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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 $R_5M_2X_{11}$, RMX_4 and $R_3M_2X_9$ chemical stoichiometries we focused on three representatives.

$[4\text{-}NH_2C_5H_4NH]SbCl_4$ 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-aminopirydinum cations interacting via hydrogen with chlorine atoms. The structure transforms from paraelectric C2/c state to incommensurate (IC) C2/c(0b0)s0 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 $Pna2_1$ phase.

The last presented crystal experiences an isomorphic 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 $(C_3N_2H_5)_3SbBr_6 \bullet H_2O$ to $(C_3N_2H_5)5Sb_2Br_{11}$ as well as physical properties, as far as $(C_3N_2H_5)5Sb_2Br_{11}$ 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.** <u>Jens Kling</u>[a], Ljubomira Schmitt[a], Hans-Joachim Kleebe[a], Manuel Hinterstein[a], Hartmut Fuess[a]. *[a]Faculty of Materials Science and Applied Geosciences, Technische Universität Damstadt, 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 $(1\text{-x-y})Bi_{0.5}Na_{0.5}TiO_3\text{-x}BaTiO_3\text{-y}K_{0.5}Na_{0.5}NbO_3$ ($0.05 \leq x \leq 0.07$ 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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Keywords: In situ experiments; ferroelectric oxides; TEM

FA2-MS05-O5

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

dielectric properties in transition-metal oxides gave rise to a significant research effort. This effort is governed by the emergence of new fundamental physics and potential technological applications [1-2].

Recently pyroxene materials with the general formula $AMSi_2O_6$ (A=Li,Na;M=Fe,Cr) have been reported as multiferroic materials [3]. This family of materials provides a large playground for physicists in condensed matter where A may be alkali or alkaline-earth elements, M being various metals with valence state 2+ or 3+ and Si^{4+} can be replaced by Ge^{4+} [4-5].

While these pyroxenes have been the subject of various studies [5-7], the complete magnetic structures are known only for few members of this class [5,7]. In order to understand and interpret properly the interplay between the dielectric and magnetic properties of this new multiferroic family, the determination of the magnetic structure of their members is necessary. It has been suggested that several members of the pyroxene family among which $LiCrSi_2O_6$ exhibit an incommensurate magnetic structure. This incommensurability of the magnetic structure would be the result of the geometrical magnetic frustration present in this family and would explain the reported multiferroic properties.

We investigated the magnetic and crystal structures of $LiCrSi_2O_6$ by powder neutron diffraction. Below T_N=11.5 K, an antiferromagnetic order appears. It is characterized by an antiferromagnetic coupling within the CrO_6 octahedra chains and a ferromagnetic coupling between the chains. The magnetic order is commensurate with the lattice with $\mathbf{k=0}$. The associated magnetic space group is $P2_1'/c$. This symmetry is in agreement with the reported magnetoelectric effect. We show that the magnetic frustration in this system is small. Finally, we discuss our results using a Landau phenomenological model and in the light of the literature [8].

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Keywords: magnetoelectricity; oxides; neutron diffraction