

## MS81.P31

*Acta Cryst.* (2011) A67, C713**In situ phase separation in bimetallic sulfates: A X-ray diffraction study**

Diptikanta Swain,<sup>a</sup> Chandrabhas Narayana,<sup>a</sup> Tayur N. Guru Row,<sup>b</sup> <sup>a</sup>*Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, (India).* <sup>b</sup>*Solid State and Structural Chemistry Unit, Indian Institute of science, Bangalore, (India).* E-mail: diptisscu@gmail.com

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  $A_2B_2(SO_4)_3$  (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] Leonites, [3] and Kröhnkite [4] have a general formula  $A_2B(SO_4)_2 \cdot XH_2O$  with the water content (X) being six in Tutton's salt, four in Leonites, and two in Kröhnkite. 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  $Na_2Mn_{1.167}(SO_4)_2S_{0.33}O_{1.167} \cdot 2H_2O$  and  $K_4Cd_3(SO_4)_5 \cdot 3H_2O$  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  $Na_2Mn_{1.167}(SO_4)_2S_{0.33}O_{1.167} \cdot 2H_2O$  is trigonal, space group  $R\bar{3}$ . 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  $Na_2Mn(SO_4)_2$ . However, the diffraction images from concentric rings could not be indexed. In the second example, the room-temperature structure is determined to be  $K_4Cd_3(SO_4)_5 \cdot 3H_2O$ , 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  $K_2Cd_2(SO_4)_3$ . 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.

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*Acta Cryst.* (2011) A67, C713**Structure and polymorphism of the  $La_2Mo_2O_9$  compounds, doped with Bi, Sb and V**

Olga Alekseeva,<sup>a</sup> Natalya Sorokina,<sup>a</sup> Natalya Novikova,<sup>a</sup> Anna Gagor,<sup>b</sup> Adam Pietraszko,<sup>b</sup> Elena Kharitonova,<sup>c</sup> Valentina Voronkova,<sup>c</sup> <sup>a</sup>*Shubnikov Institute of Crystallography, Russian Academy of Science, Moscow (Russia).* <sup>b</sup>*Institute of Low Temperatures and Structural Research, Polish Academy of Sciences, Wroclaw (Poland).* <sup>c</sup>*Moscow State University, Moscow (Russia).* E-mail: olalex@ns.crys.ras.ru

Lanthanum molybdate  $La_2Mo_2O_9$  (LM) and the doped compounds on its basis (LAMOXY) attract much attention because of the high oxygen conductivity ( $6 \cdot 10^{-2}$  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 ( $P2_13$ ) [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  $\beta_{ms}$ -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  $Sb^{+5}$  and  $V^{+5}$  ions on the crystal structure and properties of LAMOXY 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  $La_{2-x}Bi_xMo_2O_{9-y}$  ( $0 \leq x < 0.05$ ),  $La_2Mo_{2-x}Sb_xO_{9-y}$  ( $0 \leq x \leq 0.05$ ) and  $La_2Mo_{2-x}V_xO_{9-y}$  ( $0 \leq x < 0.06$ ) solid solutions samples showed that the impurities implantation results in the decrease of the  $\alpha \rightarrow \beta$  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  $\beta_{ms}$ -phase at the room temperature. Therefore the appreciable increase of conductivity of the doped  $La_2Mo_2O_9$  samples has been observed in the low-temperature area (below 500°C) in comparison with the pure  $La_2Mo_2O_9$ . The X-ray structural studies of the  $\beta_{ms}$ -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  $La_2Mo_2O_9$  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:** LAMOXY, crystal structure, oxide-ion conductivity

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*Acta Cryst.* (2011) A67, C713-C714**Synthesis, structure and properties of the  $Nd_5Mo_3O_{16}$  fluorite-like compound**

Natalya Sorokina,<sup>a</sup> Olga Alekseeva,<sup>a</sup> Nadezhda Bolotina,<sup>a</sup> Elena Kharitonova,<sup>b</sup> Valentina Voronkova,<sup>b</sup> <sup>a</sup>*Shubnikov Institute of Crystallography, Russian Academy of Science, Moscow (Russia).* <sup>b</sup>*Moscow State University, Moscow (Russia).* E-mail: nsor@ns.crys.ras.ru

High oxygen conductivity of the  $La_2Mo_2O_9$  compound (0.06 S/cm