engineering and enable new ways to manipulate energy transfers and electron leaps through defects.



Acknowledgements: The Natural Science Foundation of Zhejiang Province (Grant No. LQ21E020006), the Fundamental Research Funds for the Provincial Universities of Zhejiang (Grant No. 2021YW46), and the National Natural Science Foundation of China (Grant 62205322, 22090043). are acknowledged for the financial support.

References

[1] J.P. Fu, R. Pang, L.H. Jiang, Y.L. Jia, W.Z. Sun, S. Zhang, C.Y. Li, *Dalton Trans*. **2016**, *45*, 13317–13323.
[2] Z.W. Zhou, J.M. Zheng, R. Shi, N.M. Zhang, J.M. Chen, R.Y. Zhang, H. Suo, E.M. Goldys, C.F. Guo, *ACS Appl. Mater. Interfaces.* **2017**, *9*, 6177–6185.
[3] S. Wang, B. Devakumar, Q. Sun, J. Liang, L. Sun, X. Huang, *J. Mater. Chem. C* **2020**, *8*, 4408–4420.
[4] S.Q. Chang, J.P. Fu, X. Sun, G.C. Bai, G.Q. Liu, K.N. Wang, L.G. Xu, Q. Wei, T. Meier, M.X. Tang, *Inorg. Chem.* **2022**, *61*, 3746–3753.
[5] J.P. Fu, R. Pang, L.H. Jiang, Y.L. Jia, W.Z. Sun, S. Zhang, C.Y. Li, *Dalton Trans*. **2016**, 45, 13317–13323.

Stabilization and Migration Mechanisms of Oxygen Defects in Gallium Germanates

Xiaohui Li,[1,2] Xiaojun Kuang,[2*] Xianran Xing[1*]
[1] *Beijing Advanced Innovation Center for Materials Genome Engineering, Institute of Solid State Chemistry, University of Science and Technology Beijing, Beijing 100083, People's Republic of China.*
[2] *Guangxi Key Laboratory of Electrochemical and Magnetochemical Functional Materials, College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, People's Republic of China.*
Email: lixiaohuiftd@126.com

Oxide ion conducting materials allow the transport of oxide ions, and have been widely attracting research interest due to their promising applications in the direction of new energy and catalysis.[1-3] Recently, gallium germanate-based oxide ion conductors with tetrahedral network structures have been developed successively, due to their remarkable capability to accommodate and transport oxide ions, especially focusing on the apatite and melilite structures. Herein, we have developed new gallium germanate based oxide ion conducting materials with open structural framework, and demonstrated the stabilization and migration mechanisms of oxygen defects in different gallium germanate structural frameworks. This study provides deeper understanding and important references for the stabilization and migration mechanisms of oxygen defects in gallium germanate based oxide ion conductors. [4-5]

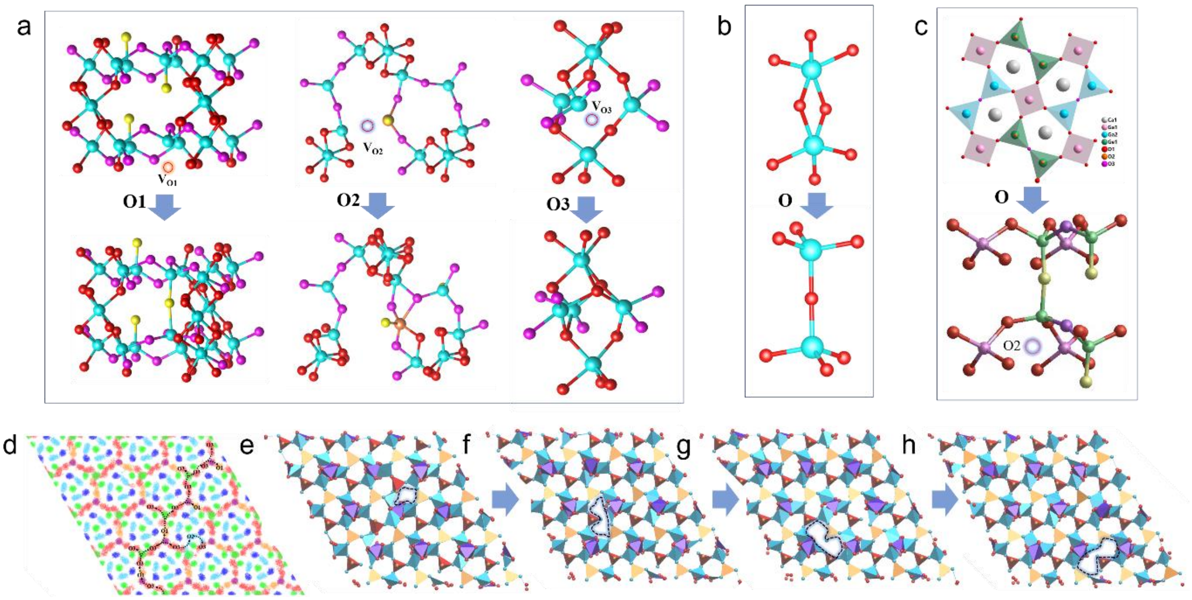


Figure 1. (a-c) Stabilization mechanisms of oxygen defects in different structures of gallium germanates. (d) Scatter plots of oxide ions and cations. (e-f) Structural evolutions of MD simulations as a function of simulattion times.

Acknowledgements: The National Natural Science Foundation of China (No. 22205017) and China Postdoctoral Science Foundation (No. 2022M720400) are acknowledged for the financial support.

References

[1] Wei, X.# **Li, X. #,*** Kuang, X.* Xing, X. *et al. ACS Appl. Energy Mater*, **2023**, *6*, 3986.
[2] **Li, X.;** Xing, X.; Sun, J.; * and Kuang, X.* *et al. J. Mater. Chem. A*, **2023**, *11*, 5615.
[3] Liang, L.; **Li, X.;#,*** Kuang, X.; and Xing, X.* *et al. Dalton Trans.*, **2023**, *52*, 7143.
[4] **Li, X.;** Xing, X.; Sun, J.; * and Kuang, X.* *et al. Sci. China Mater*, **2022**, *65 (10)*, 2737.
Li, X.; Xing, X.; Sun, J.; * and Kuang, X.* *et al. Sci. China Mater*, **2022**, *65 (11)*, 3186.
[5] Zeng, X.# **Li, X. #,*** Kuang, X.* Xing, X. *et al. Inorg. Chem. Front*, **2022**, *9*, 4486.

