

08-Inorganic and Mineralogical Crystallography

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Ternary diagrams of $\text{Li}_2\text{O}-\text{Nb}_2\text{O}_5$ with different oxides (MgO , TiO_2 , ZrO_2 , Fe_2O_3 , MnO , etc) were studied because of the interest in the electrical and optical properties of the phases obtained in those systems. In the ternary system $\text{Li}_2\text{O}-\text{Nb}_2\text{O}_5-\text{MgO}$ were founded several solid solutions regions, joint lines and new phases. $\text{Li}_6\text{MgNb}_2\text{O}_9$ is a new compound synthesized on the line $\text{Li}_3\text{NbO}_4-\text{MgO}$. It has a disordered polymorph prepared as metastable phase similar as the reported in the system $\text{Li}_3\text{NbO}_4-\text{Li}_2\text{TiO}_3$ (Aragón-Piña et al. *J. Mat. Sc. Lett.* (1984), 3, 893).

The ordered phase was prepared by reaction of the oxide starting materials at 1000°C within 120 hours. Cation disordering occurs at 1050°C within 1 hour. The disordered phase has cubic symmetry (isostructural with periclase), the precise cell parameter is $4.208(3)$ Å and statistical population of the crystallographic positions 1/3. The ordered phase has triclinic symmetry (space group P1) and cell parameters $a=7.852(3)$, $b=8.913(4)$, $c=6.050(5)$ Å, $\alpha=100.75(2)^\circ$, $\beta=97.63(3)^\circ$ and $\gamma=105.89(3)^\circ$, with crystallographic population of the positions equal one. Measurements were made in the Siemens D5000 diffractometer with $\text{Cu K}\alpha_1$ radiation. The ordered phase was indexed by TREOR 90 (P.E. Werner, University of Stockholm, private comm.) and the precise lattice parameters were refined with LSUCRI (R.G. Garvey, North Dakota State University, 1990) and PARAMETROS (R. Pomés et al, *Rev. Cub. de Física* (1981), 1, 95).

PS-08.01.25 CRYSTAL STRUCTURES OF $(\text{CH}_3)_2\text{NH}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{CD}_3)_2\text{ND}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{D}_2\text{O}$, AND $(\text{CH}_3)_2\text{NH}_2\text{Ga}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

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Crystals of $(\text{CH}_3)_2\text{NH}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (DMAS) have been reported (Kirpichnikova, L.F., Shuvalov, L.A. and Ivanov, N.R., *Ferroelectrics*, 1989, 36, 313-317) to be ferroelectric ($T_c = 150\text{K}$) and ferroelastic. DMAS represents a family of isomorphous crystals investigated in our laboratories, with the following lattice parameters:

	a(Å)	b(Å)	c(Å)	β (deg)
$(\text{CH}_3)_2\text{NH}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (T=295K)	6.403(2)	10.747(3)	11.128(2)	100.47(2)
$(\text{CD}_3)_2\text{ND}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{D}_2\text{O}$ (T=295K)	6.399(1)	10.741(2)	11.131(2)	100.44(3)
$(\text{CD}_3)_2\text{ND}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{D}_2\text{O}$ (T=130K)	6.437(1)	10.684(2)	11.116(2)	99.82(3)
$(\text{CH}_3)_2\text{NH}_2\text{Ga}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (T=295K)	6.376(3)	10.731(6)	11.365(6)	100.86(5)

In the paraelectric phase (space group $\text{P}2_1/\text{n}$) the nitrogen atom of the methylammonium molecule occupies at random two positions related by the symmetry center. The vector connecting these positions is almost parallel to the polarization vector P_s in the low temperature ferroelectric phase (space group Pn). The paraelectric-

ferroelectric phase transition is therefore of the order-disorder type and goes on with the ordering of the methylammonium molecule. The polarization reversal is connected with the switching of the nitrogen atom in the methylammonium molecule.

