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Acta Cryst. (2011) A67, C577**Structural and spectroscopic study of a series of PbMBO₄ compounds (M = Al, Fe, Mn)**

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In search of nonlinear optical materials ternary metal borates PbMBO₄ (M = Al, Cr, Fe, Ga, Mn) and their crystal structures were reported [1-3]. Systematically incorporation of transition metals into this crystal structure can reveal an extensive isomorphous miscibility (PbM_{1-x}M^{II}_xBO₄; both M^I and M^{II} are trivalent, and x = 0 - 1), which will help to tune useful physical properties. The crystal structure of PbMBO₄ is built of mullite-type infinite chains of edge-sharing MO₆ octahedra parallel to the **b**-axis, which are bridged by planar BO₃ groups. The Pb²⁺ cation occupies the apex of a PbO₄ square pyramid. Here we report syntheses, crystal structures, Fourier-transform infrared (FTIR) and micro-Raman spectroscopic investigations on three series of compounds: PbAl_{1-x}Fe_xBO₄, PbAl_{1-x}Mn_xBO₄ and PbFe_{1-x}Mn_xBO₄ for x = 0 - 1. The end-member phases (x = 0 or 1) have been synthesized by solid state reactions, and other members of the series (0 < x < 1) were produced by the glycerin method [4]. A fundamental parameter approach was implemented for the description of the reflection profiles during the structure analysis from the X-ray powder data Rietveld refinement. The refined M^I/M^{II} ratio in the compounds lies close to the stoichiometric equivalence line. The cell parameters of the end-member phases PbAlBO₄, PbFeBO₄, PbMnBO₄ showed slightly higher values than those of the reported ones calculated from neutron powder diffraction data. The change of the cell parameters is anisotropic with respect to the size/type of the M³⁺ cations in the MO₆ octahedra. A free or constrained refinement of displacement parameters between M^I and M^{II} atoms showed that their B-factors contained contributions from both thermal motion and static structural disorder. The significant difference between the octahedral radii of Al³⁺, Fe³⁺, and Mn³⁺ cations showed a wide range of M—O bond lengths, leading to a distortion of MO₆ octahedra, in particular at the mid-range of the composition (x = 0.4 - 0.6). Consequently, it imposed microstrain to the crystalline system, and to the average crystal size. Both FTIR and Raman spectra showed typical absorption bands. The incorporation of larger atoms in the MO₆ octahedra leads to shifts of the M—O stretching and bending modes toward lower wave numbers due to the decrease of the vibrational force constants. Assignments of the B—O stretching and bending modes clearly revealed the trigonal planar geometry of BO₃ group. Absorptions caused by the vibrations of the heavy Pb-atom are seen in the far-IR region. The intensity, *FWHM* and positions of bands in the region between 100 cm⁻¹ and 400 cm⁻¹ indicates the 6s² electronic lone pair is stereochemically active, which leads to the PbO₄ pyramids possessing covalent and somewhat directional Pb—O bonds.

[1] H. Park, J. Barbier, *J. Acta Cryst.* **2000**, E57, i82-i84. [2] H. Park, R. Lam, J.E. Greedan, J. Barbier, *J. Chem. Mater.* **2003**, 15, 1703-1712. [3] H. Park, J. Barbier, R.P. Hammond, *Solid State Sci.* **2003**, 5, 565-571. [4] Th. M. Gesing, R.X. Fischer, M. Burianek, M. Mühlberg, T. Debnath, C.H. Rüschler, J.-Ch. Buhl, H. Schneider. *J. Eur. Ceram. Soc.* **2011**, accepted.

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Acta Cryst. (2011) A67, C577**Crystal-chemical and structural characterization of fluorapatites****from Somma-Vesuvius volcanic complex**

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Ca₁₀(PO₄)(F, Cl, OH)₂ apatite crystals occurring in ejecta from Somma – Vesuvius volcanic complex were investigated by means of a multi-methodological approach based on morphological, textural, and geochemical analyses, indicating five main types of ejecta. Morphological data set highlight the presence of well-developed hexagonal prismatic habit and, more rarely, skeletal acicular forms. The crystals are yellow (type 1), transparent and colorless (type 2 and type 3), green (type 4) and aquamarine colored (type 5). Chemical compositions for the different apatites here investigated, using EMPA-WDS technique, show variable amounts of Na, REE, Mg, Sr, Fe replacing Ca, Si and S replacing P, and significant substitution of F from OH and Cl at the so-called ‘halogen site’. Crystals representative of each single apatite type were successively analyzed by single crystal X-ray diffraction. Their crystal structure was refined within the *P6₃/m* space group. [1] The present investigation allowed us to better focus the Somma-Vesuvius apatites, by means also of a comparative crystallochemical analysis carried out with available isostructural phases reported in literature.