Synthesis and Investigation on Proton Conduction in Acceptor Doping $LaVO_4$ Ceramics

Xinyue Geng,[1, #] Gaoqing Hang,[1, #] Alberto Jose Fernández-Carrión[1], Xiaojun Kuang[1, 2], Xiaoyan Yang[1,*]
[1] *MOE Key Laboratory of New Processing Technology for Nonferrous Metal and Materials, Guangxi Key Laboratory of Optical and Electronic Materials and Devices, College of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, P. R. China.*
[2] *College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, P. R. China.*
Corresponding author: yangxy@glut.edu.cn

Rare-earth vanadate has been attracted great interest due to their electronic properties[1], luminescence[2], and catalytic activity[3]. In 2011, it was firstly reported that Ca^{2+} solubility on La^{3+} sites in monoclinic $LaVO_4$ mixed oxide ion and proton conductor, exhibited the solubility of Ca^{2+} no exceed than 0.01 mol and the conductivity of $La_{0.99}Ca_{0.01}VO_{3.995}$ near to 6×10^{-4} S cm^{-1} at 900°C under wet O_2[1], but no further investigation on defect stabilization and ion migration in this study. Herein, polycrystalline ceramics of $LaVO_4$ and $La_{0.99}A_{0.01}VO_{3.995}$ (A = Ca, Sr and Ba) were synthesized by conventional high temperature solid-state reaction method, and the proton conductivities as well as the proton defect stabilization and migration were investigated. Among them, $La_{0.99}Sr_{0.01}VO_{3.995}$ presents the best conductivity with the value of ~10^{-3} S cm^{-1} at 900°C under wet O_2 (Figure 1). Energetics of proton defect formation and migration were computed based on first-principal calculations using the PAW method implemented in the VASP code. The results reveal protons prefer to form hydrogen bonds with the oxygen sites close to dopants A^{2+}, then transport through continuous jumping and rotation between inter- and intra-tetrahedral VO_4 tetrahedra. This study provides a useful guide for understanding and clarifying the stabilization and conduction mechanism of proton defects in acceptor doping $LaVO_4$.

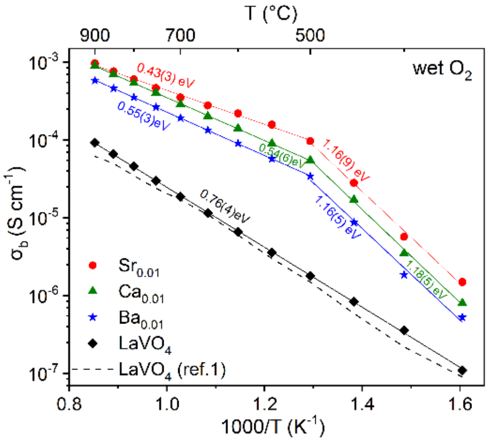


Figure 1. Arrhenius plot of the conductivities for $LaVO_4$ and $La_{0.99}A_{0.01}VO_{3.995}$ (A = Ca，Sr，Ba) under wet O_2.

Acknowledgements: National Natural Science Foundation of China (22005073); Guangxi Natural Science Foundation (2020GXNSFAA297050); Open Foundation of Guangxi Key Laboratory of Optical and Electronic Materials and Devices (20AA-1); Scientific research start-up fund of GLUT (GUTQDJJ 2017011) are acknowledged for the financial support.

References

[1] M Huse, T Norby, R Haugsrud. *J. Electrochem. Soc*. **2011**, 158, 867.
[2] Z Feng, B B Lou , Q Chen, et al. *Inorg. Chem.* **2021**, 60, 16614.
[3] Zhang M Y, Pham H K, Fang Y A, et al. *J. Mater. Chem. A*. **2019**, 7, 14816.

High-Pressure Synthesis of Highly Oxidised Transition-Metal Nitrides

Yao Yuan,[1] Simon D. Kloß,[2] J. Paul Attfield [1*]
[1] *Centre for Science at Extreme Conditions and School of Chemistry, University of Edinburgh, Edinburgh, UK.*
[2] *Department of Chemistry, Ludwig-Maximilians-Universität München, Munich, Germany.*
Corresponding author: j.p.attfield@ed.ac.uk

Mixed A (alkali metal, alkaline earth or rare earth) – M (transitional metal) oxides give rise to many important properties and have a diverse chemistry due to the stabilisation of a wide range of oxidation states, e.g. from +2 in $K_2Mn_2O_3$ to +7 in $KMnO_4$ for manganese. High oxidation state A-M-nitride counterparts are however much rarer or unknown as synthesis of solid nitrides, and in particular those with high nitrogen contents, is impeded by unfavourable nitride thermodynamics; nitride formation enthalpies are generally lower than in similar oxides due to the stable N≡N triple bond.[1] Sodium azide (NaN_3) is a versatile nitrogen source and it has recently been shown that high pressure high temperature (HPHT) reactions using NaN_3 can lead to the synthesis of stoichiometric ternary nitrides of transition metals in high oxidation states such as Ca_4FeN_4, Ca_2NiN_2, and $LaReN_3$.[2-4]

Using the above method we have recently discovered another highly oxidised Mn nitride, La_3MnN_5, based on Mn^{VI}. This has the Cs_3CoCl_5 structure type with $a = 6.8341(1)$, $c = 11.2356\ (2)$ Å. The powder X-ray structure reveals MnN_4 tetrahedra with $d(\text{Mn-N}) = 1.724(18)$ Å. La_3MnN_5 is notable as the first ternary nitride of its structure type (ICSD shows 141 reported Cs_3CoCl_5-type structures for halides, oxides, sulphides and some mixed anion examples), and La_3MnN_5 is also the highest oxidation state nitride reported to date.

