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**Keywords:** high-pressure synthesis, binary compounds, metastable phases

## MS20-O2 Crystal chemistry of postperovskite-type $AMX_3$ compounds

Yuichi Shirako<sup>1,2,3</sup>, Youguo Shi<sup>4,5</sup>, Jianshi Zhou<sup>2</sup>, Kazunari Yamaura<sup>4</sup>, Masashi Hasegawa<sup>3</sup>, Masaki Akaogi<sup>1</sup>

1. Department of Chemistry, Gakushuin University, Japan
2. Texas Materials Institute, Cockrell School of Engineering, University of Texas at Austin, USA
3. Department of Crystalline Materials Science, Nagoya University, Japan
4. Superconducting Properties Unit, National Institute for Materials Science, Japan
5. Institute of Physics, Chinese Academy of Science, P. R. China

email: shirako@numse.nagoya-u.ac.jp

Since the discovery of postperovskite type  $MgSiO_3$ ,  $AMX_3$  compounds with the postperovskite structure have attracted special attention for a recent decade in not only mineral physics but also condensed matter physics and materials science due to its alternative layered structure (ref. 1-6). Crystal chemistry of the postperovskite compounds has been quickly developed to seek for new postperovskite materials that are potentially useful in a variety of technology and science, regarding such as superconductivity and correlated electronics. It has been argued that ionic size and covalency are significant in stabilizing the postperovskite structure (ref. 7-10). Regarding ionic size, one can easily understand its effects on the tolerance factor and octahedral-site rotation of perovskite which may affect stability of the perovskite structure, leading to the perovskite to the postperovskite transition. However, in contrast, effects of bond covalency seem to be studied little over the perovskite-postperovskite transition. Therefore, no postperovskite compounds have been designed from a view point of covalent character except strong covalency in contrast to that of ionic size.

In this presentation, crystal chemistry of postperovskite materials in terms of nature of covalent bonds is discussed. These results indicate that the electron count of outermost shell of the cation which makes stronger covalent bond with anion than the other cation or total number of valence electrons of cluster ions is important as well as the electronegativity. It seems to be qualitatively similar with what was developed by Burdett et al for the other, some solid-state structures (ref. 11, 12). In addition, we will also report on a new material which was predicted based on these considerations.

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## MS20-O3 High pressure synthesis of bismuth disulfide, structural solution and its physical properties

Martin Bremholm<sup>1</sup>, Simone M. Soendergaard-Pedersen<sup>1</sup>, Morten B. Nielsen<sup>1</sup>, Lars F. Lundegaard<sup>2</sup>, Davide Ceresoli<sup>3</sup>, Yu-Sheng Chen<sup>4</sup>

1. Center for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, Denmark
2. Haldor Topsoe, Lyngby, Denmark
3. Center for Materials Crystallography and Institute of Molecular Science and Technology (CNR-ISTM), Milano, Italy
4. ChemMatCARS, The University of Chicago, Advanced Photon Source, Argonne, USA

email: bremholm@chem.au.dk

High pressure synthesis is an important method in the search for new compounds and in many cases pressure-stabilized compounds can be quenched to ambient conditions. Therefore high pressure syntheses push the boundaries of solid state chemistry. There is a large current interest in the metal dichalcogenides due to their crystal structures and electrical properties.<sup>1,2</sup> The most sulfur rich phase in the Bi-S phase diagram is Bi<sub>2</sub>S<sub>3</sub>.<sup>3</sup> Unlike the transition metal dichalcogenides, the Bi<sub>2</sub>S<sub>3</sub> atoms in BiS<sub>2</sub> have anisotropic charge distribution and more complex structures are expected when comparing the layered structures of transition metal. The recent discovery of superconductivity in La(O,F)BiS<sub>2</sub> which consists of layers of insulating La(O,F) which donates electrons to superconducting layers of BiS<sub>2</sub>, adds further motivation for studies of Bi dichalcogenides.<sup>4</sup> Furthermore, bismuth chalcogenides, such the compound Bi<sub>2</sub>S<sub>3</sub>, are known to be good thermoelectric materials.<sup>5</sup> The possibilities of using high pressure synthesis to discover new compounds in the Bi-S binary system were investigated as early as the 1960's.<sup>6</sup> The research led to discovery of a compound with BiS<sub>2</sub> stoichiometry, but no structure solution of BiS<sub>2</sub> was reported. In this research the BiS<sub>2</sub> compound was synthesized by a high pressure and high temperature method using a multi-anvil large volume press and the structure was solved by single crystal x-ray diffraction. The structure contains Bi atoms in distorted square-based pyramidal coordination to five surrounding sulfur atoms. The structure, physical properties and theoretical calculations will be discussed and compared to other metal dichalcogenide compounds.

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**Keywords:** High pressure, BiS<sub>2</sub>, structure solution, metal dichalcogenides