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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^I_{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.

Keywords: metal borate, x-ray, spectroscopy

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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.

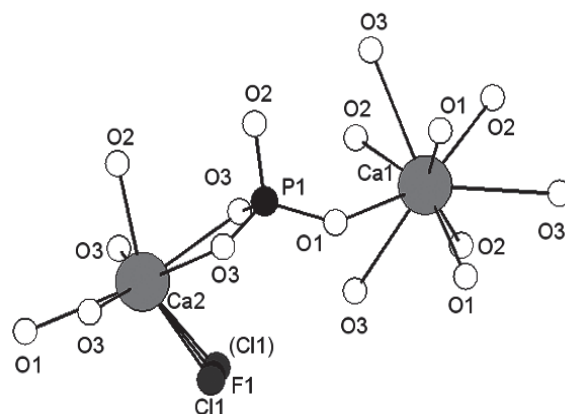


Figure 1. Cl-rich fluorapatites. Environment of P1, Ca1 and Ca2 atoms.

[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