Reactions between LaN and NaN_3 at 800 °C under 8 GPa pressure have led to the discovery of two defect rocksalt phases which are the first reported ternaries in the La-Na-N system.[5] One phase is $La_{1-x}Na_{3x}N$ with vacancies at octahedral La sites and interstitial tetrahedral Na cations. This phase has a tetragonally distorted rocksalt structure (space group $I4/mmm$, $a = 3.8704(2)$ and $c = 5.2098(3)$ Å) and the distortion decreases with increasing Na content, giving a cubic $Fm\bar{3}m$ phase ($a = 5.3055(2)$ Å). The latter composition coexists with another cubic $Fm\bar{3}m$ phase ($a = 5.1561\ (5)$ Å) that is based on a rocksalt type form of Na_3N with N-vacancies, '$NaN_{1/3}$', stabilised by a small amount of La at interstitial sites; $NaLa_yN_{(1+3y)/3}$ with $y < 1\%$. These initial investigations reveal that the high pressure La-Na-N phase diagram may be rich in defect rocksalt type materials.

Acknowledgements: The authors acknowledge EPSRC for funding. Y.Y. would like to thank the Talent Training Project of the Dalian Institute of Chemical Physics for support.

References

[1] R. Niewa, G. V. Vajenine, F. J. DiSalvo, H. Luob and W. B. Yelon, *Z. Naturforsch. B* **1998**, *53*, 63–74.
[2] S. D. Kloß, A. Haffner, P. Manuel, M. Goto, Y. Shimakawa and J. P. Attfield, *Nat. Commun.* **2021**, *12*, 571.
[3] S. D. Kloß and J. P. Attfield, *Chem. Commun.* **2021**, *57*, 10427-10430
[4] S. D. Kloß, M. L. Weidemann and J. P. Attfield, *Angew. Chem. Int. Ed.* **2021**, *60*, 22260-22264.
[5] Y. Yuan, S. D. Kloß and J. P. Attfield, *Phil. Trans. R. Soc. A.* **2023**, *381*, 20220329.

Frenkel Defect-modulated Anti-thermal Quenching Luminescence in Lanthanide-doped $Sc_2(WO_4)_3$

Yang Wei,[2] Ling Huang[1*]

[1] State Key Laboratory of Chemistry and Utilization Carbon Based Energy Resources, College of Chemistry, Xinjiang University, No.666 Shengli Road, Tianshan District, Urumqi, China.

[2] College of Engineering and Applied Sciences, Nanjing University, No. 163 Xianlin Avenue, Qixia District, Nanjing, China.

Corresponding author: lhuang@xju.edu.cn

Although large amount of effort has been invested in combating thermal quenching that severely degrades the performance of luminescent materials particularly at high temperatures, not much affirmative progress has been realized. Herein, we demonstrate that the Frenkel defect formed via controlled annealing of $Sc_2(WO_4)_3$:Ln (Ln = Yb, Er, Eu, Tb, Sm), can work as energy reservoir and back-transfer the stored excitation energy to Ln^{3+} upon heating. Therefore, except routine anti-thermal quenching, thermally enhanced 415-fold downshifting and 405-fold upconversion luminescence are even obtained in $Sc_2(WO_4)_3$:Yb/Er, which has set a record of both the Yb^{3+}-Er^{3+} energy transfer efficiency (> 85%) and the working temperature at 500 and 1073 K, respectively. Moreover, this design strategy is extendable to other hosts possessing Frenkel defect, and modulation of which directly determines whether enhanced or decreased luminescence can be obtained. This discovery has paved new avenues to reliable generation of high-temperature luminescence.

Acknowledgements: The National Natural Science Foundation of China (No. 21871137, 91956107) is acknowledged for the financial support.

References

[1] Y. Wei, Y. Pan, E. Zhou, Z. Yuan, H. Song, Y. Wang, J. Zhou, J. Rui, M. Xu, L. Ning, Z. Liu, H. Wang, X. Xie, X. Tang, H. Su, X. Xing, L. Huang, *Angew. Chem. Int. Ed*. **2023**, *62*, e202303482.

[2] L. Chen, X. Chen, R. Ma, K. Lin, Q. Li, J.-P. Lang, C. Liu, K. Kato, L. Huang, X. Xing, *J. Am. Chem. Soc*. **2022**, *144*, 13688.

[3] X. Cheng, J. Zhou, J. Yue, Y. Wei, C. Gao, X. Xie, L. Huang, *Chem. Rev*. **2022**, *122*, 15998.

[4] R. Zheng, Y. Wei, Z.-C. Zhang, Z.-Y. Wang, L.-L. Ma, Y. Wang, L. Huang, Y.-Q. Lu, *Responsive Mater*. **2023**. (DOI: DOI: 10.1002/rpm.20230017)

The Perfect Kagomé Lattice by the Substitution for Triangle Slab Exhibiting Heisenberg Spin Glass

Wenbin Guo[1], Xiaohui Yan[1], Alberto J. Fernández-Carrión[1], Meiyan Cui[2], Zhangzhen He[2], Congling Yin[1], and Xiaojun Kuang[1,3]*

[1] MOE Key Laboratory of New Processing Technology for Nonferrous Metal and Materials, Guangxi Key Laboratory of Optic and Electronic Materials and Devices, College of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, P. R. China

[2] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China

[3] College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, P. R. China.

Corresponding author: kuangxj@glut.edu.cn

Two-dimensional kagomé antiferromagnets with $S = 1/2$ are promising materials to discover the candidates of quantum spin liquid states[1]. Based on the substitution for triangle slabs in $Na_2BaMg(PO_4)_2$[2], a geometrically perfect kagomé lattice in vanadate of $Pb_{2.62}Mn_3Mg_2V_2O_{15.62}$ was constructed. Crystal structure and magnetic properties were characterized by a combination of single-crystal X-ray diffraction, nuclear magnetic resonance, magnetic susceptibilities, and specific heat measurements. NMR and TG data indicate oxygen vacancy stemming from VO_4 groups. Each MgO_6 polyhedron shares a corner with six MnO_6 and three VO_4 tetrahedra to form a sandwich-like slab $\{[Mg(VO_4)][Mn_3O_8][Mg(VO_4)]\}_\infty$, where the perfect kagomé lattice building by edge-sharing MnO_6 polyhedra is sandwiched within the slabs. The strong geometrical frustration and Heisenberg spin-glass transition around 4.5 K coexist in this compound. Our work provides a feasible strategy to substitute the kagomé for a triangle lattice.

