

### Isomorphism: The implications of understanding structural changes at extreme physical conditions

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Structural behaviors of minerals at extreme physical conditions have been often discussed with reference to isomorphism. Although they may not show actual structural aspects necessarily, however, those observed at relatively lower pressures and/or temperatures, even at ambient conditions, will give us a significant implication to the interpretation of structural behaviors which will appear at difficult experimental conditions.

Minerals in the transition zone and/or the lower part of the earth's mantle have been also investigated by various isomorphous substances.  $\text{Co}_2\text{SiO}_4$  is one of examples which showed the transformation from olivine- to spinel-type phase under high-pressure and also the presence of 'β-phase' between olivine- and spinel-type phases<sup>1)</sup>. The system of  $\text{NiAl}_2\text{O}_4$  -  $\text{Ni}_2\text{SiO}_4$ , in which each end-member phase of  $\text{NiAl}_2\text{O}_4$  and  $\text{Ni}_2\text{SiO}_4$  is spinel- and olivine-type, respectively, showed another interesting structural behavior at high-pressure and high-temperature. In this system, new spinel-related structures in addition to β-phase have been found and structurally systematized as 'spineloids'<sup>2)</sup>. A series of these phases may imply an intermediate stage of structural change at high pressures.

Perovskite-type phase is now considered as one of main constituent minerals in lower mantle of the Earth. However, crystal structures of perovskite-type phases are variously distorted depending on the chemical compositions, and also temperature and pressure conditions, resulting in various crystal structures with orthorhombic, tetragonal, rhombohedral, cubic lattices and so on. Remarkable thing is that their lattice distortions from an ideal cubic are very small to each other, so that their crystal system may sometimes tend to be erroneously designated. Expects of structural changes of perovskite-type  $\text{ABO}_3$  at high-pressure have been experimentally made by appropriate selections of cation sizes of A or B. Trivalent or tetravalent lanthanoid ions of La through Lu and  $\text{Zr}^{4+}$  were applied to control the structures. Structural changes from orthorhombic to trigonal system has been found in  $(\text{Nd}, \text{Sm}_{1-x})\text{AlO}_3$  by substituting  $\text{Sm}^{3+}$  for  $\text{Nd}^{3+}$  which are in 8- to 12-coordinations<sup>3)</sup> and those from orthorhombic to cubic through trigonal system were observed in  $\text{Ba}(\text{Ln}1, \text{Ln}2)\text{O}_3$ , where Ln are  $\text{Ce}^{4+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Zr}^{4+}$  which occur in octahedral coordinations<sup>4)</sup>. It is interesting to note that structural diagram represented by temperatures against ionic radii implies a temperature-pressure phase diagram.

#### References

- 1) Akimoto, S. and Y. Sato, Phys. Earth Planet. Inter., **1**, 498-504(1968).
- 2) Akaogi, M., et. J. Solid State Chem., **44**, 257-267(1982).
- 3) Yoshikawa, et. J. Solid State Chem., **126**, 221-226(1996)
- 4) Horiuchi, H., et. Materials Sci. & Eng., **A312**, 237-243(2001)

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### Crystal structure and bonding in the new mineral $\text{AsSbO}_3$ .

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A new mineral with ideal chemistry  $\text{AsSbO}_3$ , has been found with leucite, ludlockite, and quartz in a vug in massive tennantite from the Tsumeb mine, Namibia. The symmetry is monoclinic,  $P2_1/n$ , with  $a = 4.5757(4)$  Å,  $b = 13.1288(13)$  Å,  $c = 5.4216(5)$  Å,  $\beta = 95.039(4)^\circ$ ,  $V = 324.44(5)$  Å<sup>3</sup>,  $Z = 4$ , and  $d_{\text{calc}} = 5.009$  g/cm<sup>3</sup>. The new mineral forms adamantine, colorless bladed crystals to 6 mm, bound by {010}, {110}, {111}, and {-101}. The crystal structure consists of corrugated sheets of corner-sharing  $\text{AsO}_3$  and  $\text{SbO}_3$  trigonal pyramids with average  $\langle R(\text{AsO}) \rangle$  and  $\langle R(\text{SbO}) \rangle$  bond lengths 1.782 Å and 1.993 Å, respectively. We compare the crystal structure of  $\text{AsSbO}_3$  with a new crystal structure refinement of the isostructural mineral claudetite,  $\text{As}_2\text{O}_3$ . Claudetite also has monoclinic symmetry,  $P2_1/n$ , with  $a = 4.5460(4)$  Å,  $b = 13.0012(14)$  Å,  $c = 5.3420(5)$  Å,  $\beta = 95.329(2)^\circ$ , and  $V = 314.83(5)$  Å<sup>3</sup> with  $Z = 4$ . Bader (1998) defines a bonded interaction if and only if there exists both a bond path and a saddle point in the electron density between a pair of atoms. A bond path is a line, not necessarily straight, of continuous local maxima in the perpendicular plane between the atoms. The saddle point, referred to as a bond critical point (bcp), is a local minimum along the bond path. The analysis of the electron density distributions from ab initio quantum calculations confirm the classical short range bonding of the  $\text{AsO}_3$  and  $\text{SbO}_3$  groups, and also shows several long-range interactions between As and O and Sb and O. The bonds are ranked into three separate groups by the electron density at the bond critical points. The strongest of these bonds are associated with close contacts between As and Sb with O. A distinctly weaker group of bonds stabilize the corrugation of the structural sheets. A yet distinctly weaker pair of bonds holds the sheets together and is associated with the observed cleavage plane (010). The analysis provides insight to the bonding and topology systematic of arsenite and antimonite minerals in general.

