

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.

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

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

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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

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

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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.  $P2/c$  (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.

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

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

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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.

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

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

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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