08-Inorganic and Mineralogical Crystallography

PS-08.01.23 CRYSTAL STRUCTURE OF LiI$_2$-xH$_2$O$_3$ BY X-RAY AND NEUTRON DIFFRACTION. J. Le Roy*, C. Rosso*, J. Bouillot*, J. M. Cretete*, J.X. Bouschat* and M. Bonnet*.

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The lithium iodate crystal α-Li I O$_3$ (space-group P6$_3$) is widely used in applied physics owing to its nonlinear optical properties and strong piezolectric behaviour. The lithium iodate hydrogenic solution Li$_{1-x}$H$_2$O$_3$ (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 α-Li I O$_3$.

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 Li$_{1-x}$H$_2$O$_3$ 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. Cretete, E. Cazet and J. Boillot, Solid State Com., 1990, Vol.75, 7, 539-543). All these experiments confirm the well-known Li I O$_3$ structure, and show that the hydrogene atom not located 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 (Ba$_2$Fe$_2$SiO$_6$) undergoes a structural phase transition from the room-temperature 4H/mc structure to an orthorhombic (P2$_1$2$_1$2$_1$) structure on ice pressure. This transition has been studied at Daresbury synchrotron radiation source using energy-dispersive diffraction of powder pressed 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 and corresponding to the ferroelastic process (O$_2$) and one to a coupled volume-changing process (O$_3$) 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 the diverging reported values of P$_r$. The Ba$_2$ 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 disclastic.

PS-08.01.24 ORDER-DISORDER TRANSFORMATION OF Li$_2$GeO$_4$DO$_9$

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Ternary diagrams of Li$_2$O-B$_2$O$_3$ with different oxides (MgO, TiO$_2$, SrO$_2$, Fe$_2$O$_3$, MnO, etc.) were studied because of the interest in the electrical and optical properties of the phases obtained in these systems. In the ternary system Li$_2$O-B$_2$O$_3$-MgO we found several solid solutions regions, joint lines and new phases. Li$_2$MgB$_2$O$_6$ is a new compound synthesized on the line Li$_2$B$_2$O$_7$-MgC. It has a disordered polymorph prepared as metastable phase similar to the reported in the system Li$_2$MgB$_2$O$_6$-Ti$_2$O$_3$-A$_2$O$_3$-P$_2$O$_5$-Si$_2$O$_5$-Al as a (J. Mat. Sc. Lett. 1984, 3, 693).

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 cation parameter is 4.208(3) Å and statistical occupation of the crystallographic positions 1/3. The ordered phase has trigonal symmetry (space group P3$ar{1}$) and cell parameters a = 0.752(3), b = 0.913(4), c = 0.650 (5) Å, α = 100.75(2), β = 97.63(2) and γ = 105.89(3)°, with crystallographic phase population of the equal one. Measurements were made in the Siemens D500 diffractometer with Cu K$_\alpha$ radiation. The ordered phase was indexed by SHARP 90 (P.F. Buerger, University of Stockholm, private communication) and the precise lattice parameters were refined with LERCC (J.G. Garvey, North Dakota State University, 1990) and PARAMETROS (R. Pordes et al., Rev. Cub. de Fisica 1981, 1, 95).

**PS-08.01.25 CRYSTAL STRUCTURES OF (CH$_3$)$_2$NH$_2$SO$_3$(SO$_4$)$_2$, 6H2O (CH$_3$)$_2$NH$_2$AsO$_3$(SO$_4$)$_2$, 6H2O (CH$_3$)$_2$NH$_2$GaO$_3$(SO$_4$)$_2$, 6H2O A. Petraszkow and K. Lukaszewicz, Institute of Crystallography, Academy of Sciences, Wroclaw P.O. Box 937, Poland, and L.F. Kripjankina, Institute of Crystallography, Academy of Sciences of Sciences, Moscow, 117533, Russia. Crystals of (CH$_3$)$_2$NH$_2$AsO$_3$(SO$_4$)$_2$, 6H2O (NAMAS) have been reported (Kirkphajjukova, L.F., Shveleva, L.A. and Ivanov N.N., Ferroelectrics, 1989, 86, 319-317) to be ferroelectric (Tc = 150K) and ferroelastic. NAMAS represents a family of two-dimensional crystals, investigated in our laboratories, with the following lattice parameters: a(Å) b(Å) c(Å) β(deg) (CH$_3$)$_2$NH$_2$Al(EO)$_6$THF (T=295K) 6.40(2) 10.74(2) 12.18(2) 100.47(2) (CH$_3$)$_2$NH$_2$Al(EO)$_6$THF (T=295K) 6.40(1) 10.74(1) 12.18(1) 100.47(1) (CH$_3$)$_2$NH$_2$Al(EO)$_6$THF (T=295K) 6.40(1) 10.74(1) 12.18(1) 100.47(1) (CH$_3$)$_2$NH$_2$Al(EO)$_6$THF (T=295K) 6.40(1) 10.74(1) 12.18(1) 100.47(1) (CH$_3$)$_2$NH$_2$Al(EO)$_6$THF (T=295K) 6.40(1) 10.74(1) 12.18(1) 100.47(1) In the paraelectric phase (space group Pm3m) 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 Pm3a) the paraelectric-

