

### MS14-P3 High-temperature behaviour of astrophyllite and magnesioastrophyllite from Khibiny massif (Kola peninsula, Russia)

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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 $\alpha$ ) 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 $\alpha$ . Unit cell parameters of original astrophyllite are  $a = 5.3752(1)$ ,  $b = 11.8956(3)$ ,  $c = 11.6554(3)$  Å,  $\alpha = 113.157(2)$ ,  $\beta = 94.530(2)$ ,  $\gamma = 103.112(2)$  °,  $V = 655.47(3)$  Å<sup>3</sup>. Unit cell parameters of high-temperature phase are  $a = 5.3287(4)$ ,  $b = 11.790(1)$ ,  $c = 11.4332(9)$  Å,  $\alpha = 112.530(8)$ ,  $\beta = 94.539(6)$ ,  $\gamma = 103.683(7)$  °,  $V = 633.01(9)$  Å<sup>3</sup>. 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)

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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 $\theta$  ( $\lambda=0.39992$  Å).

Crystals were found to have monoclinic sidorenkite structure (P2<sub>1</sub>/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;  $\beta$  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.