Ternary diagrams of Li₂O-Nb₂O₅ with different oxides (MgO, TiO₂, SrO, FeO, MnO, etc) were studied by means of the interest in the electrical and optical properties of the phases retained in the three systems. In the ternary system Li₂O-Nb₂O₅-MgO, there were several well-defined regions, joint lines, and new phases. Li₇MgNbO₁₂ is a new compound synthesized on the line Li₇MgO₄-Nb₂O₅. It has a disordered polyhedral phase similar to that reported in the system Li₇MgO₄-L₂TiO₄ by Anowled-Piña et al. J. Mat. Soc. Lett. (1984), 3, 693).

The ordered phase was prepared by reaction of the oxide starting materials at 1000°C within 12 hours. Cation disordering occurs at 750°C within 1 hour. The disordered phase has cubic symmetry (isostructural with periclase), the precise cell parameter is 4.288(3) Å and the statistical population of the crystallographic positions I/3. The ordered phase has trigonal symmetry (space group P31) and cell parameters a=7.542(3), b=8.913(4), c=6.050(5) Å, β=100.75(2), γ=105.89(4)°, with crystallographic parameters of the ordered phase equal to those of the disordered phase. Measurements were made in the Siemens D5000 diffractometer with Cu Kα radiation. The ordered phase was indexed by the 124 target (F.E. Amer, University of Stockholm, private communication) and the precise lattice parameters refined with LSCUCI R.G. Garve, North Dakota State University, 1990) and XRD methods (R. Poonen et al., Rev. Cub. de Fysica (1981), 1, 95).

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

PS-08.01.25 CRYSTAL STRUCTURES OF (Cu₃Al₁₂)(SO₄)₄·6H₂O (Cu₃Al₁₂)(SO₄)₄·6H₂O, and (Cu₃Al₁₂)(SO₄)₄·6H₂O

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Crystals of (Cu₃Al₁₂)(SO₄)₄·6H₂O (IMAS) have been reported (Kirpichnikova, L.F., Shuvalov, L.A. and Ivanov N.R., Ferroelectrics, 1989, 14, 339-347) to be ferroelectric (Tc = 15.0 K) and ferroelastic. IMAS represents a family of luminescent crystals investigated in our laboratories, with the following lattice parameters:

a(Å) b(Å) c(Å) β(deg)
(Cu₃Al₁₂)(SO₄)₄·6H₂O (T=295K) 6.40(2) 10.74(2) 11.12(2) 100.47(2)
(Cu₃Al₁₂)(SO₄)₄·6H₂O (T=295K) 6.39(1) 10.74(1) 11.13(2) 100.44(2)
(Cu₃Al₁₂)(SO₄)₄·6H₂O (T=295K) 6.47(1) 10.69(2) 11.16(2) 99.82(3)
(Cu₃Al₁₂)(SO₄)₄·6H₂O (T=295K) 4.36(3) 10.73(6) 11.65(6) 100.86(5)

In the paraelectric phase (space group Pnma), 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. In the low temperature ferroelectric phase (space group Pn), the paraelectric-

PS-08.01.27 Potassium deficient phases of rhombohedral K₃BO₃

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A series of single crystals of rhombohedral K₃BO₃ 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., 1943, No. 5), with space group R₃̅ and cell dimensions a = 5.3762(2), c = 18.2545(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 R₃̅ 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 ARBAAB... sequence were also studied. They have space group R3c with c twice that of the R₃̅ phase. The cell dimensions of this phase vary, but for all the crystals studied a is shorter and c longer than the corresponding R₃̅ values, e.g. a = 5.3254(4), c = 37.333(9) 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 c or a. The lowest K/3b ratio observed in four different crystals was 0.88.

One of the R₃̅ 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 incommensurate with the a of the R₃̅ phase.