

MS14-P3 High-temperature behaviour of astrophyllite and magnesioastrophyllite from Khibiny massif (Kola peninsula, Russia)Elena S. Zhitova¹, Maria G. Krzhizhanovskaya¹, Sergey V. Krivovichev^{1,2}, Victor N. Yakovenchuk²1. Saint Petersburg State University
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The thermal behaviour of natural astrophyllite and magnesioastrophyllite (Khibiny massif, Kola peninsula, Russia) was studied using in situ high-temperature XRD in the range 25-1000 °C by means of Rigaku Ultima IV powder X-ray diffractometer (CuK α) with a high-temperature camera. The first reflections of new high-temperature phase were detected at 500 °C and 550 °C for astrophyllite and magnesioastrophyllite, respectively. Peaks of new phase were shifted in the high-angle region. Reflections of both, initial minerals and its high-temperature phase presented in the diffraction pattern at the temperature of the phase transition. In the temperature range 525- 775 °C only high-temperature phase remained. Both minerals decompose at 775 °C. Single crystal X-ray diffraction of astrophyllite was carried out for both phases using single-crystal diffractometer Bruker APEX II, MoK α . Unit cell parameters of original astrophyllite are $a = 5.3752(1)$, $b = 11.8956(3)$, $c = 11.6554(3)$ Å, $\alpha = 113.157(2)$, $\beta = 94.530(2)$, $\gamma = 103.112(2)$ °, $V = 655.47(3)$ Å³. Unit cell parameters of high-temperature phase are $a = 5.3287(4)$, $b = 11.790(1)$, $c = 11.4332(9)$ Å, $\alpha = 112.530(8)$, $\beta = 94.539(6)$, $\gamma = 103.683(7)$ °, $V = 633.01(9)$ Å³. Thermal behaviour of studied material changes from thermal expansion for initial phases to contraction for high-temperature phases. The decrease of the unit-cell parameters is probably the result of change of oxidation of iron that leads to the shortening of the Fe-O bond lengths.

The XRD studies have been performed at the X-ray Diffraction Centre of St. Petersburg State University.

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Keywords: thermal behaviour of natural layered titanosilicates, Kola alkaline massifs, astrophyllite

MS14-P4 Synthesis, structure and low temperature behaviour of Sidorenkite/Bonshtedtite-like sodium carbonophosphates containing Ni(II), Fe(II) and Mn(II)Sephira Riva¹, Serena Margadonna¹

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Recent predictions highlighted the promising features of sidorenkite ($Na_3Mn(PO_4)(CO_3)$)- and bonshtedtite ($Na_3Fe(PO_4)(CO_3)$)-like compounds for the development of new, low cost, Na-based batteries. These materials are characterized by high theoretical specific energy and stability at air exposure; moreover, they can undergo reversible Na-ion intercalation/de-intercalation by changing the oxidation state of the central transition metal.

$Na_3M(PO_4)(CO_3)$ [M=Ni, Mn, Fe] were synthesised via hydrothermal synthesis. Temperature, starting concentrations, reaction time and stirring were modulated to obtain pure samples.

Compounds were characterised using synchrotron radiation (ID31 at the ESRF), with temperature ranging from 10K to 290K. Data were collected in transmission mode by using 0.5mm glass capillaries and scanning from 0 to 30 2 θ ($\lambda=0.39992$ Å).

Crystals were found to have monoclinic sidorenkite structure (P2₁/m). Each cell unit consists of a transition metal octahedron sharing four vertices with the tetrahedral PO_4 group and an edge with the CO_3 group. The connection of transition metal octahedra, PO_4 tetrahedra and planar CO_3 groups create a two-dimensional subunit, which extends along the [1 0 0] plane. Sodium ions occupy two distinct interstitial positions between the double layers formed by tetrahedral PO_4 groups and MO_6 octahedra. These sites are coordinated by 7 (multiplicity 2) and 6 (multiplicity 4) oxygen atoms.

The dependence of cell volume and interatomic distances from temperature was quantified from cell parameters variations (a , b and c lattice parameters; β angle). The carbonophosphates structure was proven extremely stable, with no phase transitions occurring in the selected temperature region.