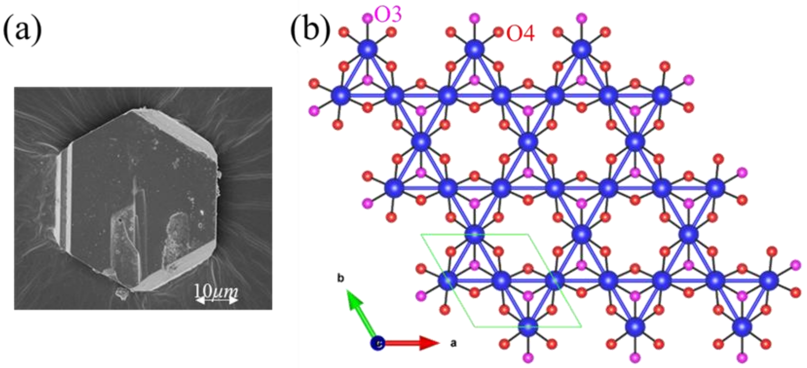


Figure 1. (a) The SEM picture of a single crystal, (b) the kagomé lattice building by edge-sharing MnO_6 at *ab* plane.

Acknowledgments: The China Postdoctoral Science Foundation (No.2022MD713743), Guangxi Science Foundation (No.AD222035120), and National Natural Science Foundation of China (No. 21875049, 11864008, and 12264011) are acknowledged for the financial support.

References

[1] C. Broholm, R. Cava, S. Kivelson, D. Nocera, M. Norman, T. Senthil, *Science* **2020,** *367* (6475), eaay0668.
[2] A. Boukhris, M. Hidouri, B. Glorieux, M. Ben Amara, *J. Rare Earths*, **2013**, *31*, 849.

Research Progress of AMO_4-Based Scheelite Solid-State Oxygen Ion Conductors

Changliang Ou, Gaoqing Hang, Xinyue Geng, Xiaoyan Yang*
[1] *MOE Key Laboratory of New Processing Technology for Nonferrous Metal and Materials, Guangxi Key Laboratory of Optical and Electronic Materials and Devices, College of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, P. R. China*
Corresponding author: yangxy@glut.edu.cn

Solid oxygen ion conductors are the core component of solid oxide fuel cells, gas sensors and other related devices, which play a decisive role in corresponding devices applications[1]. AMO_4-based (A = alkaline earth metal, rare earth metal, Pb and Bi; M = W, Mo, V, P, Nb *etc.*) scheelite compounds have received extensive attention due to their structures feature the isolated tetrahedral moieties, which have been demonstrated to exhibit relatively high tolerance for deformation and rotation[2-4]. Here we review the research progress of AMO_4-based scheelite solid-state oxygen ion conductors, includes the crystal structure, conductivity, interstitial oxygen and oxygen vacancy defects stabilization, as well as oxygen ion migration mechanisms (Figure 1). Furthermore, we mention the potential application of AMO_4-based compositions in related devices and the possibility of theoretical prediction for the development of new excellent solid-state oxygen ion conductors. It would provide reference and guidance for the subsequent research in the field of inorganic solid-state ionic conducting materials.

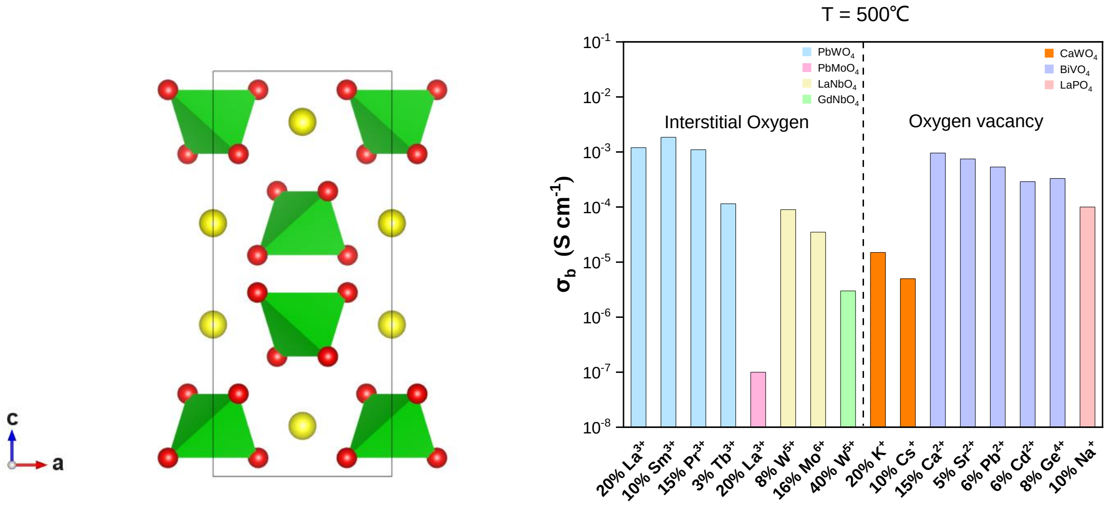


Figure 1. Crystal structure of AMO_4-based scheelites and comparison of the conductivities for different AMO_4-based scheelite compositions.

Acknowledgements: National Natural Science Foundation of China (22005073), Guangxi Natural Science Foundation (2020GXNSFAA297050); Open Foundation of Guangxi Key Laboratory of Optical and Electronic Materials and Devices (20AA-1); Scientific research start-up fund of GLUT (GUTQDJJ 2017011) are acknowledged for the financial support.

References

[1] X.Y. Yang, A.J. Fernandez-Carrion, X.J. Kuang, *Chem. Rev.*, **2023**, 123, 9356.
[2] S. Takai, M. Satou, T. Yoshida, et.al, *Electro. chem*. **2011**, 79, 696.
[3] X.Y. Yang, X.L. Zeng, X. Ming, et.al, *Inorg. Chem.* **2022**, 9, 2644.
[4] J. Li, F.J. Pan, S.P. Geng, et.al, *Nat. Commun*. **2020**, 11, 4751.

