

**P.10.02.9***Acta Cryst.* (2005). A61, C369**Ternary Phases in the Yb-Zn-Al System**

Maria L. Fornasini, Pietro Manfrinetti, Donata Mazzone, *Department of Chemistry and Industrial Chemistry, University of Genoa, Italy*. E-mail: cfmet@chimica.unige.it

The facility of ytterbium to form compounds with zinc (eight phases in the Yb-Zn system) and the presence of YbAl<sub>2</sub> with intermediate valence in the Yb-Al system have led to the study of the ternary Yb-Zn-Al system with the aim of finding compounds with possible interesting magnetic properties.

The alloys were prepared by melting the elements and annealing at 600-750°C. All samples were examined by optical and microprobe analysis and the crystal structure was determined by X-ray powder and single crystal methods.

Thirteen phases were identified. Six of them correspond to phases already present in the Yb-Zn or Yb-Al system [1], where the third element substitutes the Zn or Al atoms, more or less extensively, maintaining the same structure. Examples are YbZn<sub>0.88</sub>Al<sub>1.12</sub> (MgCu<sub>2</sub>-type) and Yb<sub>3</sub>Zn<sub>4.48</sub>Al<sub>6.16</sub> (La<sub>3</sub>Al<sub>11</sub>-type). Six ternary compounds crystallize with other known structure types. Examples are YbZnAl (MgNi<sub>2</sub>-type) with all mixed Zn/Al occupations of the Ni sites and Yb<sub>8</sub>Zn<sub>48.5</sub>Al<sub>17.5</sub> isotypic with Yb<sub>8</sub>Cu<sub>17</sub>Al<sub>49</sub> [1], with partial ordering of the Zn atoms. A new hexagonal structure is observed for YbZn<sub>7.3</sub>Al<sub>0.5</sub>, by taking nine CaCu<sub>5</sub> cells and substituting some of the Yb atoms (28.9%) with mixed Zn/Al pairs. This substitution mechanism, known for a long time, is found also in YbZn<sub>7.8</sub>Al<sub>0.4</sub> and YbZn<sub>9.2</sub>Al<sub>1.3</sub> with structures derived from the U<sub>2</sub>Zn<sub>17</sub> and SmZn<sub>11</sub> types, respectively.

[1] *CRYSTMET, Structure and Powder Database for Metals*, 2004.

**Keywords:** crystal chemistry and structure, intermetallic compounds, ternary alloys

**P.10.02.10***Acta Cryst.* (2005). A61, C369**An Unconventional Look at Sulfides and Selenides: Anion-centred Polyhedra**

Emil Makovicky, *Geological Institute, University of Copenhagen, Denmark*. E-mail: emilm@geol.ku.dk

Lower sulfides of palladium, Pd<sub>4</sub>S, Pd<sub>3</sub>S, and Pd<sub>16</sub>S<sub>7</sub>, resemble alloys with “clathrated” S atoms and a very complex metal framework. In terms of anion-centred polyhedra, however, Pd<sub>4</sub>S consists of corner-connected SP<sub>8</sub> bisdisphenoids (CN=8), Pd<sub>3</sub>S of corner-connected complex CN=6 polyhedra whereas Pd<sub>16</sub>S<sub>7</sub> contains clusters of tetrahedrally arranged trigonal prisms SP<sub>6</sub>, interconnected by flattened SP<sub>4</sub> tetrahedra. Edge- and corner-sharing SM<sub>4</sub> tetrahedra in various arrangements form the structures of PdS, PdSe and PtS. Clusters of tetrahedra as well as 4- and 6-petal rosettes of tall CN=5 coordination prisms SM<sub>5</sub> are in the structure of Rh<sub>17</sub>S<sub>15</sub> and Ni<sub>10</sub>Pd<sub>7</sub>S<sub>15</sub>; the same six-petal rosettes, interconnected by tetrahedra, form the structure of pentlandite Co<sub>9</sub>S<sub>8</sub>. Surprisingly simple structures formed by anion-centred polyhedra are found in tetrahedrite, Ag<sub>2</sub>S, Cu<sub>3</sub>Se<sub>2</sub>, and also Bi<sub>2</sub>S<sub>3</sub>, Cu<sub>2</sub>S and talnakhite.

