

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 SiO_2 and thus exhibit numerous structural analogies to 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

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Iron Substituted Hydroxyapatite by Two Powder Preparation Method: a Comparison

Adolfo Speghini^a, G. Salviulo^b, M. Bettinelli^a, L. Nodari^c, U. Russo^c, ^aDST, Univ. Verona, Verona, Italy. ^bDip. Mineral. Petrol., Univ. Padova, Padova, Italy. ^cDip. 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 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

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$\text{Rb}_5\text{In}(\text{MoO}_4)_4$: 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 $A_5M^{\text{III}}(\text{XO}_4)_4$ ($A = \text{Rb, K, Tl}; M^{\text{III}} = \text{REE, Bi, Fe, In}; X = \text{Mo, W}$) 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- M^{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, $\beta = 113.74(3)^\circ$, $V = 924.0(3)$ Å³, $Z = 2$). Compound **I** is characterised by a layered structure in which decorated kröhnkite-like [100] chains are built from a distorted InO_6 octahedron ($\langle\text{In-O}\rangle = 2.136$ Å) corner-linked to two non-equivalent 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

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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, AlO_4 -tetrahedra tend to avoid each other, leading to alternating AlO_4 - and 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 Al^{3+} replaces 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

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

Gabriella Salviulo^a, A. Speghini^b, M. Bettinelli^b, L. Nodari^c, U. Russo^c, ^aDip. Mineral. Petrol. Univ. Padova. ^bDST, Univ. Verona, ^cDip. 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 ⁵⁷Fe 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

for $\text{Fe} \leq 0.1\%$ (higher than 60%), and is absent for $\text{Fe} \geq 1\%$. It is emphasized that the composition $\text{Fe} = 0.5\%$ is crucial: because Ca- and Sr- samples are a mixture of apatite and triphosphate, while Ba-sample is 100% barium triphosphate. The accurate cell constant determination allows some considerations about a and c parameters dependence on chemical composition. Preliminary Mössbauer results indicate the presence of oxidic iron species and of substituted hydroxyapatite and phosphate in amounts that are function of both the iron amount in the starting material and the type of cation, in agreement with the X-ray powder diffraction data.

Keywords: apatites, Mössbauer spectroscopy, X-ray diffraction

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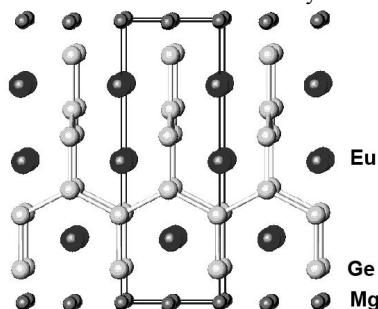
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Synthesis and Crystal Structure of the New Zintl Phase $\text{Eu}_3\text{Mg}_2\text{Ge}_6$

Michael Wörle, Christof Kubata, Frank Krumeich, Reinhard Nesper, *Inorganic Chemistry, ETH Zürich, Switzerland*. E-mail: woerle@inorg.chem.ethz.ch

The new Zintl phase $\text{Eu}_3\text{Mg}_2\text{Ge}_6$ was prepared and structurally characterized. The compound crystallizes in the tetragonal space group $P-4m2$ (No. 115) with $a = 4.476(1) \text{ \AA}$ and $c = 12.794(3) \text{ \AA}$. The structure contains the novel Zintl anion $^{1-}_4[\text{Ge}_6^{10-}]$ with an infinitely branched chain of linked perpendicular zig-zag chains, related to sections of the $\alpha\text{-ThSi}_2$ structure type.

The occurrence of diffuse scattering in the $[0kl]$ -layer points to the presence of stacking faults. Different models for stacking faults were developed and discussed, favouring one possibility, which yields a good qualitative explanation of the diffuse scattering intensities [1] and also for the observed residual electron density.



[1] Proffen Th., Neder R.B., *J. Appl. Cryst.*, 1997, 30, 171.

Keywords: germanides, diffuse scattering, Zintl phase

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Metallic Clusters Interactions: Structures of $\text{Co}(\text{H}_2\text{O})_6\text{K}_2\text{M}_2\text{W}_4\text{O}_{19}\cdot x\text{H}_2\text{O}$ ($\text{M}=\text{V}, \text{Nb}$)

Mongi Debbabi^a, Hafedh Driss^a, René Thouvenot^b, ^a*Laboratoire de Physico-Chimie des Matériaux, Faculté des Sciences de Monastir. Monstir 5019 Tunisia*. ^b*Laboratoire de Chimie inorganique et Matériaux Moléculaires case courrier 42, 4 place Jussieu Université Pierre & Marie Curie 75252 Paris Cedex 05*. E-mail: mngdbb@enim.rnu.tn