Combining Different Structural Motifs Tailoring in $Ca_nBi_{n+2}O_{2n+2}Cl_{n+2}$ (n = 1,2) van der Waals Semiconductors with photocatalytic activity

Bin Cheng[1], *Cécile Geneois*[2], *Jia Yang*[3], *Lunhua He*[4], *Congling Yin*[1*], *Mathieu Allix*[2*], *and Xiaojun Kuang*[1,3*]

1. MOE Key Laboratory of New Processing Technology for Nonferrous Metal and Materials, Guangxi Key Laboratory of Optical and Electronic Materials and Devices, College of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, P. R. China

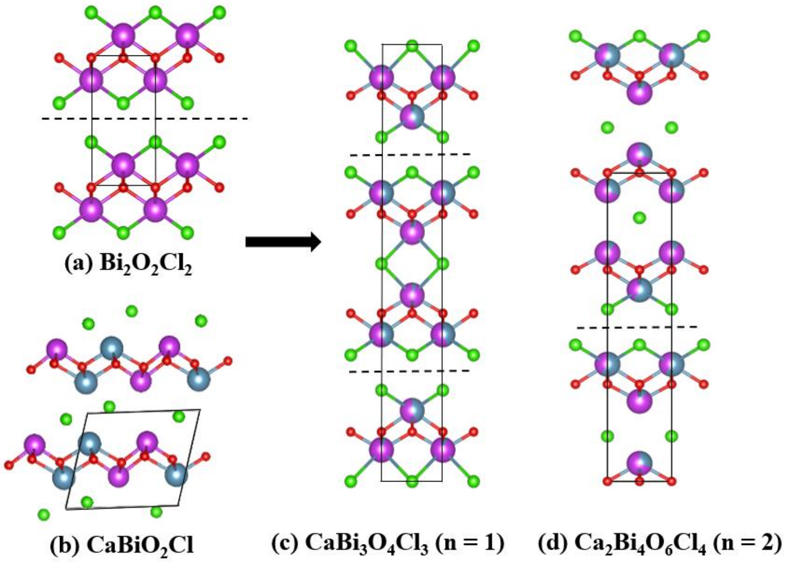
2. CNRS, CEMHTI UPR3079, Univ. Orléans, F-45071 Orléans, France

3. Guangxi Key Laboratory of Electrochemical and Magnetochemical Functional Materials, College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, P. R. China

4. Spallat Neutron Source Sci Ctr, Dongguan 523803, P. R. China

Abstract

Both layered multiple-anion compounds and homologous series are of interest for their electronic properties, including the ability to tune the properties by changing the nature or number of the layers. Here, we successfully synthesized the layered oxyhalides compounds $CaBi_3O_4Cl_3$ and $Ca_2Bi_4O_6Cl_4$, which are a 1:1 and 1:2 superlattice of the structural units present in van der Waals insulators $Bi_2O_2Cl_2$ and $CaBiO_2Cl$. Ca and Bi were mixed in all the cationic sites, and the ideal $[Ca_{0.5}Bi_{1.5}O_2]$ block was formed in the unit cell, which plays a key role in the stability of these phases. Additionally, both $CaBi_3O_4Cl_3$ and $Ca_2Bi_4O_6Cl_4$ display indirect band gaps of 2.4-2.6 eV. $CaBi_3O_4Cl_3$ showed photocatalytic H_2 evolution activity under visible-light.


(a) $Bi_2O_2Cl_2$

(b) $CaBiO_2Cl$ (c) $CaBi_3O_4Cl_3$ (n = 1) (d) $Ca_2Bi_4O_6Cl_4$ (n = 2)

Fig.1. The crystal structures of (a) $Bi_2O_2Cl_2$, (b) $CaBiO_2Cl$, (c) CaBi3O4Cl3, (d) $Ca_2Bi_4O_6Cl_4$.

Acknowledgements: National Guangxi Natural Science Foundation (2020GXNSFAA297050);

Reference:

[1] L.G. Sillén, *Naturwissenschaften* **1942**, 22, 318-324.

[2] H.Suzuki, M.Higashi, O.Tomita, Y,Ishii, T.Yamamoto, D.Kato, T.Kontani, D.Ozaki, S.Nozawa, K.Nakashima, K.Fujita, A.Saeki, H.Kageyama and R.Abe, *Chem Mater*, **2021**, 33, 9580-9587.

$Bi_{2+2n}O_{2+2n}Se_nX_2$ van der Waals Semiconductors with Low Thermal Conductivities

Ji Ruiwen[1], Cécile Genevois[2], Mathieu Allix[2], Congling Yin[1]*, Xiaojun Kuang[1] *

[1] *College of Materials Science and Engineering, Guilin University of Technology, Guilin 541004 P. R. China*

[2] *Université d'Orléans, Faculté des Sciences, Avenue du Parc Floral, 45067 Orléans Cedex 2, France*