PS-08.01.26 SYNTHESIS AND CRYSTAL STRUCTURE OF $\text{F-Er}_2\text{S}_3$

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$\text{F-Er}_2\text{S}_3$ crystals were obtained by vapor transport in the presence of foreign atoms (Nb and Cl). The structure of $\text{F-Er}_2\text{S}_3$ was determined by single crystal X-ray diffraction. $\text{F-Er}_2\text{S}_3$ is monoclinic, space group $\text{P}2_1/\text{m}$, $Z = 4$,

$a = 10.901(1)$ Å, $b = 3.896(1)$ Å, $c = 11.167(1)$ Å, $\beta = 108.804(5)^\circ$, $R_F = 0.046$ for 2838 observed reflections with $I > 2.5\sigma(I)$. All atoms are located at the mirror planes. There are four crystallographically independent erbium atoms in $\text{F-Er}_2\text{S}_3$, half of them in six coordination, one quarter in seven and one quarter in eight coordination by sulfur. Half of the six types of sulfur atoms are coordinated in four, the other half in five by erbium atoms. From the bond valence calculation of $\text{F-Er}_2\text{S}_3$ and the $\text{D-Er}_2\text{S}_3$ (the stable phase at ambient conditions), it was found that the Er-S distances and bonding valences of the six- and seven-coordinated erbium atoms in $\text{F-Er}_2\text{S}_3$ are close to those in $\text{D-Er}_2\text{S}_3$. The eight-coordinated Er atom in $\text{F-Er}_2\text{S}_3$ is much weaker bonded to sulfur than expected and has a rather low valence ($V = 2.5$).

Three different stoichiometric Er_2S_3 phases are found to occur: D-, U- and $\text{F-Er}_2\text{S}_3$. $\text{D-Er}_2\text{S}_3$ is isostructural with $\text{D-Ho}_2\text{S}_3$, half of the Er atoms in six, the other half in seven coordination by sulfur. The molar volume of $\text{D-Er}_2\text{S}_3$ amounts to $69.71 \text{ cm}^3/\text{mol}$ (to compare with $V_m = 67.90 \text{ cm}^3/\text{mol}$ for $\text{F-Er}_2\text{S}_3$). $\text{U-Er}_2\text{S}_3$ was obtained under high pressure conditions (10.9 Kbar, 900°C). The molar volume is $62.87 \text{ cm}^3/\text{mol}$. It might be concluded that $\text{D-Er}_2\text{S}_3$ is the normal temperature and pressure phase, $\text{U-Er}_2\text{S}_3$ the high-pressure form. $\text{F-Er}_2\text{S}_3$ is a medium-pressure modification.

PS-08.01.27 Potassium deficient phases of rhombohedral KSbO_3
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A series of single crystals of rhombohedral KSbO_3 have been investigated with X-ray diffraction. The structure is of the ilmenite type with approximate hexagonal close packing of oxygen atoms (Spiegelberg, *Arkiv Kemi Mineral. Geol.*, 1940, No. 5), with space group $R\bar{3}$ and cell dimensions $a = 5.3762(2)$, $c = 18.2505(8)$ Å in the hexagonal description. Each of the cations occupies two thirds of the octahedral interstices in every second layer along c . However, some of the $R\bar{3}$ samples showed disorder in the oxygen arrangement, which could be interpreted as disorder in the stacking sequence of oxygen layers along c . In this way the coordination around potassium is modified from distorted octahedral to distorted trigonal prismatic in some of the layers.

Several crystals with an ordered ABBAABB... sequence were also studied. They have space group $R\bar{3}c$ with c twice that of the $R\bar{3}$ phase. The cell dimensions of this phase vary, but for all the crystals studied a is shorter and c longer than the corresponding $R\bar{3}$ values, eg. $a = 5.3254(4)$, $c = 37.338(3)$ Å. There is an approximately linear relationship between the c and a dimensions, as well as between the refined occupancy of one of the potassium sites and a or c . The lowest K:Sb ratio observed in four different crystals was 0.88.

One of the $R\bar{3}$ crystals used for structure determination showed additionally a small number of diffuse spots in the Weissenberg photographs, that could be indexed on a trigonal cell with $a = 5.37$ Å but with a c that is incommensurable with the c of the $R\bar{3}$ phase.