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Acta Cryst. (2011) A67, C713**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 $A_2B_2(SO_4)_3$ (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**

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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 α -phase ($P2_1$) and high-temperature β -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 α -phase or as the metastable cubic β_{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 β_{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 β_{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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Acta Cryst. (2011) A67, C713-C714**Synthesis, structure and properties of the $Nd_5Mo_3O_{16}$ fluorite-like compound**

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

at 800°C) was established by the Lacorre et al [1]. There is no such a compound in the Nd_2O_3 - MoO_3 system, but there is one with the fluorite-like structure near the Nd_2MoO_6 [2], [3], [4]. Chemical composition and crystal structure of the $\text{Nd}_5\text{Mo}_3\text{O}_{16}$ compound were studied before on polycrystals [4] as well as similar structure of $\text{Pr}_5\text{Mo}_3\text{O}_{16}$ [5]. It was found that the $\text{Pr}_5\text{Mo}_3\text{O}_{16}$ crystals have a fluorite-like superstructure in 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. Overrated thermal parameters are given in [5] for the Pr2 ($B_{\text{eq}}=1.32(16) \text{ \AA}^2$) and Mo ($B_{\text{eq}}=0.98(7) \text{ \AA}^2$) atoms, while $B_{\text{eq}}=0.71(4) \text{ \AA}^2$ for the O2 atom.

Single-crystal structure refinement of $\text{Nd}_5\text{Mo}_3\text{O}_{16}$ and study of the physical properties have been performed. Dark-violet cubical $\text{Nd}_5\text{Mo}_3\text{O}_{16}$ single crystals were grown by spontaneous flux crystallization. The conductivity of the compound is hypothetically anionic and reaches approximately 10^{-2} S/cm at 800°C.

The structure of $\text{Nd}_5\text{Mo}_3\text{O}_{16}$ single crystal was studied by the X-ray techniques (XCalibur S CCD-diffractometer, $T=293 \text{ K}$). The unit cell was found to be cubic with $a=11.028(1) \text{ \AA}$, which relates to that of fluorite CaF_2 as $a \approx 2a_f$. 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 $\text{Nd}_5\text{Mo}_3\text{O}_{16}$ 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 ($R=3.6\%$, $R_w=3.27\%$, $S=1.99$, $B_{\text{eq}}=0.24(1) \text{ \AA}^2$ for the Pr2 atom).

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Synthesis and structure of new vanadium(IV) complex based on isonicotinic hydrazide

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Although the biological significance of vanadium was recognized long ago, the coordination chemistry of this element continues to attract the attention of researchers, not least because of the discovery that vanadium is present at the active site of several enzymes, such as some peroxidases, as models for bromoperoxidase, nitrogenases and other biological systems.

The crystalline coordination compound $\text{VO}_2\text{L}\cdot 2\text{H}_2\text{O}$ has been obtained as the result of interaction of 2,4-pentanedione isonicotinic hydrazone (HL) with $\text{VOSO}_4\cdot 3\text{H}_2\text{O}$. This compound is soluble in

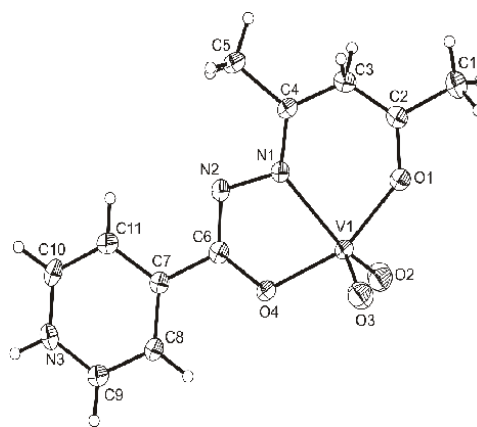
chloroform, dimethylformamide, less soluble in EtOH and MeOH.

The product $\text{VO}_2\text{L}\cdot 2\text{H}_2\text{O}$ is characterized using IR spectroscopy, elemental analysis and X-ray method.

The disappearance of the band at 1624 cm^{-1} ($\nu(\text{C}=\text{O})$) and the absence of oscillations bands of N-H, as well as the appearance of absorbance in the regions $2700\text{-}2500$ and $2250\text{-}2000 \text{ cm}^{-1}$ attributed to vibrations of $=\text{C}=\text{NH}^+$ in the spectrum of $\text{VO}_2\text{L}\cdot 2\text{H}_2\text{O}$ as compared to that of the uncoordinated ligand, indicates upon the coordination L in enolic form with proton migration (from NH) to the heterocyclic nitrogen. The presence of a narrow band of moderate intensity at 1636 cm^{-1} confirms the formation $=\text{C}=\text{N}-\text{N}=\text{C}$. The new band at 1520 cm^{-1} may be attributed to the oscillations of coordinated $\nu(\text{C}=\text{O})_{\text{acac}}$.

The crystallization water molecules are associated ($\nu(\text{OH})=3215 \text{ cm}^{-1}$), forming three hydrogen bonds. The oscillations $\nu(\text{V}=\text{O})$ are manifested at 908 cm^{-1} and is the most intensive band in the spectrum.

According to the x-ray single crystal study, the isolated compound $\text{VO}_2\text{L}\cdot 2\text{H}_2\text{O}$ has a molecular structure composed by neutral $[\text{VO}_2\text{L}]$ complexes and solvate water molecules in 1:2 ration. Vanadium atom adopts a NO_4 trigonal-bipyramidal environment, being coordinated by two oxygen atoms and one tridentate Schiff-base ligand L.



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X-Ray studies in a manganese lawsonate coordination polymer

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Lawsonate (2-hydroxy-1,4-naphtoquinone) 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 $[\text{Mn}(\text{C}_{10}\text{H}_5\text{O}_3)_2]_n$ 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 phenoxy 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