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, Langbeinite, with a general formula $A_2B_2(SO_4)_3$ (where $A =$ Li, Na, K, Rb, Cs, NH$_4$, etc. and $B =$ Mn$^{2+}$, Fe$^{3+}$, 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] K$_2$Bi$_2$$[SO_4]_3$·$2$H$_2$O and K$_2$Cd$_2$SO$_4$·3H$_2$O by using in situ variable-temperature single-crystal X-ray diffraction. With two examples, we illustrate the possibility of generating structural frameworks following deformation in bimetallic sulfates, which refer to the possible precursor phases at that temperature leading to the mineral formation. The room temperature structure of Na$_2$Mn$_{12}$$(SO_4)_{25}$S$_3$O$_{136}$·2$H_2$O and K$_2$Cd$_2$(SO$_4$)$_3$·3$H_2$O by using in situ variable-temperature single-crystal X-ray diffraction. On healing the crystal in situ on the diffractometer, the diffraction images display spherical spots and concentric rings suggesting phase separation, with two examples, we illustrate the possibility of generating structural frameworks following deformation in bimetallic sulfates, which refer to the possible precursor phases at that temperature leading to the mineral formation. The room temperature structure of Na$_2$Mn$_{12}$$(SO_4)_{25}$S$_3$O$_{136}$·2$H_2$O is trigonal, space group R 3. On heating the crystal in situ, the diffraction images display spherical spots and concentric rings suggesting phase separation, with the spherical spots getting indexed in a monoclinic space group, $C2/c$. The structure determination based on this data suggests the formation of Na$_2$Mn$_{12}$$(SO_4)_{25}$S$_3$O$_{136}$·2$H_2$O. However, the diffraction images from concentric rings could not be indexed. In the second example, the room-temperature structure is determined to be K$_2$Cd$_2$(SO$_4$)$_3$·3$H_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 $P2_13$, and the structure is K$_2$Cd$_2$(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$_2$Mo$_3$O$_{10}$ compounds, doped with Bi, Sb and V

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Lanthanum molybdate La$_2$Mo$_3$O$_{10}$ (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 $\alpha$-phase ($P2_1$) and high-temperature $\beta$-phase ($P2_12_1$) [1]. Depending on the cooling rate of the samples after preparing they can exist at the room temperature as the stable monoclinic $\alpha$-phase or as the metastable cubic $\beta$-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$^{3+}$ ions for Sb$^{5+}$ and V$^{3+}$ 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 colorimetric analysis of the La$_2$Bi$_2$Mo$_3$O$_{10}$ (0 ≤ x ≤ 0.05), La$_2$Mo$_3$Sb$_2$O$_{10}$ (0 ≤ x ≤ 0.05) and La$_2$Mo$_3$V$_2$O$_{10}$ (0 ≤ x ≤ 0.06) solid solutions showed that the impurities implantation results in the decrease of the $\alpha$-$\beta$ 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 $\beta$-phase at the room temperature. Therefore the appreciable increase of conductivity of the doped La$_2$Mo$_3$O$_{10}$ samples has been observed in the low-temperature area (below 500°C) in comparison with the pure La$_2$Mo$_3$O$_{10}$. The X-ray structural studies of the $\beta$-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$_2$Mo$_3$O$_{10}$ 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. This study was supported in part by RFFR (grant No. 11-03-00243-a), by the Department of Physical Sciences of the Russian Academy of Sciences within the Program in Support of Fundamental Research and the Council on Grants of the President of the Russian Federation for the Support of Leading Scientific Schools (project no. NSh 4034.2010.5).


Keywords: LAMOX, crystal structure, oxide-ion conductivity

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Synthesis, structure and properties of the Nd$_2$Mo$_3$O$_{10}$fluorite-like compound

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High oxygen conductivity of the La$_2$Mo$_3$O$_{10}$ compound (0.06 S/cm)