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In situ phase separation in bimetallic sulfates: A X-ray diffraction study
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The ubiquitous role of water in the formation of hydrates of complex inorganic materials, in particular minerals, is well-recognized but little understood. It is well-recognized that the variability in the levels of hydration results in intricate structural frameworks with hydrogen-bonded water molecules providing linkers between octahedral and tetrahedral units in mineral samples. Further bimetallic sulfates, for example, Langbeinites, with a general formula A$_2$B$_2$(SO$_4$)$_3$. (Where A = Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$, NH$_4^+$, etc. and B = Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, etc.), show interesting ferroelectric properties and phase transitions at low temperatures [1]. Compounds like Tutton’s salt, [2] Leontites, [3] and Krohnkite [4] have a general formula A$_2$B$_2$(SO$_4$)$_3$.2H$_2$O with the water content (X) being six in Tutton’s salt, four in Leontites, and two in Krohnkite. It is appropriate to suggest that the temperature, pressure, and amount of hydration (sometimes even fractional) generate phases required for mineral formation, providing pointers to the origin of minerals in the earth’s crust. Here, we have investigated phase separation resulting in a single-crystal-single-crystal transition accompanied by a polycrystalline phase following the dehydration of hydrated bimetallic sulfates Na$_2$Mn$_{1-x}$Mo$_x$(SO$_4$)$_3$.S$_{1.5}$O$_{11.5}$.2H$_2$O and K$_2$Cd(SO$_4$)$_3$.3H$_2$O by using in situ variable-temperature single-crystal X-ray diffraction. With two examples, we illustrate the possibility of generating structural frameworks following dehydration in bimetallic sulfates, which refer to the possible precursor phases at that temperature leading to the mineral formation. The room temperature structure of Na$_2$Mn$_{1-x}$Mo$_x$(SO$_4$)$_3$.S$_{1.5}$O$_{11.5}$.2H$_2$O is trigonal, space group R 3. On heating the crystal in situ on the diffractometer, the diffraction images display spherical spots and concentric rings suggesting phase separation, with the spherical spots getting indexed in a monoclinic space group, C2/c. The structure determination based on this data suggests the formation of Na$_2$Mn(SO$_4$)$_3$. However, the diffraction images from concentric rings could not be indexed. In the second example, the room-temperature structure is determined to be K$_2$Cd(SO$_4$)$_3$.3H$_2$O, crystallizing in a monoclinic space group, P2$_1$/n. On heating the crystal in situ, the diffraction images collected also have both spherical spots and diffuse rings. The spherical spots could be indexed to a cubic crystal system, space group P2$_1$3, and the structure is K$_2$Cd(SO$_4$)$_3$. The study of the dehydration regime of the two compounds brings out a unique phase separation strategy based on symmetry-directed pathways and facile energy changes, keeping the lattice changes within the single-crystal to single crystal transformation.

Keywords: phase separation, mineral, sulfate

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Structure and polymorphism of the La$_2$MoO$_4$ compounds, doped with Bi, Sb and V

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Lanthanum molybdate La$_2$MoO$_4$ (LM) and the doped compounds on its basis (LAMOX) attract much attention because of the high oxygen conductivity (6×10$^{-2}$ Sm/cm), which was found by Lacorre group in 2000 year [1]. LM has the proper oxygen vacancies [2]. LM has the first-order phase transition at about 580°C and two phases: low-temperature monoclinic α-phase (P2$_1$), high-temperature β-phase (P2$_1$2$_1$2$_3$) [1]. Depending on the cooling rate of the samples after preparing, they can exist at the room temperature as the stable monoclinic α-phase or as the metastable cubic β$_m$-phase or as the mixture of these phases [3], [4].

