

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.

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

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