

MS15-P20 Synthesis and Characterizations of new quaternary selenide Sn₄(In/Sb)₁₄Se₂₅

Chi-Shen Lee¹, Guan-Ruei Chen¹

1. National Chiao Tung University

email: chishen@mail.nctu.edu.tw

New quaternary selenide Sn₄(In/Sb)₁₄Se₂₅ was synthesized by a solid state chemistry reaction with stoichiometric mixture of elements (Sn:In:Sb:Se = 5:4:9:25). The structure is constructed with two building units called NaCl¹⁰⁰-type () and NaCl¹¹¹-type (), respectively. Due to similar atomic numbers of indium, tin and antimony atoms, the valence and coordination environments of atomic sites were utilized to assign metal positions. Five-coordinated (square pyramid) sites in NaCl¹⁰⁰ units were considered as mixed occupied Sn²⁺/Sb³⁺, while six-coordinated (octahedron) sites in NaCl¹¹¹ units were assigned as In³⁺/Sb³⁺. The result gave a charge-balanced formula Sn₄In₅Sb₉Se₂₅. Sn₄In₅Sb₉Se₂₅ crystallizes in the monoclinic space group C2/m in a new structure type and shows the property of preferred orientation with columnar appearance. This compound exhibits black color and physical property measurements suggest semiconducting property with a narrow band gap. The value of the band gap obtained by UV-Vis-NIR spectroscopy and the electrical conductivity is ~0.52 eV. Band structure calculations from a model structure also showed the result of nearly semiconducting property. The as prepared compound is stable at room temperature under ambient condition. And it is melted and decomposed in temperature near 600°C under vacuum.

Keywords: crystal structure, selenide, solid state chemistry, crystallography

MS15-P21 Synthesis, structure and band structure calculation of the new sodium sulfido ferrates Na₂[Fe₂S₆] and Na₇[Fe₂S₆]

Pirmin Stüble¹, Caroline Röhr¹

1. Albert-Ludwigs-Universität Freiburg, Germany

email: pirmin@pyrite.chemie.uni-freiburg.de

In the course of a systematic study of alkali chalcogenido metalates, the new compounds Na₂[Fe₂S₆] and Na₇[Fe₂S₆] were synthesized by heating natural pyrite and elemental sodium enclosed in corundum crucibles under an argon atmosphere at a maximum temperature of 800°C. In this reductive approach, lower iron valences were obtained extending once again the structural diversity of this well investigated class of compounds. The crystal structures were determined by means of single crystal X-ray diffraction. DFT+U band structure calculations were performed using the FP-LAPW method.

The orthorhombic compound Na₂[Fe₂S₆] (K₂Mn₂ structure type, space group *Ibam*, *a*=643.3, *b*=1140.4, *c*=562.9 pm, *Z*=4, *R*₁=0.037) contains linear anionic chains of Fe₂S₄ tetrahedra connected via two opposite edges (Fig. a), relating it structurally to the mixed valent Na₂[Fe₂S₆] with corrugated chains [1]. Na₂[Fe₂S₆] is isotypic to the cobaltates A₂[Co₂S₆] (*A*=Na,K,Rb,Cs) [2] and is the first alkali chalcogenido ferrate with anionic chains exclusively containing Fe^{II}.

Corresponding to the known magnetism of the cobaltates DFT calculations were carried out with antiferromagnetic spin ordering in the linear chains.

The triclinic diferrate Na₇[Fe₂S₆] (new structure type, space group *P-1*, *a*=764.2, *b*=1153.7, *c*=1272.6 pm, *α*=62.3, *β*=72.83, *γ*=84.64°, *Z*=3, *R*₁=0.019) contains binuclear [Fe₂S₆]⁷⁻ anions formed by two edge sharing FeS₄ tetrahedra (Fig. b). Two crystallographically different [Fe₂S₆]⁷⁻ anions can be distinguished, one of them is centrosymmetric. Nevertheless, averaged terminal and bridging Fe-S distances are well comparable in both, indicating one Fe^{II} and one Fe^{III} in each dimer (Fig. c). This mixed valency is unique among the alkali chalcogenido metalate dimer compounds, previously containing only M^{III}, like e.g. the diferrates A₆[Fe₂Q₆] (*A*=Na,K,Rb,Cs; *Q*=O,S,Se) [3-6] and Rb₁₂[Fe₂Q₆](Q₂)₃ (*Q*=S,Se) [6].

Due to the antiferromagnetic spin ordering in the dimers in the reference compound Na₆[Fe₂S₆] [3], we found ferrimagnetic spin ordering for Na₇[Fe₂S₆] coinciding with its macroscopic magnetic behaviour.

[1] K. Klepp, H. Boller. *Monatsh. Chem.* 112, 83-89 (1981).