Corresponding author: congling.yin@glut.edu.cn and kuangxj@glut.edu.cn

Layered materials coupling a two-dimensional strong-bonding layered network with much weaker van der Waals (vdW) interaction between the layers are sought after for the development of nanoelectronics and energy conversion devices. It is important to elucidate the layer stacking rules in these vdW materials and control the thickness of the strong-bonding layers for tuning the nanosheet height during exfoliation and therefore tailor physical properties. Here we show that the single Bi_2O_2Se ionic layer in the three-anion vdW semiconductor $Bi_4O_4SeCl_2$ showing extremely low thermal conductivity can be expanded to higher-order layers forming a homologous series $Bi_{2+2n}O_{2+2n}Se_nX_2$ (X = Cl, Br) with variable ionic layer thicknesses. $Bi_4O_4SeX_2$ (n = 1) and $Bi_6O_6Se_2X_2$ (n = 2) were isolated as single-phase materials, while materials with larger layer thicknesses such as $Bi_8O_8Se_3Cl_2$ (n = 3) contain different defect-intergrowth structures at the crystallite scale. The anionic disorder of Se and X within the Bi_2O_2Se and $Bi_2O_2X_2$ slabs is a critical factor in the stabilization of $Bi_{2+2n}O_{2+2n}Se_nX_2$. The ~50% Se substitution by X anions in the Bi_2O_2Se slab as related to the weak interlayer interaction can serve a stabilization criterion of $Bi_{2+2n}O_{2+2n}Se_nX_2$. All these materials show similar optical indirect band gaps of ~ 1.05 eV, originating from the electronic states in the Bi_2O_2Se slabs. Pellets prepared from these vdW materials possessed low bulk resistivities (100 Ω.cm) and exceptionally low and tunable thermal conductivities (0.66 W/mK and lower) parallel to the pressing axis of the pellets (heavier the halogen is, lower is the thermal conductivity). The results presented here provide important multiple anion chemistry for tailoring the ionic-bonding network into different thicknesses in the vdW layered structures and therefore their physical properties.

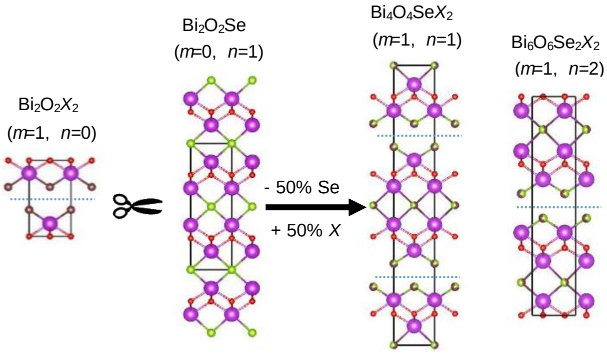


Figure 1. the ionic Bi_2O_2Se layer can be cut by $Bi_2O_2X_2$ vdW slab into different heights

Acknowledgements: The National Natural Science Foundation of China (No. 22161014, 21850410458) is acknowledged for the financial support.

References

[1] H. Kageyama, K. Hayashi, K. Maeda, J. P. Attfield, Z. Hiroi, J. M. Rondinelli, K. R. Poeppelmeier, *Nat. Commun*. **2018**, *9*, 772.

[2] Q. D. Gibson, T. Zhao, L. M. Daniels, H. C. Walker, R. Daou, S. Hébert, M. Zanella, M. S. Dyer, J. B. Claridge, B. Slater, M. W. Gaultois1, F. Corà, J. Alaria, M. J. Rosseinsky *Science* **2021**, *373*, 1017–1022.

[3] R.W Ji, M. Lei, C. Genevois, W.D. Zhang, X. Ming, L.H. He, M. Allix, C.L. Yin, X.J. Kuang, and X.R. Xing, *Chem. Mater.* **2022**, *34*, 4751-4764.

Lists of delegates

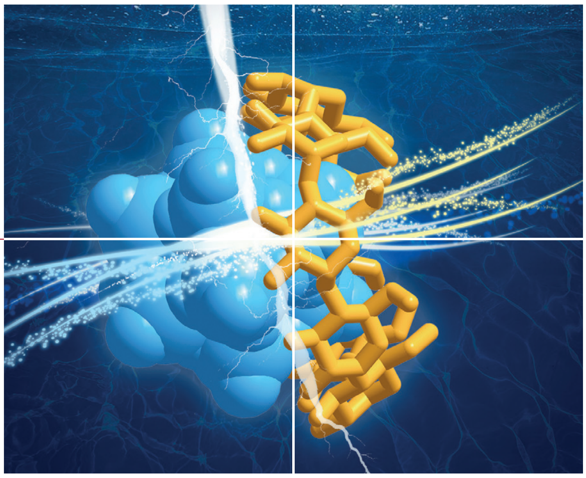
No.	Delegate	Organization	Email
1	Alberto J. Fernández Carrión	University of Seville	alberto@glut.edu.cn
2	Anucha Koedtruad	Institute of High Energy Physic, Chinese Academy of Science	anuchakoedtruad@ihep.ac.cn
3	Artem R. Oganov	Skolkovo Institute of Science and Technology	A.Oganov@skoltech.ru
4	Bin Cheng	Guilin University of Technology	2120210256@glut.edu.cn
5	Bin Huang	Guilin University of Technology	bin@glut.edu.cn
6	Changliang Ou	Guilin University of Technology	
7	Changqing Jin	Institute of Physics, Chinese Academy of Sciences	Jin@iphy.ac.cn
8	ChangZheng Hu	Guilin University of Technology	huchzh@glut.edu.cn
9	Chen Li	Center for High Pressure Science and Technology Advanced Research	Chen.li@hpstar.ac.cn
10	Chengxin Xu	Center for High Pressure Science&Technology Advanced Research	Chengxin.xu@hpstar.ac.cn
11	Chenjie Lou	Center for High Pressure Science and Technology Advanced Research, Beijing	chenjie.lou@hpstar.ac.cn
12	Chenliang Ye	Tsinghua University	
13	Chun-Hai Wang	Northwestern Polytechnical University	chwang81@gmail.com
14	Congling Yin	Guilin University of Technology	congling.yin@glut.edu.cn
15	Deyang Xu	Guilin University of Technology	
16	En Chen	Center for High Pressure Science and Technology Advanced Research	en.chen@hpstar.ac.cn
17	Fenghua Ding	Kyoto University	dingfenghua-csu@hotmail.com
18	Fupei Liang	Guilin University of Technology	liangfupei@glut.edu.cn
19	Guo-Cong Guo	Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences	gcguo@fjirsm.ac.cn
20	Guohong Zou	Sichuan University	zough@scu.edu.cn
21	He Zhu	Nanjing University of Science and Technology	hezhu@njust.edu.cn
22	Hiroshi Kageyama	Kyoto University	kage@scl.kyoto-u.ac.jp
23	Hongcheng Lu	Huazhong University of Science and Technology	HCL@hust.edu.cn
24	Huajie Luo	University of Science and Technology Beijing	hjluo@ustb.edu.cn
25	Irina Cherepanova	Ural Federal University	
26	J. Paul Attfield	University of Edinburgh	j.p.attfield@ed.ac.uk
27	Jian Li	Peking University	jian.li@nju.edu.cn
28	Jiawang Hong	Beijing Institute of Technology,	hongjw@bit.edu.cn
29	Ji-Jing Xu	Jilin University	jijingxu@jlu.edu.cn
30	Jin Wang	Shenzhen University	2023043@ahnu.edu.cn
31	Jinghai Liu	Inner Mongolia Minzu University	jhliu2015@imun.edu.cn
32	Jingtai Zhao	Guilin University of Electronic Technology	jtzhao@shu.edu.cn
33	Jinxiao Zhang	Guilin University of Technology	jxzh@glut.edu.cn
34	Jipeng Fu	China Jiliang University	fujipeng@cjlu.edu.cn
35	Jun Chen	Hainan University	junchen@ustb.edu.cn
36	Jungu Xu	Guilin University of Technology	xujungu@126.com
37	Junliang Sun	Peking University	junliang.sun@pku.edu.cn

