Correlation between crystal structures and polar (ferroelectric) properties of hybrids of haloantimonates(III) and halobismuthates(III)

R. Jakubas, M. Rok, K. Mencel, G. Bator and A. Piecha-Bisiorek*

Halogenoantimonates(III) and halogenobismuthates(III) are a highly versatile class of organic–inorganic hybrid materials, applicable in optoelectronics and switchable dielectric devices. In this review, we discuss the rich chemistry of molecular–ionic halide complexes of Bi(III) and Sb(III) focusing on the correlations between their crystal structures and ferroelectric properties as well as on an explanation of the molecular mechanism of the paraelectric–ferroelectric phase transition. This review summarizes the current state of the art in the field of ferroelectricity among organic–inorganic hybrids based on Bi(III) and Sb(III) halides, which has become one of the key exploration areas of modern materials chemistry.

1. Introduction

Materials whose physical properties can be controlled by external stimuli have attracted considerable interest due to their potential applications in substrate-film interfaces,1–3 high-strain states, electrocaloric circuits,4,5 nanotubes and nanowires,6 ferroelectric random access memories (FeRAMs),7 dynamic random access memory (DRAM) capacitors,8–10 electron emitters,2,8 solar cell components,11 and weak-magnetic field sensors.12–16 Ferroelectrics are of importance in the design of thermo-sensitive multifunctional switching materials because they are often accompanied by multiple switchable physical properties, e.g. piezoelectricity, pyroelectricity, dielectric constant and second harmonic generation (SHG). Ferroelectrics are polar substances in the solid state (crystalline or amorphous) or liquid-crystalline state (liquid crystals), in which a spontaneous polarization ($P_s$) is generated and it is reversible in an external electric field ($E$). The relationship between an electric shift ($D$) or polarization ($P$) and the electric field intensity leads to a hysteresis loop ($D$–$E$ loop) between the oppositely charged layers. Such an electrical bistability can be used in non-volatile memory parts. It refers in particular to the ferroelectric computer memory type, FeRAM, which is crucial for...
the application of novel materials. In principle all ferroelectrics have a Curie temperature, $T_c$, connected with the phase changes from the ferroelectric to paraelectric phase but some of them decompose before achieving $T_c$. When the temperature approaches $T_c$, the dielectric constant fulfilling the Curie–Weiss law undergoes an abnormal increase; this is a quantity, which can be used in capacitors. Pyroelectricity is another important quantity. The change of the piezoelectric $e$-current with temperature, when the crystal is being heated or cooled down, generates mechanical phenomena. The stress generates electric polariz- tion $e$-current known as the piezoelectric $e$- current. The pyroelectric $e$-effect is particularly enhanced especially of hybrid molecular ferroelectrics still represents a great challenge, among which the lack of spatial-inversion symmetry is one of them. Among the 32 point groups, 11 belong to the centrosymmetric and the remaining 21 are noncentrosymmetric. One should note, that the lack of spatial-inversion symmetry observed in the noncentrosymmetric group of crystals is most sought for in applications. It is important for the ferroelectric phase to adopt one of the 10 polar point groups, from which 68 space groups and 32 point groups, which describe both the macro- and microscopic symmetries of crystal structures. Among the 32 point groups, 11 belong to the centrosymmetric classes, while the remaining 21 are noncentrosymmetric.17 One should note, that the lack of spatial-inversion symmetry observed in the noncentrosymmetric group of crystals is most sought for in applications. It is important for the ferroelectric phase to adopt one of the 10 polar point groups, from which 68 space groups are formed (see Table 1).