The compounds $[\text{Co}(\text{H}_2\text{O})_6]\text{K}_2\text{V}_2\text{W}_4\text{O}_{19}\cdot 3\text{H}_2\text{O}$ (**1**) and $[\text{Co}(\text{H}_2\text{O})_6]\text{K}_2\text{Nb}_2\text{W}_4\text{O}_{19}$ (**2**) crystallizes respectively in the Orthorhombic system, space group Cmcm and the Hexagonal system, space group R-3m . The cell parameters for (**1**) are $a=11.645(1)\text{ \AA}$, $b=13.242(1)\text{ \AA}$, $c=15.417(1)\text{ \AA}$, $V=2377(3) \text{ \AA}^3$ with $Z=4$ and $a=9.887(2) \text{ \AA}$, $c=24.242(1) \text{ \AA}$, $V=2052.4(2) \text{ \AA}^3$ with $Z=4$ for (**2**). The structure of the anion $[\text{M}_2\text{W}_4\text{O}_{19}]^{4-}$ ($\text{M}=\text{V}$ or Nb) is essentially that of Lindqvist^[1], the metals positions are disordered, occupancies of V or Nb and W were refined and are close to the theoretical values. The crystal structure shows that the oppositely charged polyhedral ions are arranged alternately and have their faces parallel to each other for maximal interactions (face-to-face interaction)^[2]. The crystal (**1**) has large mono-directional channels along the $[001]$ axis with a sectional area of $10.23 \times 6.35 \text{ \AA}^2$ that are filled by cobalt. The crystal (**2**) has also mono-directional quasi squared channels along the $[012]$ axis

with a sectional area of $(4.52)^2 \text{ \AA}^2$ that are filled by cobalt.

[1] Lindqvist, *I. Ark. Kemi.*, 1952, 5, 247. [2] Son J., Kwon Y., *Inorg. Chem.*, 2004, 43, 1929-1932.

Keywords: polyoxometalate structures, inorganic clusters, interactions

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Hydrogen Bonds in Triclinic $\text{MH}(\text{XO}_4)$ Compounds

Herta Effenberger, Tamara Mihajlović, *Inst. f. Mineralogie und Kristallographie, Univ. Wien, Althanstraße 14, A-1090 Wien, Austria*. E-mail: herta.silvia.effenberger@univie.ac.at

The crystal structure of triclinic SrHAsO_4 was re-investigated from single crystal X-ray data. The strong reflections of the present investigation are in agreement with a former description [1]. However, additional weak superstructure reflections are responsible for a unit cell with four-fold cell volume. The non-standard space-group setting

$F\bar{1}$ ($a = 14.697(3)$, $b = 28.230(5)$, $c = 14.920(3) \text{ \AA}$, $\alpha = 95.20(3)$, $\beta = 104.78(3)$, $\gamma = 88.11(3)^\circ$, $Z = 64$) was chosen to facilitate the comparison with CaHPO_4 (monetite), CaHAsO_4 (weilite), $\alpha\text{-SrHPO}_4$, NaHSO_4 , and HgHAsO_4 . Their unit cells correspond with the average cell of SrHAsO_4 . The arrangements of the M and X atoms ($M = \text{Na}, \text{Ca}, \text{Sr}, \text{Hg}$; $X = \text{S}, \text{P}, \text{As}$) compare well; their coordination figures are qualitatively maintained. Despite a structural analogy, isotropy is not verified. Essential differences are evident for the hydrogen bonds. The

parental structure has space group $P\bar{1}$ ($Z = 4$) and exhibits three crystallographically different hydrogen bonds. Only half of the H atoms p.f.u. forms conventional hydrogen bonds. Two hydrogen

bonds are restricted by $\bar{1}$ symmetry ($\text{O}\cdots\text{O} \geq 2.40 \text{ \AA}$). Distinct order phenomena in the structurally related compounds are observed. In SrHAsO_4 the formation of a superstructure violates these inversion centres and all hydrogen bonds have distinct donor and acceptor atoms. However, some short contacts $\text{O}\cdots\text{O}' \geq 2.47 \text{ \AA}$ are maintained. Financial support of the Austrian science foundation (FWF) is gratefully acknowledged (Grant P15875-N03).

[1] Nabar M.A., Dalvi A.P., *Bull. Soc. fr. Min. Crist.*, 1977, 100, 353.

Keywords: $\text{MH}(\text{XO}_4)$, hydrogen bonding, crystal chemistry of inorganic compounds

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Structural and Electron Density Studies of Stuffed Tridymite

Hiroshi Yamada^a, H. Kubozono^b, C. N. Xu^{ac}, ^a*AIST Japan*. ^b*Saga University Japan*. ^c*JST, Japan*. E-mail: hiro-yamada@aist.go.jp

Stuffed tridymite materials, MA_2O_4 ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$) are one of the most important matrices for luminous materials because of easily introducing various dopant ions into the framework structure and can realize various luminous colours. Utilizing these matrices, we have developed newly functional materials, which show strong mechano-, electro-, and photo-luminescence in one material [1,2]. Their physical properties are largely related to the crystal structure because the luminescent properties are strongly sensitive to its local atomic configuration and the local polarization state around dopant ions. Therefore the structural study of these materials is important for controlling their mechanical, luminescent and optical properties.

We have determined the accurate structural parameters of MA_2O_4 ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$) by Rietveld refinements using high resolved powder diffraction data with synchrotron X-ray radiation (SPring-8 BL02B2). It was found that their structural features were strongly dependent on cation size. The shape of AlO_4 tetrahedra that constitute of the framework structure was almost independent to the cation size meanwhile the void space around cation was variable, suggesting that the framework structure in stuffed tridymite may be easily deformed. Furthermore the charge density distribution was also calculated from the observed form factors F_o using the maximum entropy method (MEM), demonstrating that the cation ions were isolated ions