08-Inorganic and Mineralogical Crystallography

PS-08.01.21 CRYSTAL STRUCTURE OF Li$_2$H$_4$IO$_5$ BY X-RAY AND NEUTRON DIFFRACTION.
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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 piezoelectric behaviour. The lithium iodate ionic solid solution Li$_{1-x}$H$_x$I 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$_3$ 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 Li$_{1-x}$H$_x$I O$_3$ forms a single phase only with x in the range 0.22 to 0.16, 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. Crétez, E. Casquet and J. Bouillot. Solid State Com., 1990, Vol.79, 7, 539-543). All these experiments confirm the well known Li I O$_3$ structure, and show that the hydrogen 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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Gillespie (BaFe$_2$Si$_2$O$_8$) undergoes a structural phase transition from the room-temperature orthorhombic (Pbca) to an orthorhombic (Pnma) structure. This transition has been studied at Daresbury synchrotron radiation source using energy-dispersive diffraction of powder pressed at 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 gillespie is described by two order parameters, one corresponding to the ferroelastic O$_3$ process and one to a coupled volume-changing process (O$_2$) 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 Pr. The Ba site undergoes extensive reconversion while the ferroelastic framework topology remains constant through the rapid reversible transition. In this sense the high-pressure transition is similar to others recently described in chains silicates, and seems to be best described as displacive.

PS-08.01.24 ORDER-ORDER TRANSFORMATION OF Li$_x$Mg$_{2}$O$_9$.
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