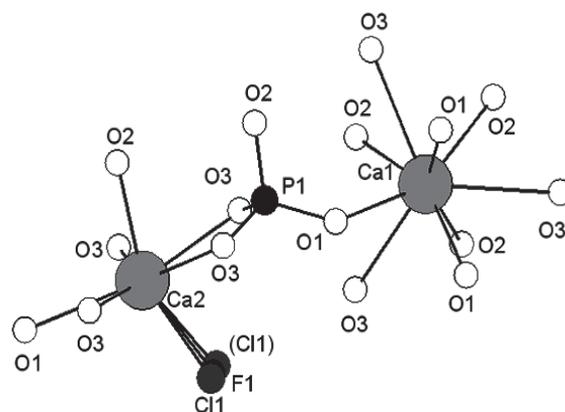


Figure 1. Cl-rich fluorapatites. Environment of P1, Ca1 and Ca2 atoms.

[1] M. Rossi, M.R. Ghiara, G. Chita, F. Capitelli, *American Mineralogist* **2011**, accepted.

Keywords: fluorapatite, Somma-Vesuvius volcanic complex, X-ray crystal structure

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Acta Cryst. (2011) A67, C577-C578**Effect of Ti-doping on electron configuration and ADPs in synthetic titanomagnetites**

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Single crystals of three Ti-doped magnetite specimens [Fe_{2.992}Ti_{0.054}O₄, *a* = 8.4029(3) Å; Fe_{2.8668}Ti_{0.1194}O₄, *a* = 8.4087(3) Å; Fe_{2.6864}Ti_{0.2955}O₄, *a* = 8.4298(3) Å] were prepared by floating zone method, and their structural parameters were compared to each other and also to nearly stoichiometric one [Fe_{2.998}O₄, *a* = 8.3972(3) Å]. Ti

and cation vacancies were found at the octahedral cation site (B site). Change in cell dimension was smooth and monotonous, while structure refinements utilizing only high angle data (147 out of 182 Bragg points with $\sin\theta/\lambda \geq 0.6$) showed that the most of structural parameters have different trends with Ti doping higher and lower than 2%.

Anisotropy in ADPs at the octahedral cation site (B site) was high in the stoichiometric specimen [1] and this high anisotropy was kept in Ti 2% specimen. This anisotropy, however, got smaller with increasing Ti doping as it was reported on cation-deficient magnetite [2]. ADPs at the tetrahedral cation site (A site) and that at the oxide ion site along $\langle 111 \rangle$ increased steeply with Ti doping at concentrations higher than 5%.

As it has been repeatedly reported, the A-O and B-O distances in magnetite are longer and shorter than ${}^{\text{iv}}\text{Fe}^{2+}$ -O and average of ${}^{\text{vi}}\text{Fe}^{2+}$ -O and ${}^{\text{vi}}\text{Fe}^{3+}$ -O distances, respectively, in hitherto reported Fe-bearing spinels [3]. The A-O distance increased moderately with Ti doping, indicating transfer of remnant electron from the B site due to substitution of Fe^{2+} by Ti^{4+} . Change in the B-O distance showed convex feature with an amount of Ti: the B-O distance abruptly increased with Ti doping from 0 to 2%, then it turned into moderate convex trend with further Ti doping. Intercept at $\text{Ti} = 0\%$ extrapolated from Ti 5% and 10% data [$d(\text{B-O}) = 2.0610(6) \text{ \AA}$ at $\text{Ti} = 5\%$ and $2.0607(6) \text{ \AA}$ at $\text{Ti} = 10\%$] was 2.0615 \AA . While the value (2.0615 \AA) was still smaller than the average of $d({}^{\text{iv}}\text{Fe}^{2+}\text{-O})$ and $d({}^{\text{vi}}\text{Fe}^{3+}\text{-O})$ estimated from bond-valence scheme (2.078 \AA), this trend itself indicated change in nature of Fe-O bonding in the B-O bond (semi-metallic to ionic nature) with a little amount of Ti doping.