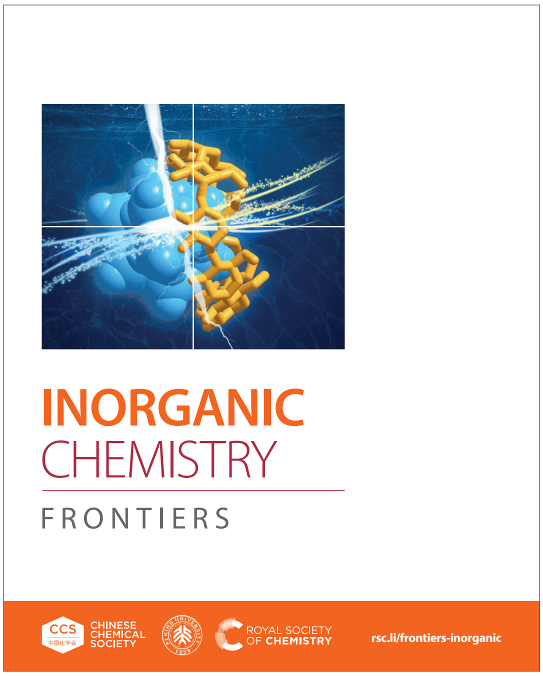
38	Junling Wang	Southern University of Science and Technology	jwang@sustech.edu.cn
39	Kailin Deng	Royal Society of Chemistry, UK（Deputy Editor)	dengk@rsc.org
40	Keke Huang	Jilin University	kkhuang@jlu.edu.cn
41	Kun Lin	University of Science and Technology Beijing	xing@ustb.edu.cn
42	Kuo Li	Center for High Pressure Science and Technology Advanced Research	likuo@hpstar.ac.cn
43	Ligang Xu	Center for High Pressure Science&Technology Advanced Research	ligang.xu@hpstar.ac.cn
44	Lin Gu	Tsinghua University	lingu@tsinghua.edu.cn
45	Ling Chen	Beijing Normal University	chenl@bnu.edu.cn
46	Ling Huang	Nanjing Tech University	iamlhuang@njtech.edu.cn
47	Liying Wang	City University of Hong Kong	
48	Man Xue	Guilin University of Technology	
49	Man-Rong Li	Hainan University	limanrong@hainanu.edu.cn
50	Mathieu Allix	CEMHTI-CNRS	mathieu.allix@cnrs-orleans.fr
51	Ming Li	University of Nottingham	ming.li@nottingham.ac.uk
52	Minghua Zeng	Guangxi Normal University	zmh@mailbox.gxnu.edu.cn
53	Minghui Yang	Dalian University of Technology	myang@dlut.edu.cn
54	Mingxue Tang	University of Science and Technology Beijing	mingxue.tang@hpstar.ac.cn
55	Olga Sidorova	Ural State Pedagogical University	
56	Ping Miao	Institute of High Energy Physics, Chinese Academy of Sciences	miaoping@ihep.ac.cn
57	Qiang Li	University of Science and Technology Beijing	qiangli@ustb.edu.cn
58	QingZhen Huang	China Spallation Neutron Source (CSNS)	huangqz@ihep.ac.cn
59	Ru-Shi Liu	National Taiwan University	rsliu@ntu.edu.tw
60	Sangen Zhao	Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences	zhaosangen@fjirsm.ac.cn
61	Sergii Khmelevskyi	Vienna University of Technology	sk@cms.tuwien.ac.at
62	Shu-Fen Hu	Taiwan Normal University	sfhu.hu@gmail.com
63	Sihao Deng	Spallation Neutron Source Science Center	dengsh@ihep.ac.cn
64	Susana García Martín	Universidad Complutense	sgmartin@quim.ucm.es
65	Takafumi Yamamoto	Tokyo Institute of Technology	yama@msl.titech.ac.jp
66	Tang Ya	Shanghai University	tangya0709@shu.edu.cn
67	Tao Yang	Chongqing University	taoyang@cqu.edu.cn
68	Tianyao Pei	Center for High Pressure Science & Technology Advanced Research	Tianyao.pei@hpstar.ac.cn
69	Valeriy Sidorov	Ural State Pedagogical University	sidorov@uspu.ru
70	Vladimir Cherepanov	Ural Federal University	v.a.cherepanov@urfu.ru
71	Weiwei Cao	University of Science and Technology Beijing	caoweiwei@ustb.edu.cn
72	Wenbin Guo	Guilin University of Technology	
73	Wenda Zhang	Guilin University of Technology	wenda.zhang@hpstar.ac.cn
74	Xiangfei Kong	Guilin University of Technology	xiangfei.kong@glut.edu.cn
75	Xianran Xing	University of Science and Technology Beijing	xing@ustb.edu.cn
76	Xiao Ma	Guilin University of Technology	
77	Xiaohui Li	University of Science and Technology Beijing	lixiaohuiftd@126.com
78	Xiaojun Kuang	Guilin University of Technology	kuangxj@glut.edu.cn
79	Xiao-Ming Wang	Shaanxi Normal University	xmwang@snnu.edu.cn