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**PS-08.01.25 SYNTHESIS AND CRYSTAL STRUCTURE OF F-Fe$_3$S$_3$**

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F-Fe$_3$S$_3$ crystals were obtained by vapor transport in the presence of foreign ions (Ni and Cl). The structure of F-Fe$_3$S$_3$ was determined by single crystal X-ray diffraction. F-Fe$_3$S$_3$ is monoclinic, space group P2$_1$/c, Z = 4, a = 10.90(1) Å, b = 18.65(2) Å, c = 11.761(1) Å, β = 108.860(8)°. Rp = 0.046 for 2838 observed reflections with I > 2σ(I). All atoms are located at the mirror planes. There are four crystallographically independent sulfur atoms in F-Fe$_3$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 sulfur atoms. From the bond valence calculation of F-Fe$_3$S$_3$ and the D-Fe$_3$S$_3$ (the stable phase at ambient conditions), which was found that the B-O distances and bonding valences of the six- and seven- coordinated sulfur atoms in F-Fe$_3$S$_3$ are close to those in D-Fe$_3$S$_3$. The eight-coordinated sulfur in F-Fe$_3$S$_3$ is much weaker bonded to sulfur than expected and has a rather low valence (V = 2.5).

Three different stoichiometric Fe$_3$S$_3$ phases are found to occur: Fe$_3$S$_3$, L-Fe$_3$S$_3$, and D-Fe$_3$S$_3$. D-Fe$_3$S$_3$ is isostructural with D-Fe$_3$S$_3$, half of the Fe atoms in six, the other half in seven coordination by sulfur. The molar volume of D-Fe$_3$S$_3$ amounts to 69.7 cm$^3$/mol (to compare with V$_{Fe_3S_3}$ = 67.9 cm$^3$/mol for Fe$_3$S$_3$). U-Fe$_3$S$_3$ was obtained under high pressure conditions (0.9 GPa, 900 °C). The molar volume is 68.7 cm$^3$/mol. It might be concluded that D-Fe$_3$S$_3$ is the normal tetragonal, and pressure phase, U-Fe$_3$S$_3$ the high-pressure form. F-Fe$_3$S$_3$ is a medium-pressure modification.

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**PS-08.01.27 Potassium deficient phases of rhombohedral K$_8$O$_3$**

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A series of single crystals of rhombohedral K$_8$Na$_3$ have been investigated with X-ray diffraction. The structure is of the imenite type with approximulate hexagonal close packing of oxygen atoms (Spiegellberg, Arkiv Kemi Mineral. Geol., 1943, No. 5), with space group R$\overline{3}$ and cell dimensions a = 5.3762(2), c = 18.250(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$\overline{3}$ 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 octahedra to distorted trigonal prismatic in some of the layers. Several crystals with an ordered ARBAAABB... sequence were also studied. They have space group R$\overline{3}$c with c twice that of the R$\overline{3}$ phase. The cell dimensions of this phase may vary, but for all the crystals studied a is shorter and c longer than the corresponding R$\overline{3}$ values, e.g. a = 5.3254(4), c = 37.335(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:Na ratio observed in four different crystals was 0.88. One of the R$\overline{3}$ 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 incommensurate with the c of the R$\overline{3}$ phase.