### Crystal-chemical behaviour of Ge and Ga in Pb–Fe members of the alunite supergroup

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Jarosite-like Pb–Fe arsenates, phosphates, sulphates and their solid solutions exist widely in nature and form part of the  $\text{AB}_3(\text{XO}_4)_2(\text{OH}, \text{H}_2\text{O})_n$  alunite supergroup (space group R-3m). In this supergroup the A site can be occupied by monovalent Na, K, Ag,  $\text{NH}_4$  or  $\text{H}_3\text{O}$ , divalent Pb, Ca, Sr or Ba, or trivalent (Bi, REE) ions; the octahedrally coordinated B site can be occupied by either Al,  $\text{Fe}^{3+}$ ,  $\text{V}^{5+}$  or Ga, whilst the tetrahedrally coordinated X site is occupied by either  $\text{P}^{5+}$ ,  $\text{As}^{5+}$ ,  $\text{S}^{6+}$  or, reportedly, Ge. These minerals are commonly found in the oxidised zones of ore deposits, but can also occur in soil horizons and as precipitants from acid mine drainage. Gallobeudantite, the Ga analogue of beudantite, and Ge-bearing beudantite from Tsumeb, Namibia, present novel variants of the well-established species in the Pb–Fe subgroup. This contribution reports the results of a crystal-chemical investigation into the roles of Ge and Ga in natural and synthetic Pb–Fe members.

Several  $\text{AsO}_4$ -dominant Pb–Fe members were hydrothermally synthesised (Teflon vessels, 220°C, 7 days, pH 0.5 to 1.0) at the Institute for Mineralogy and Crystallography, University of Vienna. Several specimens of Ge-bearing beudantite and segnitite in the collection of the Museum Victoria have been analysed and compared with the synthesised compounds.

The results of the single-crystal structure refinements show that the partitioning of Ge in the synthetic Pb–Fe members is not a straightforward substitution for As in the X site. Instead, in the absence of any other minor elements (e.g. Al), Ge prefers octahedral over tetrahedral coordination in Ge-rich members. This is in contrast to previous considerations that all the Ge sits on the X site. However, in natural samples, minor amounts of  $\text{Al} \approx \text{Cu}$  or  $\text{Zn}$  commonly occupy the octahedral site, while Ge occupies the tetrahedral site.

The results for a synthetic Ge- and Ga-rich segnitite confirm that Ga substitutes for Fe in the octahedral site; however, this synthetic sample shows higher symmetry (R-3m) than that proposed for gallobeudantite (R3m). The synthetic members also have the Pb atom on the origin — the first such example among Pb–Fe members. The unit-cell parameters for the synthetic Ge-rich segnitite and Ge- and Ga-rich segnitite are  $a = 7.276$ ,  $c = 17.058$  Å and  $a = 7.240$ ,  $c = 17.054$  Å, respectively, and are similar to those of the As-dominant members of the group.

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### Periodic Nets and Crystal Structures

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Non-molecular crystal structures consist of periodic arrays of atoms joined by bonds. The atoms and bonds correspond respectively to the vertices and edges of a special kind of graph (simple, connected, periodic) called a net. Increasingly, the language and methods of graph theory are being used to describe such structures and combined with the methods of combinatorial tiling theory. In this presentation I will describe recent developments in the taxonomy of nets and in the enumeration of possible structures using these new methods. Special attention will be given to the topics of regularity, transitivity, natural tilings, and dual structures. Illustrations will focus particularly on three-periodic, four-coordinated nets such as are the underlying topologies of important minerals such as quartz, feldspar and related framework aluminosilicates, and zeolites.