80	Xiaoyan Yang	Guilin University of Technology	yangxy@glut.edu.cn
81	Xinyue Geng	Guilin University of Technology	yangxy@glut.edu.cn
82	Xiping Jing	Peking University	xpjing@pku.edu.cn
83	Xueming Li	Guilin University of Technology	lixueming@glut.edu.cn
84	Xueyuan Chen	Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences	xchen@fjirsm.ac.cn
85	Yang Ren	City University of Hong Kong	yangren@cityu.edu.hk
86	Yang Wei	Nanjing University	yangwei20630@163.com
87	Yao Yuan	University of Edinburgh, Edinburgh	yuanyao11@outlook.com
88	Yaoqing Zhang	Nature Publishing group	Yaoqing.Zhang@nature.com
89	Yijia Sunhuang	Guilin University of Technology	
90	Yili Cao	University of Science and Technology Beijing	yilicao@ustb.edu.cn
91	Yilin Wang	Nanjing Tech University	iamyilinwang@njtech.edu.cn
92	Ying Tang	Guilin University of Technology	tangyinggl001@aliyun.com
93	Yongping Liu	Guilin University of Technology	liuyp624@163.com
94	Yu Cao	Kyoto University	cao.yu.8y@kyoto-u.ac.jp
95	Yuichi Shimakawa	Kyoto University	shimak@scl.kyoto-u.ac.jp
96	Zhenhong Tan	Institute of High Energy Physics, Chinese Academy of Sciences	tanzh@ihep.ac.cn
97	Zhihua Sun	Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences	sunzhihua@fjirsm.ac.cn
98	Zhiqun He	Beijing Jiaotong University	zhqhe@bjtu.edu.cn
99	Zi-En Cheng	Chongqing University	1606488220@qq.com
100	Zuheng Jin	Guilin University of Technology	huchzh@foxmail.com

INORGANIC
CHEMISTRY
FRONTIERS

The international, high quality journal for interdisciplinary research between inorganic chemistry and related subjects





INORGANIC
CHEMISTRY
FRONTIERS

CCS CHINESE CHEMICAL SOCIETY · ROYAL SOCIETY OF CHEMISTRY · rsc.li/frontiers-inorganic

rsc.li/frontiers-inorganic
InorgChemFrontiersED@rsc.org
@InorgChemFront

微信搜一搜
FrontiersRSC

2-year Impact Factor: **7.0** *
Article Publications: **670***
Best IF Quartile: **Q1** (Chemistry, Inorganic & Nuclear)
CiteScore: **10.1** **
Median time to 1st decision: **29** days ***

* 2022 Journal Citation Reports (Clarivate Analytics, 2023)
** CiteScore 2019-22 (Elsevier, 2023)
*** For submissions in 2022 that underwent peer review only

中科院一区Top期刊|入选中国科技期刊卓越行动计划

Journal Scope

Inorganic Chemistry Frontiers values cutting-edge research at the interfaces between inorganic chemistry and related fields, such as materials science, biochemistry, nanotechnology, and catalysis. Significant advances in inorganic chemistry are essential.

Editorial Board

Editor-in-Chief
Song Gao（高松）
Peking University&Sun Yat-sen University, China

Editorial board members
Xianran Xing（邢献然）
University of Science and Technology Beijing, China
Hiroshi Kitagawa
Kyoto University, Japan
Yu Tang （唐瑜）
Lanzhou University, China
Nanfeng Zheng（郑南峰）
Xiamen University, China

Associate Editors
Jun Chen (陈军)
Nankai University, China
Paula Diaconescu
University of California, Los Angeles, USA
Svetlana Mintova
CNRS, France
Zhiping Zheng (郑智平)
Southern University of Science and Technology, China
Justin J. Wilson
Cornell University, USA
Teppei Yamada
University of Tokyo, Japan

CCS 中国化学会 CHINESE CHEMICAL SOCIETY
ROYAL SOCIETY OF CHEMISTRY

Guilin University of Technology (GUT)

Founded in 1956, Guilin University of Technology (GUT) is situated in Guilin, a world-famous tourist destination and a convenient transportation hub connecting southern China. It takes 3 hours to reach nearly all major cities in Asia. It is one of the gateway cities of the China-Asean Free Trade Zone and an important connection point between "One Belt One Road" and Guizhou, Guangdong, Hunan, and Guangxi provinces.

GUT has been managed and invested by the national and local governments with its daily affairs managed mainly by Guangxi Zhuang Autonomous Region, the provincial government. Covering more than 220 hectares, GUT has four campuses, namely Pingfeng (in Guilin), Yanshan (in Guilin), Anji (in Nanning), and Konggang (in Nanning). With nearly 3,000 teachers and staff, the university has 19 faculties and provides Ph.D, postgraduate, and undergraduate degree programs as well as high vocational programs for over 40,000 full-time students. The GUT has developed into a university of multiple disciplines. The education of postgraduate, undergraduate, higher vocation, and adult continuing education have been developing harmoniously.

GUT aims to cultivate practice-oriented advanced professional talents, holding the key majors with distinctive features, such as Geology, Environment, Material, Civil Engineering, Surveying and Mapping, Tourism and Management. Some majors have obtained the top list in the national ranking, which are Surveying and Mapping Engineering, Tourism Management, as well as Business Administration.

Focusing on quality-oriented education, GUT also has paid attention to expanding the scale of education and developing research programs. The university has won the highest award of Guangxi scientific research achievement of higher education and the National Scientific Progress Prize. For more than half a century, the university has brought up nearly 100,000 professional and technical talents. The rate of graduate employment has reached 90% every year. Our graduates are welcomed by enterprises and institutions due to their solid professional basic knowledge and hands-on abilities.

For the purposes of promoting international exchanges and cooperation, GUT has insisted on an opening-up policy and actively built an international cooperation system that is all-round, multi-level, and in various forms. So far the university has established cooperative relations with over 100 colleges from 30 countries, including the United States, UK, Australia, Japan, Russia, Malaysia, and so on. It also signed academic exchanges, personnel training, and scientific research cooperation agreements with 50 famous universities. International education has developed steadily- so far there are over 6600 students have had courses at GUT from more than 60 countries.