The anion-centred configurations depend on the cation:anion ratio (metal-rich sulfides have higher CN) and on the type of cation. Especially Cu and Ag form typical anion-based polyhedra. Uniformity and small number of configurations suggest that the directional bonds of an anion may be equally important as those of the cation present. It means that an insight deeper than the usual anion-packing considerations might be necessary. Cation-lined interspaces between the anion-centred polyhedra and the contracted polyhedron edges with metal-metal bonds are of special interest.

**Keywords:** coordination and inorganic compounds, sulfides, selenides

**P.10.02.11***Acta Cryst.* (2005). A61, C369**The Term Systematics**

Nina L. Smirnova, *Department of Geology, Moscow State University, Moscow, Russia*. E-mail: snl194@mail.ru

Every science is represented by its terms. Systemic terms are used in all sciences and other terms in concrete sciences. The term sequence is used in all sciences. The sequence  $s < f < d < p$  elements is the basis of chemical compounds, mineral systematics.

Many terms represent different sequences in chemistry, crystallography. These are series: homologous, linear, polytypic, heteropolytypic, pseudopolytypic, polysomic, modular, plesiotypic, meroplesiotypic, space modulated; series of: mixed layer structures (s.), syntactic s., fragment s, transmineral s., symbiotic s., sonar s., super space s., long period s., chemical twin s., topological s., related s., topology related s., gray isomorphic s., partial isotypic s., intergrowth at the level of unit cell s., crystallographic shear s., multistory s., O, OD, MDO s., superstructures, cluster substructures, matrix combinations, sminal structure types, structure type spectra, ordered isomorphs, 0-3 dimensional isomorphs, 0-3 dimensional elements, details, domains, V-D domains, as trees of polymorph structure types, as trees of symmetry groups, as Belov classes, subclasses, as planar static waves, as concentration waves, as elastic waves, as standing waves, as homologous structure type classes, as refrain series of merons, as series of supramolecular syntons.

The term systematics (a branch of systematics) allows finding and solving discrepancies between mineral species and external form terms, revealing relationship, difference, synonymy, constructing skeletal part of science.

**Keywords:** systematics, term, science

**P.10.02.12***Acta Cryst.* (2005). A61, C369**Alkaline Earth Aluminates/Gallates and Perovskites: Two Sides of the Same Coin**

Volker Kahlenberg, *Institute of Mineralogy and Petrography, University of Innsbruck, Innsbruck, Austria*. E-mail: volker.kahlenberg@uibk.ac.at

The crystal chemistry of alkaline earth oxoaluminates and gallates covers a large variety of different structure types. However, most of the compounds are based on [AlO<sub>4</sub>]- or [GaO<sub>4</sub>]-tetrahedra with various degrees of connectivities. The structures of the materials are similar to those observed in silicates (which have been studied in much more detail) and can be classified using the same concepts proposed by Liebau [1].

However, many of the alkaline earth rich compounds can be related to the perovskite structure type as well. For example, the “cyclo-gallate” Sr<sub>3</sub>Ga<sub>2</sub>O<sub>6</sub> containing isolated six-membered [Ga<sub>6</sub>O<sub>18</sub>]-rings can be alternatively regarded as an example for a defect ABO<sub>3</sub>-perovskite with 12.5% vacancies in the A-substructure and 25% oxygen vacancies: (Sr<sub>7/8</sub>□<sub>1/8</sub>)(Ga<sub>3/4</sub>Sr<sub>1/4</sub>)(O<sub>3/4</sub>□<sub>1/4</sub>)<sub>3</sub>.

This new concept has been successfully applied to about ten recently determined crystal structures of oxoaluminates/gallates. Using the classical description based on the connectivity of the tetrahedra, the crystal structures look quite different. The “perovskite-approach” offers an elegant way to relate these structures in a simple way.

