FA2-MS16-P32

3-D transition metal phosphate zeotypes: piezochromicity, polymorphism and magnetism.

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Materials with both magnetic and electric orders such as the magnetoelectric (ME) multiferroics have received significant attention in recent years. [1-2] The coupling of such behaviours should give rise to technological uses but also lead to rich physics. Often, ferroelectric and magnetic phases have very different ordering temperatures, which suggest that the processes are driven by different microscopic interactions, but for a significant number of materials these coincide and ferroelectricity can be generated by long-range order. Phosphate based materials have been discovered with applications across the whole range of solid state chemistry and physics from battery materials to solid oxide fuel cells and proton conductors. The lithium orthophosphates (LO) $LiMPO_4$ with M = Mn, Fe, Co and Ni are a prototypical iso-structural group of antiferromagnets (AFs) that show ME below their Néel temperatures. [3-7] Here we present initial work on materials of the type $ABPO_4$ with A = Rb and Cs and B = Co, Ni and Cu that show novel frameworks based on structures intermediate between that of zeolite ABW and the natural mineral olivine that have the potential to yield interesting properties. In the Cu system, polymorphic piezo-chromic behaviour is observed at RT driven by coordination changes in the Cu polyhedra. The structure can be locked into one of the polymorphs by doping with Ni and the dimensionality of the structure can be tuned by substitution of the A site cation. [8]

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Keywords: powder diffraction, phosphates, phase transitions and structure.

FA2-MS16-P33

The crystal structure of magnesioneptunite in the context of neptunite crystal chemistry.

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The mineral neptunite represents the silicate of titanium and is usually described with an idealized formula $LiNa_2K(Fe,Mg,Mn)_2Ti_2O_2[Si_4O_{10}]_2$. Its crystal structure has been investigated before by different authors [1-4] and different techniques. For the moment, two structural models of the mineral exist: one is centrosymmetric (space group $C2/c$) and the second is acentric (space group Cc). A new Mg-rich variety of the mineral was found in changed sandstone xenolite, dividing larnite skarn from ignimbrite, at Verhnechegemskaya Caldera, Lakargi Mountain locality (North Caucause, Russia). It is formed over ilmenite and accompanied by later less magnesium neptunite. The crystal structure of magnesioneptunite was determined by single crystal X-ray diffraction: a = 16.3271(7), b = 12.4788(4), c = 9.9666(4) Å, β=115.651(1)°, V=1830.5(1) Å^3 at 293 K, and refined till wR_2 = 0.0615, R = 0.0251 in the framework of the space group $C2/c$. The found formula corresponds to $LiK_{0.6}Na_{2.4}(Fe_{0.5}Mg_{0.5})_2Ti_2O_2[Si_4O_{10}]_2$, Z=4.

There are two nonequivalent octahedral positions for transition metals (and Mg) in the structure. The first type of octahedra are occupied by iron and magnesium, the second one contain titanium. An ordered distribution of Ti and Fe(Mg) atoms correlate with sizes of polyhedra. Thus, Ti octahedra are more distorted, Ti – O bond lengths change from 1.884(2) to 2.245(2) Å, while M – O distances in (Fe, Mg) polyhedra lie in the interval 1.962(2) – 2.180(2) Å. Alternating pairs of sharing edges Ti and (Fe, Mg) octahedra form columns that are alongated in [1-10] and [110] directions of the unit cell. SiO_4 tetrahedra share the part of oxygen vertices with a formation of an anionic paraframework. Alkaline cations Li^+, Na^+ and K^+ are distributed in different positions and are surrounded by 6 (Li and Na) or 10 (K) oxygen atoms in the first coordination sphere. In addition to the high amount of magnesium, the new variety of mineral is enriched by sodium: 2.4 atoms per formula (apf) distributed among three different structural positions compared to the usual 2 apf. Accordingly, an amount of potassium is reduced: 0.6 apf against 1 apf found for another neptunites.

Crystal structure peculiarities of the neptunite are discussed in correlation with the chemical diversity of mineral varieties.

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Keywords: crystal structure, X-ray diffraction, magnesioneptunite.

FA2-MS16-P34

Structural Refinement of $M_2Si_5N_8$:Eu^{2+} (M=Ca, Sr, Ba) Phosphor for Light Emitting Diode

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The chip based light emitting diodes (LEDs) as a new light source which have many advantages in energy efficiency, long life time, compactness and environmentally good features over conventional incandescent and fluorescent lamps. Among suitable phosphor materials to produce white light, red color-emitting nitride phosphor $M_2Si_5N_8$:Eu^{2+} (M=Ca, Sr, Ba) synthesized by a solid state reaction between metallic nitrides showed the emission peak around 650 nm under blue light (480 nm) excitation. The amount of Eu^{2+} ions occupying the crystal lattice in $M_2Si_5N_8$:Eu^{2+} (M=Ca, Sr, Ba) is closely related to the performance of phosphors such as decay time, color shift and concentration quenching. Hence, this work is focused on determining the site preference and the amount of Eu^{2+} ions in host lattice by means of the combined structural