Difference Fourier synthesis on the stoichiometric specimen showed positive residues on B-O bonds, particularly in the vicinity of the B site (at $1/2, 1/2, 1/2$), and also positive residues on non-bonding directions in the vicinity of the A site. These features, however, were not clearly seen on Ti 2% and 5% specimens and vanished on Ti 10% specimen.

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Structural properties of gahnite doped with cobalt, manganese or titanium

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Oxide spinels include a very large group of structurally related compounds having a considerable technological importance. Among them, zinc aluminate (ZnAl_2O_4), known by the mineral name gahnite, is of interest due its good combination of semiconducting and optical properties which makes it useful in various photoelectronic devices [1]. When doped with some transition-metal cations or rear-earth cations, it exhibits luminescence and can be used as a cathodoluminescence material [2]. Gahnite possesses a cubic spinel-type structure, space group $Fd\bar{3}m$ [3]. Although gahnite doped with various cations already has wide applications, some cases of doping are not completely elucidated.

Three series of nanocrystalline powder gahnite samples were

prepared by a sol-gel technique: (i) samples doped with 0-100 at% Co (substituted for Zn), (ii) samples doped with 0-60 at% Mn (substituted for Zn), (iii) samples doped with 0-12.5 at% Ti (substituted for Al). Structural changes due to Co, Mn and Ti incorporation in the gahnite lattice were studied by XRD. Crystal structures were refined by the Rietveld method [4], including the analysis of diffraction line broadening. Valence state and location of dopant cations in the gahnite lattice were determined by EPR spectroscopy.

Unit-cell parameter of gahnite increased on doping with Co, Mn and Ti. Doping with cobalt and manganese induced a partial inverse spinel structure, with Co^{2+} and Mn^{2+} cations residing on both tetrahedral and octahedral cation sites of the gahnite structure respectively. On the other hand, Ti^{4+} dopant cations occupied only octahedral sites substituting for Al^{3+} . In the latter case the excess Zn^{2+} cations (included during the synthesis procedure) were also situated on octahedral cation sites due to charge compensation. On cobalt doping as well on titanium doping, the metal-oxygen distances in gahnite structural tetrahedra decreased while in structural octahedra increased. In the case of manganese doping the situation is just opposite: metal-oxygen distances in structural tetrahedra increased and in structural octahedra decreased. Such behavior is a consequence of ionic radii of involved dopant cations and their contents on the respective cation sites.

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Structure and spectroscopic study of $\text{A}_{0.50}\text{SbFe}(\text{PO}_4)_3$ (A = Mn, Ca, Cd, Sr) Nasicon phosphates series

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The Nasicon-type family has been the subject of intensive research due to its potential applications as solid electrolyte, electrode material, low thermal expansion ceramics and as storage materials for nuclear waste [1-4]. The structure of such materials with general formula $\text{A}_x\text{XX}'(\text{PO}_4)_3$ consists of a three-dimensional network made up of corner-sharing $\text{X}(\text{X}')\text{O}_6$ octahedra and PO_4 tetrahedra in such a way that each octahedron is surrounded by six tetrahedra and each tetrahedron is connected to four octahedra. Within the Nasicon framework, there are interconnected interstitial sites usually labelled M1 (one per formula unit) and M2 (three per formula unit) through which A cation can diffuse, giving rise to a fast-ion conductivity. The crystallographic formula can be written as $[\text{M1}][\text{M2}]_3\text{XX}'(\text{PO}_4)_3$.

$\text{A}_{0.50}\text{SbFe}(\text{PO}_4)_3$ (A = Mn, Ca, Cd, Sr) samples were obtained by solid state reaction in air. The structural characteristics by powder X-ray diffraction (XRD) study using the Rietveld method show that $\text{A}_{0.50}\text{SbFe}(\text{PO}_4)_3$ (A = Mn, Ca, Cd, Sr) compounds are isostructural and crystallise in the $R\bar{3}$ space group. In all samples, A^{2+} cations occupied one-half of the M1 sites and the Sb^{5+} and Fe^{3+} cations are orderly distributed within the $\text{SbFe}(\text{PO}_4)_3$ framework. A globally structural comparison between $\text{A}_{0.50}\text{SbFe}(\text{PO}_4)_3$ phases are presented. In order to obtain further structural information about the nature of bonding in studied phosphates an assignment of Raman and Infrared bands was also realised.