

MS16-04 A pair distribution function study of lead-free piezoelectrics. Dean S Keeble,^a Emma R. Barney^b, David A. Keen^c, Matt G. Tucker^c, Jens Kreisel^{a,d} and Pam A. Thomas^a, ^aUniversity of Warwick, UK, ^bISIS Facility, Harwell Oxford, UK, ^cUniversity of Nottingham, UK, ^dLaboratoire des Matériaux et du Génie Physique, Grenoble INP, France. E-mail: d.s.keeble@warwick.ac.uk

ABO_3 perovskite-type solid solutions display a large variety of structural and physical properties, which can be tuned by chemical composition, or external parameters such as temperature, pressure, strain, electric or magnetic fields. Some solid solutions show remarkably enhanced physical properties like colossal magnetoresistance or giant piezoelectricity. It has been recognized that structural distortions, competing on the local level, are key to understanding and tuning these remarkable properties, yet, it remains a challenge to observe experimentally such local structural details. Here, from neutron pair-distribution analysis, we report a temperature-dependent 3D atomic-level model of the lead-free piezoelectric perovskite $Na_{0.5}Bi_{0.5}TiO_3$ (NBT). Our statistical analysis of this model shows how local distortions compete, how this competition develops with temperature and, in particular, how different polar displacements of Bi-cations coexist, highlighting the interest of Bi-based materials in the search for new lead-free piezoelectrics.

Keywords: pair distribution function; piezo- and ferroelectric materials; physics of disordered systems

MS16-05 $M_mH_n(XO_4)_{(m+n)/2}$ crystals: structure, phase transitions, hydrogen bonds, conductivity.

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Hydrogen bonds are of great interest due to their importance in functional properties of crystalline materials, ranging from inorganic to biological chemistry. The interest in compounds of $M_mH_n(XO_4)_{(m+n)/2}$ ($M = K, Rb, Cs, NH_4; X = S, Se, P$) is related to the solution of fundamental problems of physics of condensed state: structural phase transitions, establishing the structural conditionality of anomalies of physical properties and the influence of hydrogen subsystems. In most hydrogen-containing crystals, hydrogen atoms form a regular net of hydrogen bonds. Superprotonic crystals form a peculiar class in which changes occur in the system of hydrogen bonds at phase transitions, which lead to radical changes in their properties, in particular, to the high conductivity of $\approx 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at relatively low temperatures. These crystals are unique in a class of proton conductors, since superprotonic conductivity is related to the structural features of these compounds, instead of consequence of impurity doping process.

X-ray structural data evidence the distinction of structural mechanisms of conductivity in $M_mH_n(XO_4)_{(m+n)/2} \cdot xH_2O$ compounds. In $M_3H(XO_4)_2$ crystals high proton conductivity is caused by the formation of dynamically disordered network of hydrogen bonds in which both positions of the centers of hydrogen bonds and their orientations are disordered, that enables protons to move over vacant crystallographically equivalent positions [1], [2], and also at further heating by the formation of a multiphase state. In $K_9H_7(SO_4)_8 \cdot H_2O$ crystals, the only known representative of the $M_9H_7(XO_4)_8 \cdot xH_2O$ family, a superprotonic phase transition at $T \approx 400$ K is related to the diffusion of crystallization water and motion of K ions [3], as well as to the transformation of the system of hydrogen bonds. The stabilization of the high-temperature superprotonic phase and its supercooling to low temperatures are due to the presence of channels for the motion of K ions and slow backward diffusion of water in the crystal. The distinction in the properties of $Cs_{S(m+n)}(HSO_4)_m(H_2PO_4)_n$ crystals is related to different net of hydrogen bonds formed between the different-occupied XO_4 tetrahedra.

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Keywords: crystal structure; superionic phase transitions; hydrogen bonds