[1] Liebau F., *Structural Chemistry of Silicates*, Springer, 1985.

**Keywords:** crystal chemistry of inorganic compounds, structural relationships, aluminum compounds

**P.10.02.13***Acta Cryst.* (2005). A61, C369-C370**Order-Disorder Phenomena in Nitridosilicates and Nitridophosphates**

Oliver Oeckler, Friedrich Karau, Florian Stadler, Christian Schmolke, Wolfgang Schnick, *Dept. of Chemistry & Bio-chemistry, LMU Munich, Germany*. E-mail: oliver.oeckler@gmx.de

Among numerous (oxo-)nitridosilicates synthesized in the past years, some compounds exhibit interesting order-disorder phenomena. Whereas the ordered structure of Ho<sub>2</sub>[Si<sub>4</sub>N<sub>6</sub>C] [1] can be derived from the highly symmetrical framework nitridosilicate BaYb[Si<sub>4</sub>N<sub>7</sub>] [2] by “chemical twinning”, the same N<sup>[4]</sup>(SiN<sub>3/2</sub>)<sub>4</sub> (X = N, C) building

blocks form microdomains with different interconnection in  $\text{Sm}_2[\text{Si}_4\text{N}_6\text{C}]$ , leading to pronounced diffuse scattering. A change of cations can impede long-range order in layered oxonitridosilicates as well.  $\text{Ca}[\text{Si}_2\text{N}_2\text{O}_2]$  constitutes a well-ordered compound, the same anionic layers in  $\text{Eu}[\text{Si}_2\text{N}_2\text{O}_2]$ , however, exhibit severe stacking disorder with the tendency to form a superstructure.

The  $[\text{PN}_2]^-$  frameworks of  $\text{M}^{\text{II}}\text{P}_2\text{N}_4$  (and other) nitridophosphates are isoelectronic with  $\text{SiO}_2$  and thus exhibit numerous structural analogies to  $\text{SiO}_2$ . The highly symmetrical tetrahedral basic structures are always distorted due to the adaptation of voids to cation size and ordering as well as due to the tendency to avoid linear P–N–P bridges. However, only in some cases these distortions lead to long-range ordering by symmetry reduction or superstructure formation. Order-disorder effects, i. e. chemical and positional disorder, diffuse scattering and modulations will be discussed on the basis of X-ray powder data and electron diffraction.

[1] Huppertz H., Schnick W., *Angew. Chem.* 1996, **108**, 2115. [2] Höpfe H.A., Kotzyba G., Pöttgen R., Schnick W., *J. Mater. Chem.* 2001, **11**, 3300.

**Keywords:** nitrides, disordered materials, inorganic structural chemistry

#### P.10.02.14

*Acta Cryst.* (2005). A61, C370

#### Iron Substituted Hydroxyapatite by Two Powder Preparation Method: a Comparison

Adolfo Speghini<sup>a</sup>, G. Salviulo<sup>b</sup>, M. Bettinelli<sup>a</sup>, L. Nodari<sup>c</sup>, U. Russo<sup>c</sup>, <sup>a</sup>DST, Univ. Verona, Verona, Italy. <sup>b</sup>Dip. Mineral. Petrol., Univ. Padova, Padova, Italy. <sup>c</sup>Dip. Sci. Chim., Univ. Padova, Padova, Italy. E-mail: adolfo.speghini@univr.it

