

Exploring Novel Functional Compounds

CAS/MPG Partner Group on Chemistry and Physics of Inorganic Solid State Materials

Shanghai-Dresden, 2006.8.1 – 2011.7.31



Inauguration ceremony for the establishment of the MPS/CAS Partner Group, August 3, 2006. From left: LUO Hongjie (then Director of SIC-CAS), ZHAO Jingtai (Partner Group Leader), LU Yongxiang (then President of CAS), Peter Gruss (President of the Max Planck Society), three members from the MPS/CAS Partner Group on Astronomy, Ruediger Kniep (then Director, now Emeritus Director of MPI-CPFS), and Yuri Grin (Director of MPI-CPFS).

The MPS/CAS Partner Group on the Chemistry and Physics of Inorganic Solid State Materials was formally established in 2006 by the Shanghai Institute of Ceramics, CAS (SIC-CAS) and the Max Planck Institute for Chemical Physics of Solids (MPI-CPFS). The work of the group focused on two research directions within the scope of solid state chemistry and physics, namely intermetallic compounds and inorganic borophosphates and related compounds. Cooperative work has been carried out at both sides, either through the exchange of students and coworkers or by sharing research facilities. The outcomes of the collaboration are justified through joint and partner group facilitated publications, joint contributions at scientific conferences, co-supervised students, exchange visits of members and joint scientific reports.

Reported by Group Leader ZHAO Jingtai



Group photo of the 3rd Shanghai Workshop on X-ray Crystallography, which was initiated and organized by the MPS/CAS Partner Group at SIC-CAS.

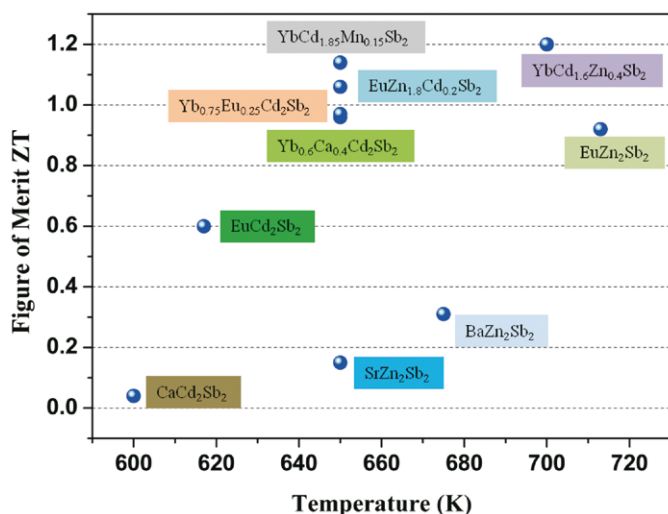
The research work within the partner group has scored great progress since its establishment. This includes the preparation and characterization of more than 30 new compounds, among which over 10 crystallize in new structure types. New synthetic methods have been developed to design and synthesize new compounds, such as rare earth borophosphates and borogermanates. New potential thermoelectric and fluorescent materials were discovered among the new families of compounds, several of them revealing promising physical behaviors. The research yielded 26 publications that have already appeared, along with several more to be published, and numerous presentations at international and national conferences. Among the ten co-supervised and exchange students, five have already obtained their Ph.D. degrees. Five post-doctoral researchers have participated or are still participating in joint research

projects within the partner group. More than 20 scientific exchange visits have been realized within this scope. The group also initiated the yearly Shanghai Workshop on X-Ray Crystallography, which have been successfully convened for four times by far. Below are two examples of our joint research work.

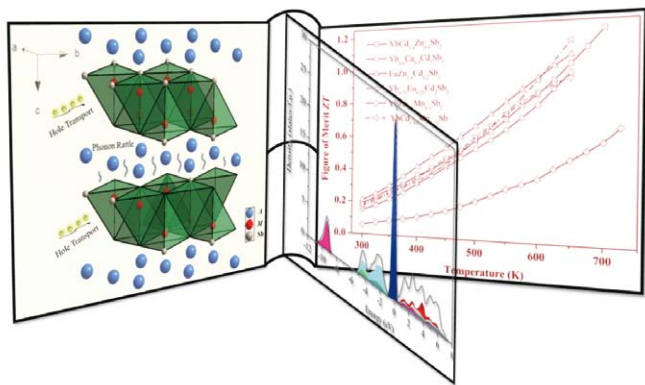
MAJOR RESEARCH THEMES

1. Synthesis, crystal structure study and thermoelectric property characterization of Zintl phases AB_2X_2 (A = Ca, Sr, Ba, Eu, Yb; B = Zn, Cd, Mn; X = Sb)

During the last few years, our attention was focused on the synthesis, structural investigation and property characterization of several series of AM_2X_2 compounds (where A is an alkaline-earth or a divalent rare-earth metal, M is Zn or Cd, and X is mainly Sb) as potential thermoelectric materials. More than nine members of the partner group participated in the research, including three faculty members, two postdocs



Thermoelectric figure-of-merit for AM₂X₂ compounds and their substitution variants.



