

PS-08.01.21 CRYSTAL STRUCTURE OF $\text{Li}_{1-x}\text{H}_x\text{IO}_3$ BY X-RAY AND NEUTRON DIFFRACTION. J. Le Roy*, C. Rosso¹, J. Bouillot¹, J.M. Crettez², J.X. Boucherle³ and M. Bonnet³.

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The lithium iodate crystal $\alpha\text{-LiIO}_3$ (space-group $P6_3$) is widely used in applied physics owing to its nonlinear optical properties and strong piezoelectric behaviour. The lithium iodate ionic acid solution $\text{Li}_{1-x}\text{H}_x\text{IO}_3$ (same space group) have also been recognized to be prospective materials for technical applications. Moreover, this solid solution is a good tool to understand the proton behaviour in $\alpha\text{-LiIO}_3$ ionic conductivity.

In this aim, several experiments using either X-Ray single crystal or neutron powder and single crystal diffraction have been performed to localize precisely the protons in this solid solution. As $\text{Li}_{1-x}\text{H}_x\text{IO}_3$ forms a single phase only with x in the range 0.22 to 0.36, we have chosen x close to 0.33 for this study. Structure refinements have been performed at various temperatures from 10K to room temperature and preliminary results have already been published (J. Le Roy, J.M. Crettez, E. Coquet and J. Bouillot, Solid State Com., 1990, Vol.75, 7, 539-543). All these experiments confirm the well-known LiIO_3 structure, and show that the hydrogen atom not locates in lithium site but takes place on particular sites which are well-refined.

The most recent experiment using single crystal neutron diffraction have even allowed to define the anisotropic Debye temperature factors associated with this site, with a final overall R factor of 0.018. The existence of these proton sites induces some significant changes on the thermal parameters of the other atoms.

All these features, including the thermal dependence of the structural parameters, are presented and discussed in this paper.

PS-08.01.22 HIGH-PRESSURE ORTHORHOMBIC-TETRAGONAL TRANSITION IN GILLESPIE: ORDER PARAMETER BEHAVIOUR FROM SYNCHROTRON POWDER DIFFRACTION

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Gillespite ($\text{BaFeSi}_4\text{O}_{10}$) undergoes a structural phase transition from the room-pressure $P4/ncc$ structure to an orthorhombic ($P2_12_12$) structure on increasing pressure. This transition has been studied at Daresbury synchrotron radiation source using energy-dispersive diffraction of powders pressurized in the diamond anvil cell to approximately 10 Gpa. The anomalous compressibility arising above the transition has been interpreted

in terms of ferroelastic and coelastic spontaneous strain. Powder diffraction is particularly suited to this type of study since the measurement of cell distortions in the high-pressure (low-symmetry) phase is uncomplicated by problems caused by ferroelastic twinning.

The results show that the potentially ferroelastic phase transition in gillespite is described by two order parameters: one corresponding to the ferroelastic process (Q_1) and one to a coupled volume-changing process (Q_2) in the orthorhombic phase. The role of linear-quadratic coupling between these order parameters is considered within the framework of Landau theory and accounts for the strongly first-order character of the reversible transition. Order-parameter coupling also provides an explanation for widely diverging reported values of P_r . The Ba site undergoes extensive reorganization while the ferrosilicate framework topology remains constant through the rapid reversible transition. In this sense the high-pressure transition is similar to others recently described in chain silicates, and seems to be best described as displacive.

PS-08.01.23 CRYSTALLOGRAPHY OF TERNARY OXIDES IN THE SYSTEM Ba-Ti-Zn-O. By W. Wong-Ng*, R.S. Roth and C.J. Rawn, Ceramics Division, NIST, Gaithersburg, MD 20899, U.S.A.

In recent years, the ternary system BaO-ZnO-TiO_2 is of great interest in the production of microwave dielectric ceramics. The addition of ZnO to the barium polytitanates has been found to improve their dielectric property. Knowledge of crystallography of phases in the Ba-Zn-Ti-O system is important to understand the physical properties of these materials.

This system has been found to contain four ternary phases, ideally $\text{BaZn}_2\text{Ti}_4\text{O}_{11}$, $\text{Ba}_4\text{ZnTi}_{11}\text{O}_{27}$, $\text{Ba}_2\text{ZnTi}_5\text{O}_{13}$ and $\text{Ba}_x\text{Zn}_x\text{Ti}_{8-x}\text{O}_{16}$ (hollandite). The crystal structures of the first three have been determined recently in this laboratory. $\text{Ba}_4\text{ZnTi}_{11}\text{O}_{27}$ is isostructural with $\text{Ba}_4\text{Ti}_{10}\text{Al}_2\text{O}_{27}$, which is monoclinic with space group $C2/m$. The Ti and Zn ions occupy distorted octahedra and Ba^{2+} has a coordination of 11 or 12. The compound $\text{Ba}_2\text{ZnTi}_5\text{O}_{13}$ was found to be isostructural with $\text{K}_2\text{Ti}_6\text{O}_{13}$ (monoclinic $C2/m$) which crystallizes in the form of thin sheets. The overall structures can be described as consisting of zig-zag ribbons of $(\text{Ti,Zn})\text{O}_6$ octahedra running along c . Rectangular open channels can be seen running through the structure parallel to b . In $\text{BaZn}_2\text{Ti}_4\text{O}_{11}$, some Ti sites were found to be occupied by Zn, resulting to a formula of $\text{BaZn}_{2.03}\text{Ti}_{3.93}\text{O}_{10.89}$. The overall structure (orthorhombic $Pnab$) consists of a three dimensional network of distorted edge-sharing and corner-sharing octahedra with Zn filling some tetrahedral interstices.

PS-08.01.24

ORDER-DISORDER TRANSFORMATION OF $\text{Li}_6\text{MgNb}_2\text{O}_9$.

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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 F- Er_2S_3

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F- Er_2S_3 crystals were obtained by vapor transport in the presence of foreign atoms (Nb and Cl). The structure of F- Er_2S_3 was determined by single crystal X-ray diffraction. F- Er_2S_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 F- Er_2S_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 F- Er_2S_3 and the D- Er_2S_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 F- Er_2S_3 are close to those in D- Er_2S_3 . The eight-coordinated Er atom in F- Er_2S_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 F- Er_2S_3 . D- Er_2S_3 is isostructural with D- Ho_2S_3 , half of the Er atoms in six, the other half in seven coordination by sulfur. The molar volume of D- Er_2S_3 amounts to $69.71 \text{ cm}^3/\text{mol}$ (to compare with $V_m = 67.90 \text{ cm}^3/\text{mol}$ for F- Er_2S_3). U- Er_2S_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 D- Er_2S_3 is the normal temperature and pressure phase, U- Er_2S_3 the high-pressure form. F- Er_2S_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.