The aim of this work is the characterization of hydroxyapatite (HAP), nominal composition  $[(\text{Ca}_{10-x}\text{Fe}_x)(\text{PO}_4)_6(\text{OH})_y]$ ,  $x=0.0; 0.05; 0.1; 0.5; 1.0; 1.5$ , obtained by high temperature solid state reaction (HTS) and wet precipitation (WPS). The ceramic samples were prepared by firing appropriate quantities of the metal carbonate, iron(III) oxide and ammonium hydrogen phosphate at 1200 °C ( $x=0.05, 0.1, 0.5$  and  $1.0$ ) for 72 hours or at 1450 °C ( $x=1.5$ ) for 48 hours. The heat treatment was repeated two more times with intermediate grinding. Materials of the same composition were prepared with a wet chemical synthesis by mixing appropriate quantities of solutions of the metal nitrate and ammonium phosphate at pH=10.5. The precipitates were dried at 80 °C and fired at 550°C in  $\text{O}_2$  flux for 6 hours. The X-ray diffraction patterns show for all powders obtained by HTS sharp and narrow apatite peaks, while WPS samples present broad peaks indicating a low degree of crystallinity; crystallite sizes result to be 200 and 20 nm respectively. All HTS samples show the presence of HAP and/or tricalcium phosphate, the relative amounts depending on the theoretical composition. Hydroxyapatite decreases from 100 to 39% for  $x$  varying from 0.0 to 0.5, while for  $x=1.0$  and 1.5 no hydroxyapatite peaks were detected. With decreasing hydroxyapatite content, tricalcium phosphate increases up to 96% for  $x=1.0$  and 1.5. Mössbauer spectra show the presence of iron oxidic phases, such as hematite and magnetite for HTS samples and ferrihydrite for WPS ones, not detectable by X-ray diffraction.

**Keywords:** apatites, Mössbauer, X-ray diffraction

#### P.10.02.15

*Acta Cryst.* (2005). A61, C370

#### $\text{Rb}_5\text{In}(\text{MoO}_4)_4$ : Crystal Structure of a Possible Laser Material

Ekkehart Tillmanns, Maria Wierzbicka, Uwe Kolitsch, *Institut für Mineralogie und Kristallographie, Universität Wien, Wien, Austria.* E-mail: ekkehart.tillmanns@univie.ac.at

The compounds  $A_5\text{M}^{\text{III}}(\text{XO}_4)_4$  ( $A = \text{Rb}, \text{K}, \text{Tl}; \text{M}^{\text{III}} = \text{REE}, \text{Bi}, \text{Fe}, \text{In}; X = \text{Mo}, \text{W}$ ) crystallise in a variety of layered structure types, related to the mineral palmierite,  $\text{K}_2\text{Pb}(\text{SO}_4)_2$  [1]. Some of the REE representatives are used as phosphors and laser materials [1].

During flux growth of alkali- $\text{M}^{\text{III}}$ -silicates we have obtained the compound  $\text{Rb}_5\text{In}(\text{MoO}_4)_4$  (**I**). Its crystal structure has been determined from single-crystal intensity data (Mo  $K\alpha$  X-radiation, CCD area detector, 293 K) and refined in s.g.  $P2_1/c$  (no. 13) to  $R(F) = 0.0227$  ( $a =$

$11.391(2), b = 7.983(2), c = 11.100(2)$  Å,  $\beta = 113.74(3)^\circ$ ,  $V = 924.0(3)$  Å<sup>3</sup>,  $Z = 2$ ). Compound **I** is characterised by a layered structure in which decorated kröhnkite-like [100] chains are built from a distorted  $\text{InO}_6$  octahedron ( $\langle\text{In-O}\rangle = 2.136$  Å) corner-linked to two non-equivalent  $\text{MoO}_4$  tetrahedra. The chains are similar to those in  $\text{Ba}_2\text{Ca}(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_2$  [2]. Rb atoms separate these chains in different directions. Compound **I** is isotopic with  $\text{Rb}_5\text{Er}(\text{MoO}_4)_4$  [3]. A calculated X-ray powder diffraction pattern demonstrates that the indexing and cell given for **I** on ICCD-PDF 26-1367 are incorrect. Financial support by the Austrian Science Foundation (FWF) (Grant P17623-N10) is gratefully acknowledged.

[1] Morozov V.A., Lazoryak B.I., Lebedev O.I., Amelinckx S., Van Tendeloo G., *J. Solid State Chem.*, 2003, **176**, 76. [2] Toumi M., Chabchoub S., Smiri-Doggy L., Laligant Y., *Eur. J. Solid State Inorg. Chem.*, 1997, **34**, 1249. [3] Klevtsova R.F., Glinskaya L.A., *Dokl. Akad. Nauk SSSR*, 1976, **230**, 1337.

