

**FA2-MS05-O1**

**Symmetry Studies of Ferroic Structures with the Bilbao Crystallographic Server.** Moisés I. Aroyo<sup>a</sup>, J. Manuel Perez-Mato<sup>a</sup>, Daniel Orobengoa<sup>a</sup>. <sup>a</sup>*Department of Solid State Physics, University of the Basque Country, Bilbao, Spain.*

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The Bilbao Crystallographic Server [1] is a free web site with crystallographic databases and programs available at <http://www.cryst.ehu.es>. The server is built on a core of databases that contains data of the *International Tables for Crystallography*, Vol. A (*Space-group Symmetry*), Vol. A1 (*Symmetry Relations between Space Groups*) and Vol. E (*Subperiodic Groups*). More specialized crystallographic software is also available and distributed in shells according to different topics: group-subgroup relations of space groups, solid-state physics and crystal chemistry applications or representation theory.

The aim of the contribution is to report on the databases and tools available on the server facilitating the symmetry-mode analysis of distorted structures of displacive type, the ferroic structures being a particular case. Starting from the experimental structures of the high- and low symmetry phases, it is possible to determine the global structural distortion that relates the two phases. The symmetry-modes compatible with the studied symmetry break are calculated, their orthonormalization permits the decomposition of the global distortion into symmetry-mode contributions, and the determination of the corresponding polarization vectors. This type of analysis allows the determination of the correlated atomic displacements that correspond to the structural instabilities at the origin of the ferroic distortion, *i.e.* the so-called *primary modes*, and to distinguish them from *secondary ones*, weaker distortions of limited relevance for the transition mechanism.

The server also offers online tools for the evaluation of the pseudosymmetry of a given structure with respect to a supergroup of its space group [2]. The detection of structural pseudosymmetry as the consequence of a small distortion of a higher symmetry, described by a supergroup of the crystal space group, is a powerful method for the prediction of new ferroelectric and ferroelastic materials. For example, polar structures with pseudosymmetry related to a hypothetical non-polar configuration can be considered as good candidates for ferroelectrics.

There are also computer tools for systematic studies of the possible transition paths of phase transitions with no group-subgroup relation between their phases [3]. The method is based on the assumption that the transformation involves, at least locally, an intermediate “hypothetical” configuration corresponding to a common space subgroup of the two end phases. The structure-dependent characterization of the proposed mechanisms and an evaluation of their plausibility is achieved by the analysis of lattice strains and atomic displacements involved in the transition. The procedure proves to be very useful for the study of structural relationships between different phases of ferroic materials with no group-subgroup relation between the symmetries.

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**FA2-MS05-O2**

**Compositional Heterogeneities in Relaxor Ferroelectric Oxides.** Karim Z. Baba-Kishi. *Department of Applied Physics, The Hong Kong Polytechnic University, Kowloon, Hong Kong.*

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Pb-based complex perovskite-structured relaxor oxides are a special class of ferroelectric compounds that exhibit outstanding pyroelectric properties, characterized by broad dielectric permittivity peak and diffuse phase transition. The structure of these compounds conform to the nominal chemical formula  $A(B'_{1/2}B''_{1/2})O_3$ , where the Pb atom is positioned on the A-site and the iso-valent or off-valent cations, occupy the crystallographically equivalent B' and B'' positions. Examples include  $Pb(Sc_{1/2}Ta_{1/2})O_3$  and  $Pb(Sc_{1/2}Nb_{1/2})O_3$ . There are also the compounds with B'<sup>1/3</sup> and B''<sup>2/3</sup> that include  $Pb(Mg_{1/3}Nb_{2/3})O_3$  and  $Pb(Zn_{1/3}Nb_{2/3})O_3$ . The relaxor ferroelectric state is confined to the disordered compounds in this group. As the degree of 1:1 long-range order (LRO) on the {111} planes increases, the relaxor state dissipates. Using various advanced microscopy techniques, e.g. HAADF, EELS and XEDS, including results recorded in a Cs-corrected STEM, it will be illustrated that the disorder in relaxors involve various forms of structural characteristics that include: 1:1 long-range order; mixed occupancy on the B-site positions [1]; development of superstructures related to higher chemical order (disparate from the 1:1 LRO); Pb displacement on the {110} planes that result in diffuse streaking along the <110> directions, and random occupational clustering of the Pb atoms on the A-site positions. It will be shown that a combination of these various forms of disorder may assist in establishing a unified approach to compositional heterogeneities in relaxors.

[1] K.Z. Baba-Kishi, C.W. Tai and X. Meng, *Philosophical Magazine*, 86, No.32, **2006**, 5031-5051.

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**FA2-MS05-O3**

**Beyond the Landau Theory: Unusual Phase Transitions in Some  $R_aSb_bX_{(3b+a)}$  Salts (where R: Organic Cation; M:Sb, Br; X: Br, Cl).** Anna Gagor<sup>a</sup>, Ryszard Jakubas<sup>b</sup>, Anna Piecha<sup>b</sup>, Adam Pietraszko<sup>a</sup>, Maciej Wojtaś<sup>b</sup>. <sup>a</sup>*Institute of Low Temperature and Structure Research Polish Academy of Sciences, Okólna 2, 50-950 Wrocław, Poland.* <sup>b</sup>*Faculty of*