[2] W. Bronger, C. Bomba. *J. Less-Common Met.* 158, 169-176 (1990).

[3] W. Bronger, U. Ruschewitz, P. Müller. *J. Alloys Compd.* 187, 95-103 (1992).

[4] G. Frisch, C. Röhr. *Z. Kristallogr.* 220, 135-141 (2005).

[5] M. Schwarz, M. Haas, C. Röhr, *Z. Anorg. Allg. Chem.* 369, 360-374 (2013).

[6] M. Schwarz, P. Stüble, C. Röhr (in prep.).

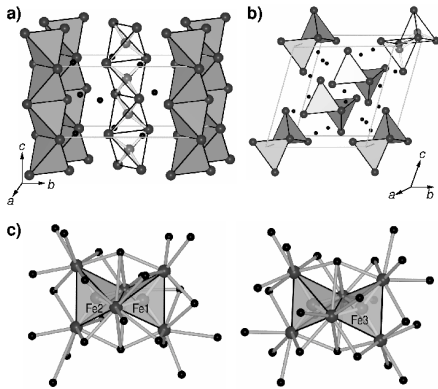


Figure 1. a) Unit cell of $\text{Na}_2[\text{FeS}_6]$. b) Unit cell of $\text{Na}_4[\text{Fe}_2\text{S}_6]$. c) Acentric dimer1 (left) and centrosymmetric dimer2 (right) with Na^+ coordination. Bridging and terminal Fe-S bond lengths of dimer1 / dimer2: $d_{\text{Fe-S}}^{\text{br}} = 234.7(3) / 235.4$ pm, $d_{\text{Fe-S}}^{\text{t}} = 228.7(1) / 229.2(2)$ pm.

Keywords: chalcogenido ferrate, diferrate, band structure, magnetism

MS15-P22 The biclinic crystal system – a hidden system in crystallography

Hejing Wang¹, Jian Zhou²

1. School of Earth and Space Sciences, Peking University, Beijing 100871, China

2. Chinese Academy of Geological Sciences, Beijing 100037, China

email: hjwang@pku.edu.cn

It is well known that there are seven crystal systems, the cubic, hexagonal, trigonal, tetragonal, orthorhombic, monoclinic and the triclinic systems. From the orthorhombic to the triclinic systems, the crystal axial angles change from orthogonal ($\alpha = \beta = \gamma = 90^\circ$) to oblique in one axis (e.g. $\beta \neq 90^\circ$) to oblique in three axes ($\alpha \neq \beta \neq \gamma \neq 90^\circ$). There is no oblique case in two axes (any two of α , β and $\gamma \neq 90^\circ$ and with the remainder = 90°). That is strange. The biclinic crystal system ($a \neq b \neq c$, $\alpha \neq \beta \neq \gamma$ and α (or β or γ) = 90°) is a real but being hidden system in crystallography. As α (or γ) = 90° ($\beta \neq \gamma \neq 90^\circ$ or $\beta \neq \alpha \neq 90^\circ$), kaolinite donates a real example of the biclinic crystal system [1]. The formation of the biclinic system is demonstrated by its equivalent biclinic-parallelepiped that is built from a pair of rectangles by shifting each other along their two edges (Fig. 1). The P1 and P-1 properties of space group are deduced from both twofold axis and mirror plane. Those formulae of the biclinic system are given for useful calculations including the metric tensor G and its reciprocal G-1, volume V, reciprocal lattice parameters a^* , b^* , c^* , α^* , β^* and γ^* , the relationships between the Miller indices, interplanar angle Φ , vector length r , intervector angle ρ and the interplanar distance d . The transformations between the biclinic and the triclinic crystal systems arisen from a little axis-angle variations are exemplified with kaolinite, heulandite and anorthite. It is summarized from those transformations that the difference, in d spacing, less than $0.05^\circ 2\theta$ in copper radiation will be no significance in distinguishing the biclinic from the triclinic system and *vice versa* [2]. It is worth noting that when use the regulations of the triclinic system to deal with these data of the biclinic system it is very easy to fall in a “no biclinic system” trap and layouts them into the triclinic system. Finally, the “missing” of the biclinic crystal system is because the P1 and P-1 space groups are classified into the triclinic system. One does not need to “refine” the data ($a \neq b \neq c$, $\alpha \neq \beta \neq \gamma$ and α or β or $\gamma = 90^\circ$) from the biclinic system to the triclinic system ($\alpha \neq \beta \neq \gamma \neq 90^\circ$). These low grade crystal systems (bi- and triclinic) would make a plentiful crystal world.

References

[1] Corlelis K, 2002, The manual of mineral science, 22th edition (New York, John wiley)

[2] Wang H, Zhou J, 2000, J. Appl. Crys. 33, 1128