**Keywords:** crystal structures, crystal growth, molybdenum compounds

#### P.10.02.16

*Acta Cryst.* (2005). A61, C370

#### Systematic Violation of Loewenstein's Rule Established

Wulf Depmeier, Lars Peters, Karsten Knorr, *Institut für Geowissenschaften, University of Kiel, Kiel, Germany.* E-mail: wd@min.uni-kiel.de

Since its formulation 50 years ago, Loewenstein's rule [1] has become a standard argument in the crystal chemistry of, notably, layer and framework silicates and zeolites. The validity of the rule is usually taken for granted, and it is used rather schematically, sometimes even without making reference to the original paper. The rule is normally used as an argument to account for two experimental observations: i) In aluminosilicates,  $\text{AlO}_4$ -tetrahedra tend to avoid each other, leading to alternating  $\text{AlO}_4$ - and  $\text{SiO}_4$ -tetrahedra for a Si : Al ratio of 1:1; ii) Except in rare cases, aluminosilicates have an Al : Si ratio smaller than or equal to 1. Observation i) could be rationalized theoretically to be due to the expenditure in elastic energy which is necessary to deform the structure when the bigger  $\text{Al}^{3+}$  replaces  $\text{Si}^{4+}$  [2]. Observation ii) is not easily explained, in fact, it does not seem that fully convincing arguments have been put forward for its explanation.

We have prepared series of compounds where Loewenstein's rule is breached systematically, and continuously. These belong either to the melilite, or to the sodalite structure type. Crystallographic, structural, chemical and physical features and properties have been determined and will be reported.

[1] Loewenstein W., *Amer. Miner.*, 1954, **39**, 92. [2] Bosenick A., Dove M.T., Myers E.R., Palin E.J., Sainz-Diaz C.I., Gupton B.S., Warren M.C., Craig M.S., Redfern S.A.T., *Mineralogical Magazine*, 2001, **65**, 193.

**Keywords:** Loewenstein's rule, aluminosilicates, sodalites

#### P.10.02.17

*Acta Cryst.* (2005). A61, C370-C371

#### Iron Substituted Ca-Sr-Ba-Apatites: Preliminary Results

Gabriella Salviulo<sup>a</sup>, A. Speghini<sup>b</sup>, M. Bettinelli<sup>b</sup>, L. Nodari<sup>c</sup>, U. Russo<sup>c</sup>, <sup>a</sup>Dip. Mineral. Petrol. Univ. Padova. <sup>b</sup>DST, Univ. Verona, <sup>c</sup>Dip. Sci. chim. Univ. Padova. E-mail: gabriella.salviulo@unipd.it

The aim of this work is the characterization of Fe-substituted Ca-Sr-Ba-hydroxyapatite of composition  $[(\text{Me}_{10-x}\text{Fe}_x)(\text{PO}_4)_6(\text{OH})_y]$ , where  $x = 0.0; 0.05; 0.1; 0.5; 1.0; 1.5$  obtained by high temperature solid state reaction. Stoichiometric quantities of the appropriate metal carbonate, iron (III) oxide and ammonium hydrogen phosphate were mixed in an agata mortar and pressed with a hydraulic press to form pellets subsequently heat treated at 1200 °C ( $x=0.05, 0.1, 0.5$  and  $1.0$ ) for 72 hours or at 1450 °C ( $x=1.5$ ) for 48 hours. The heat treatment was repeated two more times with intermediate grinding. For the most diluted samples <sup>57</sup>Fe isotopically enriched iron (III) oxide was used. The X-ray diffraction patterns show sharp and narrow apatite peaks, however none of these powders is constituted by only one crystalline phase. All samples show the presence of hydroxyapatite and/or triphosphate, the relative amounts depending on the theoretical composition. For all the series, hydroxyapatite is the dominant phase