Crystal structure and physical properties of AM₂X₂ compounds.

and four Ph.D. students. Ternary antimonides SrZn₂Sb₂, BaZn₂Sb₂, EuZn₂Sb₂, YbCd₂Sb₂, EuCd₂Sb₂, CaCd₂Sb₂ and their substitution variants were prepared by solid-state reaction techniques. The thermoelectric properties of the respective ternary Zintl compounds were improved within the quaternary solid solutions Yb_xEu_{1-x}Cd₂Sb₂, Ca_xYb_{1-x}Cd₂Sb₂, YbZn_xCd_{2-x}Sb₂, Eu(Zn_{1-x}Cd_x)₂Sb₂ and YbCd₂Sb_{2-x}Ge_x by substituting all the three crystallographic sites in the structure and introducing chemical disorder. The last, in turn, positively influenced the thermal conductivity of the materials, and allowed their thermoelectric figure-of-merit values to reach around 1.0, which is already interesting from the application point of view.

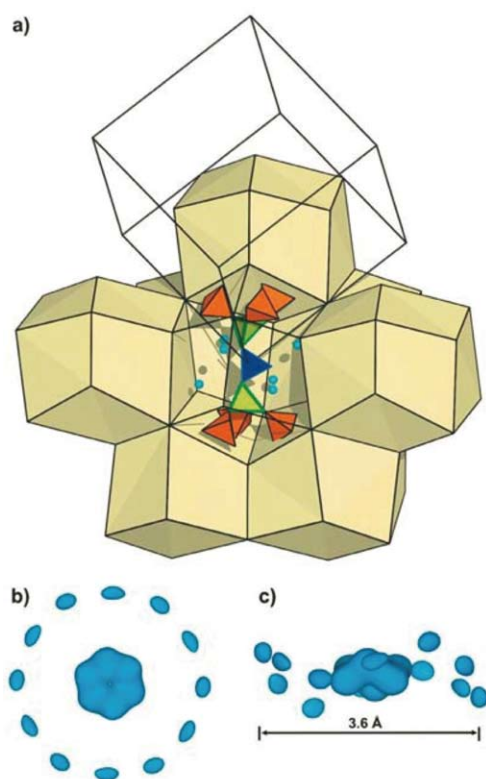
Polycrystalline antimonide BaZn₂Sb₂ was prepared and its thermoelectric prop-

erties in the temperature range from 2 to 675 K were investigated. This Zintl compound showed rather low thermal conductivity, 1.6 W m⁻¹ K⁻¹, at room temperature. The value of its thermoelectric figure-of-merit *ZT* reached 0.31 at 675 K. Its electronic structure, calculated by *ab initio* methods, suggested that the *p*-type electrical transport can be mainly ascribed to the [Zn₂Sb₂] framework. This compound provided the authors with a basic host lattice for the modification and optimization of thermoelectric properties through chemical substitution.

Already replacement of barium with europium enhanced remarkably the thermoelectric activity. The thermoelectric performance of EuZn₂Sb₂ and EuCd₂Sb₂ was further optimized by mixed occupation of the transition metal position. Samples in the solid solution

Eu(Zn_{1-x}Cd_x)₂Sb₂ with the CaAl₂Si₂-type crystal structure were prepared from the elements for compositions with *x* = 0, 0.1, 0.3, 0.5 and 1. The thermoelectric properties were investigated after densification of the products by spark plasma sintering (SPS). The samples showed low electrical resistivity, high thermopower and a low lattice thermal conductivity. The highest *ZT* value of 1.06 at 650 K was obtained for *x* = 0.1.

The thermoelectric performance of EuCd₂Sb₂ and YbCd₂Sb₂ was improved by mixed cation occupation. The composition, structure, and thermoelectric properties of Yb_xEu_{1-x}Cd₂Sb₂ (*x* = 0, 0.5, 0.75, and 1) have been investigated. Polycrystalline samples were prepared by direct reaction of the elements. Thermoelectric properties were investigated after densification of the polycrystalline



RE	a(Å)	V(Å ³)	material
Y	13.6508(9)	2543.7(3)	powder, single crystal
Er	13.5808(1)	2504.4(1)	powder, single crystal
Yb	13.5707(8)	2499.2(2)	powder
Lu	13.5490(7)	2487.3(2)	powder

Crystal structure of $K_6RE_3[BP_3O_{13}(X'')O_{13}P_3B]$. The RE ions form an arrangement of condensed rhombic dodecahedra (yellow), which are filled with K⁺ (light blue) and borophosphate groups (orange: PO_4 , green BO_4 , blue: X'' , see text). Residual electron density in the voids is shown viewed along $[111]$ (b) and perpendicular to $[111]$ (c).

materials by spark plasma sintering. These materials showed low electrical resistivity, high Seebeck coefficient, and low thermal conductivity together with high carrier concentration and high carrier mobility. The ZT values of 0.88 and 0.97 were obtained for $Yb_{0.5}Eu_{0.5}Cd_2Sb_2$ and $Yb_{0.75}Eu_{0.25}Cd_2Sb_2$ at 650 K, respectively.