Magnetic properties tests highlighted the anti-ferromagnetic behaviour of Ni, Mn, and Fe carbonophosphates; as well as the existence of several magnetic transitions at temperatures lower than 10K.

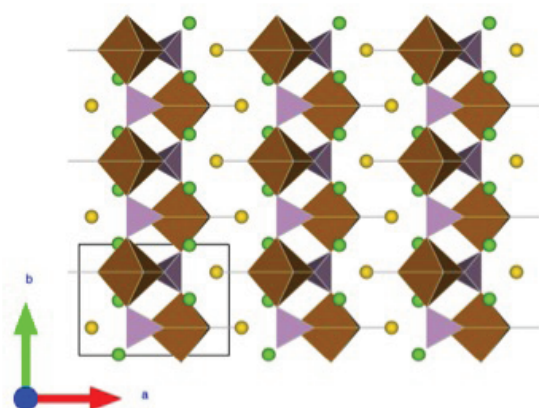


Figure 1. Structure of $Na_3Fe(PO_4)(CO_3)$ (bonshtedtite) viewed along $[0\ 0\ 1]$ plane. Fe^3 octahedra and PO_4 tetrahedra are highlighted in brown and purple respectively. Na^4 atoms occupying sites of multiplicity 2 (green) and 4 (yellow) are displayed. Oxygen atoms are hidden for clarity.

Keywords: Carbonophosphates, Low-temperature crystallography, SQUID

MS14-P5 Temperature and pressure induced phase transitions in chevkinite group. A joint XRD, XPS and EPMA structural studies

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The chevkinite group of minerals (chevkinites and perrierites) are increasingly being recognized as accessory phases in a wide range of igneous and metamorphic rocks. The general formula for the most common members of the group, is $A_4BC_2D_2(Si_2O_7)_2O_8$, where the most common cations are $A = Ca^{2+}, REE^{3+}, Sr^{2+}, Th^{4+}$; $B, C, D = Fe^{2+}, Fe^{3+}, Ti^{4+}, Al^{3+}, Mn^{2+}, Mg^{2+}$. Annealing at 750°C of niobian chevkinite-(Ce) single crystal from the Biraya rare-metal deposit (Russia) resulted in a phase transition from the space group $C2/m$ to $P2_1/a$. This may be of particular interest for researchers dealing with metamict minerals because annealing may lead to a slightly different crystal structure from the initial one, additionally a migration of cations to different crystallographic sites was observed during annealing. To confirm the new findings, next X-ray measurements on different unannealed and annealed crystals were performed.

A reversed effect of a phase transition was monitored on a single crystal of perrierite from Nettuno, Italy loaded into the diamond anvil cell. The compressibility of this mineral was analysed on the basis of fourteen X-ray diffraction (XRD) experiments from ambient pressure up to 6.4 GPa.

X-ray photoelectron spectroscopy (XPS) can give valuable results in the investigation of element valency especially when the amount of sample is insufficient for Mössbauer spectroscopy. This method can give information on any element and oxidation state, as long as the characteristic spectra for different ions are separated. This could provide crucial independent information allowing the establishment of the correct crystal structures of complex minerals. In Nb-bearing chevkinite-(Ce) iron is present as Fe^{2+} and Fe^{3+} and Ti is present as Ti^{4+} , Ti^{3+} and possibly Ti^{2+} . With this information the volumes of the first coordination spheres could be matched with the ionic radii of elements and their masses with site scattering factors in the analyzed crystal structures to obtain the most probable allocation of cations.

Empirical formulae for niobian chevkinite-(Ce) was established by joined XRD, XPS and EPMA analyses for $C2/m$: $(Ce_{1.9}^{3+}La_{1.2}Nd_{0.4}Pr_{0.2}Ca_{0.1}Sr_{0.1}Ba_{0.1})_{\Sigma 4}(Fe_{0.7}^{2+}Ca_{0.15}Mn_{0.1}Th_{0.05})(Fe_{0.7}^{3+}Ti_{0.5}^{4+}Nb_{0.6}Al_{0.1}V_{0.1})_{\Sigma 2}$