

Figure 1. Structure of $\text{Na}_3\text{Fe}(\text{PO}_4)(\text{CO}_3)$ (bonshtedtite) viewed along $[0\ 0\ 1]$ plane. Fe^{3+} octahedra and PO_4 tetrahedra are highlighted in brown and purple respectively. Na^+ 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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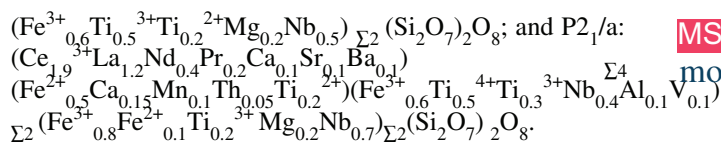
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The chevkinite group of minerals (chevkinites and perrierites) are increasingly being recognized as accessory phases in a wide range of igneous and metamorphic rocks. The general formula for the most common members of the group, is $\text{A}_4\text{BC}_2\text{D}_2(\text{Si}_2\text{O}_7)_2\text{O}_8$, where the most common cations are $\text{A} = \text{Ca}^{2+}$, REE^{3+} , Sr^{2+} , Th^{4+} ; B , C , $\text{D} = \text{Fe}^{2+}$, 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 $\text{P2}_1/\text{a}$. 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 : $(\text{Ce}_{1.9}^{3+}\text{La}_{1.2}\text{Nd}_{0.4}\text{Pr}_{0.2}\text{Ca}_{0.1}\text{Sr}_{0.1}\text{Ba}_{0.1})_{\Sigma 4}(\text{Fe}_{0.7}^{2+}\text{Ca}_{0.15}\text{Mn}_{0.1}\text{Th}_{0.05})(\text{Fe}^{3+}_{0.7}\text{Ti}_{0.5}^{4+}\text{Nb}_{0.6}\text{Al}_{0.1}\text{V}_{0.1})_{\Sigma 2}$



Keywords: Chevkinite group, composition, phase transition, oxidation state, high pressure, annealing

MS14-P6 Characterization of Mn octahedral molecular sieves by electron diffraction and Rietveld refinement

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Manganese is an extremely versatile element due to its multiple oxidation states. Tunneled octahedral manganese oxides are found in nature as alteration products in mineralized rocks. Their structures are characterized by channels walled by edge-sharing MnO_6 octahedra and hosting different ionic species (Na, K, Ba...). Small differences in manganese oxidation state are associated with a wide structural variety of framework connectivity and pore sizes [1].

Tunneled manganese oxides belong to the group of octahedral molecular sieves (OMS), due to their open framework structures recalling the better-known tetrahedral molecular sieves, i.e. zeolites. In the last years OMS raised an increasing interest for their electronic properties. While tetrahedral frameworks are typically electronic insulators, OMS are mixed electronic/ionic conductors. The octahedrally coordinated elements in OMS frameworks have easily accessible 3d orbitals. Oxidation state and band gap are structurally related and depend on position and coordination of the extra-framework ions. Manganese tunneled oxides find advanced applications in gas sensing, heterogeneous catalysis, batteries and supercapacitors [2]. Moreover, manganese OMS exhibit electric and magnetic transitions at relatively high temperatures and show a superconductive behavior connected with charge-ordering of framework and extra-framework atoms [3].

A systematic structure characterization of manganese OMS is hampered by difficulty in growing single crystals and achieving pure synthetic products. In this contribution we present the structure investigation of several natural and synthetic manganese OMS, combining X-ray powder diffraction, transmission electron microscopy and electron diffraction tomography [4]. The frameworks of unknown structures were determined ab-initio by direct methods, and extra-framework ion positions were identified during structure refinement. Intermediate phases occurring during the synthesis were tracked by thermal analysis and structurally characterized. Finally, order-disorder transitions of extra-framework atoms, eventually associated with superstructure modulations, were investigated by cryo-controlled experiments.