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Halogenoantimonates(III) and halogenobismutates(III) of the general formula  $R_aM_bX_{(3b+a)}$  constitute a promising group of materials with a nonlinear dielectric properties [1]. Spontaneous polarization in certain salts (e.g.  $(CH_3NH_3)_5Bi_2X_{11}$ ) is comparable to those found in a well-known tri-glycine sulfate (TGS) family. Numerous structural studies have shown that these metal halide salts adopt a wide diversity of the anionic substructures which are very often responsible for the polar properties. The exceptionally large number of various polymorphic forms found in  $R_aM_bX_{(3b+a)}$  family is related to the low energy barrier between different anionic substructures, starting with isolated octahedra and square pyramids through more complex separated clusters, polyanionic chains and layers. Consequently, there are complex sequences of phase transitions which not infrequently comprise of four or five phases. Most of the transformations are displacive and order-disorder type of the first and second order that perfectly meet the concepts of Landau theory of PTs. There exist, however, non-standard transformations of discontinuous type beyond this theory which are the subject of the presentation. Since ferroelectric properties are limited to the  $R_3M_2X_{11}$ ,  $RMX_4$  and  $R_3M_2X_9$  chemical stoichiometries we focused on three representatives.

$[4-NH_2C_5H_4NH]SbCl_4$  salt is a unique structurally incommensurate ferroelectric crystal that adopts five different low temperature phases. Crystal structure is made of polyanionic chains of  $(SbCl_4)^-$  and 4-aminopyridinium cations interacting via hydrogen with chlorine atoms. The structure transforms from paraelectric C2/c state to incommensurate (IC) C2/c(0b0)<sub>s0</sub> at 304/304 K (cooling/heating), next at 270.5/271 K to ferroelectric commensurate Cc(0b0), then to ferroelectric IC phase Cc(0b0) at 240/245 K and finally to non-polar low temperature phase with  $P2_1/c$  symmetry.

The second example is  $[(CH_3)_3PH]_3Sb_2Cl_9$  salt which also exists in five different phases and experiences an unusual increase in symmetry from the monoclinic to the orthorhombic form at low temperatures. The structure that is made of discrete  $(Sb_2Cl_9)^-$  units interacting via hydrogen with  $[(CH_3)_3PH]^+$  cations transforms at 382 K from hexagonal  $P6_3/mmc$  parent phase to orthorhombic Pnam, next, at 295 K to monoclinic  $P2_1/a$ ; at 216 K to modulated commensurately  $P2_1/a$ , and finally the symmetry increases to orthorhombic, polar Pna2<sub>1</sub> phase.

The last presented crystal experiences an isomorphous phase transition at low temperature and reconstructive, irreversible transformation just above the room temperature (at 317 K) changing in fact both: the structure and stoichiometry from  $(C_3N_2H_3)_3SbBr_6 \cdot H_2O$  to  $(C_3N_2H_3)_5Sb_2Br_{11}$  as well as physical properties, as far as  $(C_3N_2H_3)_5Sb_2Br_{11}$  is known as a weak ferroelectric at low temperatures [2].

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## FA2-MS05-O4

**In Situ Transmission Electron Microscopy Experiments on Ferroelectric Materials under Electrical Field.** Jens Kling<sup>a</sup>, Ljubomira Schmitt<sup>a</sup>, Hans-Joachim Kleebe<sup>a</sup>, Manuel Hinterstein<sup>a</sup>, Hartmut Fuess<sup>a</sup>. <sup>a</sup>*Faculty of Materials Science and Applied Geosciences, Technische Universität Darmstadt, Germany.*

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Ferroelectric ceramics like leadzirconate-titanate (PZT) are widely used in several industrial applications. The outstanding properties are related to their morphotropic phase boundary (MPB). Such a region of phase coexistence can be found in different systems as well. New lead-free materials, like  $(1-x-y)Bi_{0.5}Na_{0.5}TiO_3-xBaTiO_3-yK_{0.5}Na_{0.5}NbO_3$  ( $0.05 \leq x \leq 0.07$  and  $0.01 \leq y \leq 0.03$ ) (BNT-BT-KNN) [1], are developed due to the environmental problem with lead. These materials also show extraordinary properties around their MPB. But the real structure of these lead-free materials and even of PZT and its correlation to the properties is still unknown or under discussion. We perform *in situ* transmission electron microscopy experiments under electrical field to get a closer insight to the microstructure and domain structure and its behaviour under electrical field. The new electrode geometry used provides an electrical field perpendicular to the electron beam. Field strengths up to around 2,5kV/mm are possible, which is above the coercive field ( $E_c$ ) of these materials. The examined samples exhibit  $E_c$  of around 1kV/mm, dependent on their composition. Investigations are still in progress as performing these experiments need a lot of patience due to the brittleness and easy cracking of the ceramics. The results will be discussed and compared due to their properties.

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## FA2-MS05-O5

**Magnetic and Crystal Structures of the Magnetolectric Pyroxene  $LiCrSi_2O_6$ .** Gwilherm Nénert<sup>a,b</sup>, Masahiko Isobe<sup>c</sup>, Clemens Ritter<sup>b</sup>, Olivier Isnard<sup>d</sup>, Alexander N. Vasiliev<sup>e</sup>, Yutaka Ueda<sup>c</sup>. <sup>a</sup>*CEA-Grenoble INAC/SPSMS/MDN, Grenoble, France.* <sup>b</sup>*Institut Laue-Langevin, Grenoble, France.* <sup>c</sup>*Institute for Solid State Physics, University of Tokyo, Chiba, Japan.* <sup>d</sup>*Institut Néel, CNRS, Université Joseph Fourier, Grenoble, France.* <sup>e</sup>*Low Temperature Physics Department, Moscow State University, Moscow, Russia.*

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In recent years, the coupling between magnetic and