Two synthetic phases $Li_4Ni_2F_2[PO_4]_2$ and $Li_5Fe^{3+}F_2[PO_4]_2$ crystallize in the structure type found in mineral grandidierite $MgAl_3O_2[SiO_4][BO_3]$. Topologically identical three anionic subcells differ in case of grandidierite because of an ordered vacancy in the position of one O, bringing forward a triangular configuration of the borate group. The way of cations' distribution in the voids of anionic packing leads to a dense 3D framework ordered in the Ni variety. In the Fe phosphate, four of five "metallic" positions have isomorphic or vacancy defects and all of them contain Li^+ cations. Very high degree of structure defection with Li atoms in all possible positions allow to predict ionic-conductive properties for the $Li_5Fe^{3+}F_2[PO_4]_2$. The second ordered vacancy also takes place in the grandidierite structure. It corresponds to a Li octahedron fully populated in the Ni phase, stabilized by holes in the Fe variety and empty in the grandidierite.

Topologically identical units of Ti octahedral sharing vertices with six tetrahedra $\{TiT_6O_{24}\}$ which form synthetic $Cs_2\{Ti(VO_2)_3[PO_4]_3\}$ phase (T =P) are the essential fragments of the framework in mineral benitoit $BaTiSi_3O_9$ with T =Si. Three-membered rings of tetrahedra in the benitoit structure are interrupted by hexagonal rings of V polyhedra in synthetic compound changing its tetrahedral motive from circular (as in benitoit) to "ortho".

Several other cases of microporous synthetic phosphates and their mineral analogues will be shown.

MS11 O4

Pressure-induced phase transitions in phosphate-like α-quartz-type solid solutions J. Haines[a], O. Cambon[a], R. Le Parc[b], C. Levelut[b], A. S. Pereira, [c] [a]*Institut Charles Gerhardt Montpellier UMR 5253 CNRS-UM2-ENSCM-UM1, Equipe PMOF, Université Montpellier II, Montpellier, France.,* [b]*Laboratoire des Colloïdes, Verres et Nanomatériaux, UMR CNRS 5587, Université Montpellier II, Montpellier, France.,*[c]*Instituto de Fisica and Escola de Engenharia, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, Brazil.*
E-mail: jhaines@lpmc.univ-montp2.fr

Keywords: phosphates, disorder, high pressure

The high-pressure stability of α-quartz-type materials is of considerable interest for materials (piezoelectrics etc.) and Earth science. Representative compositions of two phosphorus-containing, α-quartz type, solid solutions SiO_2-PON and $AlPO_4$-$GaPO_4$ were studied at high pressure by x-ray diffraction. These materials exhibit distinct high pressure behavior as α-quartz-type $Si_{0.56}P_{0.44}O_{1.56}N_{0.44}$ was found to undergo gradual amorphization above 23 GPa, whereas $Al_{0.30}Ga_{0.70}PO_4$ transforms to a poorly-crystallized phase above 12 GPa. This difference in behavior can be linked to the initial degree of positional disorder, particularly on the site occupied by phosphorus, in the two solid solutions. Amorphization is favored in the highly disordered SiO_2-PON system, in which positional disorder is present on all cation and anion sites. In contrast, disorder affects only ½ of the cation sites in the $AlPO_4$-$GaPO_4$ system, those

occupied by Al and Ga, whereas the phosphorus site is ordered. A high degree of disorder on the site occupied by phosphorus favors amorphous forms as it inhibits the formation of ordered phases with increased cation coordination due to the relative stability of PO_4 and $PO_{4-x}N_x$ tetrahedra in the pressure range investigated at ambient temperature. In such cases, an increase in coordination number at random sites (Si positions, for example) in the disordered cation sublattice will further enhance the process of amorphization.

MS11 O5

The structural complexity of phosphates in the Na-Fe(II)-Fe(III) (+PO₄) system Frédéric Hatert[a]
[a]*Laboratory of Mineralogy B18, University of Liège, B-4000 Liège, Belgium.* E-mail: fhatert@ulg.ac.be

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The alluaudite group of minerals consists of Na-Mn-Fe-bearing phosphates which are known to occur in Li-rich granitic pegmatites. Due to their flexible crystal structure, which is able to accommodate Fe(II) and Fe(III) in variable amounts, alluaudites are very stable and crystallize from the first stages of pegmatite evolution to the latest oxidation processes. In order to assess the geothermometric potential of alluaudite-type phosphates, we performed systematic hydrothermal experiments in the Na-Fe(II)-Fe(III) (+PO4) ternary system, between 400 and 700°C, at 1 kbar. Oxygen fugacity was not buffered, and gold capsules (2 mm diameter, 25 mm length) were used in order to keep the initial Fe(II)/Fe(III) ratio constant.

Alluaudite-type phosphates were observed between 400 and 700°C, and occupy the central part of the Na-Fe(II)-Fe(III) diagram. In the Na-poor part of the diagram occur other well known Fe-phosphates, as for example $Fe_3(PO_4)_2$ (sarcopside), $Fe^{3+}_4Fe^{2+}_3(PO_4)_6$, or $Fe^{3+}_4(PO_4)_3(OH)_3$.

The hydrothermal experiments also produced three phosphates which show new exciting crystal structures. They are localized in the Na-rich part of the diagram and were investigated by single-crystal X-ray techniques. The crystal structure of $Na_3Fe(PO_4)_2$ (*P*-1, a = 5.3141(6), b = 8.5853(9), c = 8.7859(8) Å, α = 114.429(9), β = 92.327(9), γ = 106.08(1)°, R_1 = 0.028) is based on heteropolyhedral chains running along [100], and formed by Fe1 octahedra linked via corner-sharing to P1 tetrahedra. Sodium atoms (Na-O = 2.222-2.94 Å) occur between the chains, and show topologies of weakly distorted octahedra (Na2, Na4), of distorted pentagonal bipyramid (Na1), and of hexagonal bipyramid (Na3/Na3*).

$Na_4Fe^{2+}Fe^{3+}(PO_4)_3$ (*R*3, a = 8.9543(9), c = 21.280(4) Å, R_1 = 0.035) shows a structure based on trimers formed by one Na2 octahedron, sharing one face with the Fe4 octahedron and one edge with the Fe1 octahedron. The trimers are connected together via edge-sharing P1 tetrahedra, to form chains which are running along the c axis.

The crystal structure of $Na_2Fe^{3+}(HPO_4)_2(OH)$ has been solved in the *I*2/*m* space group (a = 14.605(4), b = 7.144(2), c = 15.490(4) Å, β = 90.06(2)°), up to R_1 = 0.053.