In the present work the effect of substitution of the La$^{3+}$ ions for Bi$^{3+}$ ions or Mo$^{6+}$ ions for Sb$^{3+}$ and V$^{5+}$ ions on the crystal structure and properties of LAMOX compounds was studied. Polycrystalline samples were prepared by solid state reaction. Single crystals were grown by spontaneous crystallization from flux. The X-ray results of the La$_2$Bi$_2$Mo$_3$O$_{11}$(0 ≤ x < 0.05), La$_2$Mo$_3$Sb$_3$O$_{11}$(0 ≤ x < 0.05) and La$_2$Mo$_3$V$_3$O$_{11}$(0 ≤ x < 0.06) solid solutions showed that the impurities implantation results in the decrease of the α→β phase transition temperature and to its appreciable suppression. Temperature dependent conductivity measurements confirm the fact that LM doping with Bi, Sb or V stabilizes of the cubic β$_m$ phase at the room temperature. Therefore the appreciable increase of conductivity of the doped La$_2$MoO$_4$ samples has been observed in the low-temperature area (below 500°C) in comparison with the pure La$_2$MoO$_4$. The X-ray structural studies of the β$_m$ phase of the single crystals series showed that the impurities (Bi, Sb, V) implantation into LM structure leads to the stabilization of the cubic phase at the room temperature. It was established that doping of La$_2$MoO$_4$ compound by Bi, Sb or V atoms results in the redistribution of the valence forces in the LM structure, the analogous situation takes place at high temperatures. More symmetric arrangement of the oxygen atoms around Mo atoms lead to the stabilization of the cubic phase at room temperature.

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Keywords: LAMOX, crystal structure, oxide-ion conductivity

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Synthesis, structure and properties of the Nd$_2$MoO$_4$ fluorite-like compound
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High oxygen conductivity of the Nd$_2$MoO$_4$ compound (0.06 S/cm

Keywords: LAMOX, crystal structure, oxide-ion conductivity
at 800°C) was established by the Lacorre et al [1]. There is no such a compound in the Nd₃O₇-MoO₃ system, but there is one with the fluorite-like structure near the Nd₃MoO₈ [2], [3], [4]. Chemical composition and crystal structure of the Nd₃MoO₈ compound were studied before on polycrystals [4] as well as similar structure of Pr₃MoO₈ [5]. It was found that the Pr₃MoO₈ crystals have a fluorite-like superstructure in the Pn-3n sp. gr. There are Pr1 at 12e position, Pr2 at 8c, Mo at 16f, and two kinds of oxygen atoms O1 at 48i and O2 at 16f. Overerrated thermal parameters are given in [5] for the Pr2 (Bₑ = 1.32(16) Å) and Mo (Bₑ = 0.98(7) Å) atoms, while Bₑ = 0.71(4) Å for the O2 atom.

Single-crystal structure refinement of Nd₃MoO₈ and study of the physical properties have been performed. Dark-violet cubic Nd₃MoO₈ single crystals were grown by spontaneous flux crystallization. The conductivity of the compound is hypothetically anionic and reaches approximately 10⁻¹⁰ S/cm at 800°C.

The structure of Nd₃MoO₈ single crystal was studied by the X-ray techniques (XCalibur S CCD-diffractometer, T=293 K). The unit cell was found to be cubic with a=11.028(1) Å, which relates to that of fluorite CaF₂ as a=2a₂. The structure was solved using the Pn-3n symmetry group. It was found that the Nd1 and Mo atoms are shifted from their positions on the 4-fold axis with the formation of 4 positions (0.25 occupation) around it. The Nd2 atoms are not disordered; they are located on the 3-fold axis and are surrounded by oxygens with 6 Nd2-O2 distances equal to 2.597 Å and 2 distances Nd2-O1 equal to 2.294 Å (coordination polyhedron of Nd2 – slightly distorted cube). Inclusion of Mo atoms into Nd₃MoO₈ structure, which are surrounded by O2 atoms (Mo-O2 distances from 1.695 to 1.892 Å) lead to the strong distortion of the Nd1 – polyhedron and to the deviation of the structure framework from the fluorite-like. Some shift of the Nd1 and Mo atoms from the axis appears as a result, which was established in the present work (R=3.6%, R₁=3.27%, S=1.99, Bₑ=0.24(1) Å for the Pr2 atom).

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X-Ray studies in a manganese lawsonate coordination polymer

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Lawsonite (2-hydroxy-1,4-naphthoquinone) is a natural spin carrier in metal complexes molecules. The redox properties of quinones and their complexes have been explored for applications such as the development of new drugs for cancer [1] and switches for molecular electronics [2]. Here, we describe the synthesis and the characterization of [Mn(C₇H₆O₄)₂]ₙ by infrared and ultraviolet spectroscopy, thermogravimetric analysis and single-crystal X-ray diffraction. X-ray data shows the formation of a coordination polymer with the manganese atom in a center of a fully distorted octahedron (C2/c). The carbonyl and the phenoxo oxygens (O1 and O2, respectively) chelate to the manganese, and the other carbonyl oxygen (O3) bridges to another metal center forming a 2D arrangement. Temperature dependent X-ray studies (225K and 110K) shows a significantly variation in bond distances around the metal center, which indicates change in the bond.