2. The first rare-earth borophosphates

Borates, phosphates and germanates are widely used as functional materials. Because of their more flexible crystal structures, borophosphates combining borate and phosphate groups and borogermanates combining borate and germanate groups in the same compound are attracting more and more attention as

new systems for search of functional materials. Within our Partner Group, compounds with new types of crystal structures were prepared via low-temperature synthesis in flux, and their properties were investigated.

One of the most interesting groups of compounds is the rare earth borophosphates discovered by the Partner Group. Using a two-step reactive-flux route we succeeded in the preparation of a series of isostructural rare-earth borophosphates. High-quality X-ray diffraction data (Ag $K\alpha$ -radiation) of the yttrium compound enabled us to establish a reasonable structure model, which was further supported by synchrotron and neutron diffraction data, chemical analyses, and spectroscopic studies. The "clear" part of the crystal structure contains the

K and RE positions as well as the tetrameric borophosphate units BP_3O_{13} with B and P in tetrahedral coordination. The RE sites (in octahedral coordination owing to the oxygen corners of neighboring PO_4 -groups) are arranged in form of rhombic dodecahedra which fill the space by sharing common faces. These rhombic dodecahedra are filled with potassium or tetrameric borophosphate groups. Between the two BP_3O_{13} groups we found a new triangular atomic arrangement. Yet, it can be assumed that this unidentified group interconnects the two BP_3O_{13} units and completes a borophosphate oligomer. From the point of view of charge balancing, the missing unit (named X) has to bear one positive charge. The residual electron density distribution between the two



Members of the Partner Group and the International Board after the Inauguration Symposium at Shanghai Institute of Ceramics in August 3, 2006. From left: (front rows) Prof. Dr. ZHAO Jingtai (Partner Group leader, SIC-CAS), Prof. Dr. Ruediger Kniep (Partner Group member, MPI-CPfS), Prof. Dr. Yuri Grin (Partner Group member, MPI-CPfS), Prof. Dr. Bernt Harbricht (International Board member of the Partner Group, Marburg University, Germany), Prof. Dr. Slavi Sevov (International Board member of the Partner Group, University of Notre Dame, USA), Prof. Dr. LIN Jianhua (International Board member of the Partner Group, Peking University, China); (back rows) Partner Group members at SIC-CAS: LIN Zhisheng, WANG Xiaojun, ZHANG Zhijun, XIONG Dingbang, YANG Xinxin, HUANG Yaxi, LU Yuming, LIANG Ying, YUAN Junlin, MI Jinxiao and FENG Xiqi.



Partner Group members of SIC-CAS and MPI-CPfS with the International Board members after the Mid-Term Evaluation at the CAS Shanghai Institute of Ceramics on November 21, 2008. From left to right: (First row) Partner Group members at SIC-CAS, YANG Xinxin, WANG Jiao, WANG Hong, FENG Xianjuan, CHEN Shuang, LIU Minlin, LIANG Ying; (Second row) GUO Kai (SIC-CAS), Prof. Dr. Bernt Harbricht (International Board member of the Partner Group; Marburg University, Germany), RAO Guanghui (International Board member of the Partner Group; the Institute of Physics, CAS), Prof. Dr. ZHANG Hui (SIC-CAS), Prof. Dr. HUANG Yaxi (Xiamen University, China), Prof. Dr. Ruediger Kniep (Partner Group member, MPI-CPfS), XIA Rongsen (SIC-CAS), Dr. TANG Meibo (SIC-CAS); (Third row) Prof. Dr. MAN Zhenyong (SIC-CAS), CHEN Haohong (SIC-CAS), Prof. HU Guanqin (SIC-CAS), Prof. Dr. Slavi Sevov (International Board member of the Partner Group; University of Notre Dame, USA), Prof. Dr. ZHAO Jingtai (Partner Group leader, SIC-CAS), Dr. Niels Oeschler (MPI-CPfS), Prof. Dr. Yuri Grin (Partner Group member, MPI-CPfS), Dr. Stefan Hoffmann (MPI-CPfS), and LIN Zhisheng (SIC-CAS).

neighboring BP_3O_{13} groups is characterized by 12 maxima surrounding a toroidal arrangement in the center. By taking into account the "free" oxygen corners of the neighboring BO_4 tetrahedra, it can be assumed that the two oligomers

become interconnected either by a BO^+ -group (resulting in a BO_3 -unit), or by a $B(OH)^{2+}$ -group (resulting in a $O_2B(OH)_2$ -tetrahedron), or by a PO^{2+} -unit (resulting in a PO_4 -tetrahedron). Bearing this in mind, the chemical composition of the

first RE borophosphate is best described by $K_6RE_3[BP_3O_{13}(X^{1+})O_{13}P_3B]$, with $X = BO, B(OH)_2$ and/or PO_2 . These rare earth containing compounds may provide effective hosts for luminescent materials by doping with guest elements. ◀