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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)_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 P2₁/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 P6₃/mmc parent phase to orthorhombic Pnam, next, at 295 K to monoclinic P2₁/a; at 216 K to modulated commensurately P2₁/a, and finally the symmetry increases to orthorhombic, polar Pna2₁ 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].

[1] R. Jakubas and L. Sobczyk, *Phase Transitions* 20 (1990) 163-193. [2] A. Piecha, A. Pietraszko, G. Bator, R. Jakubas, *Journal of Solid State Chemistry* 181 (2008) 1155-1166

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In Situ Transmission Electron Microscopy Experiments on Ferroelectric Materials under Electrical Field. Jens Kling^a, Ljubomira Schmitt^a, Hans-Joachim Kleebe^a, Manuel Hinterstein^a, Hartmut Fuess^a. ^a*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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[1] Zhang S.-T., Kounga A.B., Aulbach E., Granzow T., Jo W., Kleebe H.-J., Rödel J., *J. Appl. Phys.*, 2008, 103, 034107.

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Magnetic and Crystal Structures of the Magnetolectric Pyroxene $LiCrSi_2O_6$. Gwilherm Nénert^{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