The most important functionalities that make ferroelectrics so useful are the high values of the real part of complex dielectric permittivity, $\varepsilon^\ast$, spontaneous polarization, $P_s$, good mechanical and thermal resistance and small dielectric losses.18,19 This set of traits determines the transition from the

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Polar point group</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>1</td>
<td>P1, P2, P3, C2</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$m$</td>
<td>P1mm, P1, C1</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$mm2$</td>
<td>Pm, Pn, Cm, Cc</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>4</td>
<td>P4, P41, P42, P43, I4, I41</td>
</tr>
<tr>
<td>Trigonal</td>
<td>3</td>
<td>P3, P31, P32, R3,</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>6</td>
<td>P6, P61, P63, P62, P63, P6</td>
</tr>
</tbody>
</table>

Klaudia Mencel was born in 1992 in Ostrów Wielkopolski, Poland. She received her M.Sc. degree at the Faculty of Chemistry of the University of Wroclaw in 2016. She is a Ph.D. student in the Ferroelectrics and Liquid Crystals Team, Faculty of Chemistry (University of Wroclaw).

Grażyna Bator was born in 1958 in Pleszew, Poland. She completed her Ph.D. in 1986 at the Faculty of Chemistry of the University of Wroclaw, Poland. After presenting her habilitation dissertation in 2000, she obtained the title of Professor in 2007. She took scientific internships at KU Leuven in Belgium and ZIBJ in Dubna, FR, and carried out experiments on neutron scattering in cooperation with FRM II, Garching, Germany. She is the co-author of about 160 articles in the field of materials chemistry. She is the head of the specialization ‘Materials Chemistry for Modern Technologies’ at the Faculty of Chemistry of the University of Wroclaw.
paraelectric phase (which is usually high-temperature, high symmetry state) to the ferroelectric one (low-temperature, low-symmetry state) in the close vicinity of the Curie temperature ($T_C$). The paraelectric–ferroelectric PT is related to the symmetry change (e.g. some symmetry elements of the paraelectric phase are lost, when the ferroelectric phase is reached), and leads to the structurally modified (ordered) ferroelectric phase. This structural transformation (described often as symmetry-breaking), is reflected in the macroscopic properties of the material, e.g. the appearance of $P_c$ in the ferroelectric phases.

One of the classes of molecular–ionic materials are organic–inorganic hybrid ferroelectrics which are currently of particular interest, due to the desirable and modifiable characteristics of their organic and inorganic components, for exploring ferroelectric-based multifunctional materials such as multiferroics, semiconductors and photovoltaic materials.20–23 Of note, the symmetry, size, and value of the dipole moments of the cation play an important role in triggering the structural PT. Therefore, control of the ’order–disorder’ motion of the organic cations in a molecular crystal is a key issue for the design of hybrid molecular–ionic ferroelectrics.

Haloantimonates(III) and halobismuthates(III), which are the subject of the present review, defined by the general formula $\text{R}_m\text{M}_b\text{X}_{i\text{b}}\text{(III)}$ (where $\text{R}$ – organic cations, $\text{M}$ = Sb(III) or Bi(III) and $\text{X}$ = Cl, Br, I) create one of the well-recognizable groups of ferroic compounds, essential mainly from an application point of view as they combine many desirable features, e.g. facile synthesis and processing, and cost-effectiveness with promising electrical and optical properties.24–29 A characteristic feature of the compounds under consideration is that they possess the lone electron pair ($5s^2$ (Sb) and $6s^2$ (Bi)). However, its presence, which has a moderate impact on the structural properties of these salts, seems to have a tremendous effect on the physical properties of crystals. The lone electron pair deforms very easily a spherical symmetry of the orbitals, on which they are located. This leads to an increase in the length of the M–X bonds, and thus to a considerable deformation of the MX$_6$ octahedra.

The polyanionic structure of the lattice is determined by the size of the organic cation, its symmetry and ability to create hydrogen bonds of the N–H⋯X type; the size of the halogen atom, which jointly creates the lattice is also of crucial importance. The alkylammonium cations belong to a wide variety of organic cations, which crystallize with various anionic sublayers. They are characterized by the different chain lengths, from methyl- to butyl-ammonium, and they may form five- or six-membered rings in the aromatic cations (e.g. imidazolium, pyridinium and its substituted derivatives) as well as saturated heterocyclic amines (e.g. pyrrolidine) (Fig. 1).

An analysis of these compounds has revealed a richness of the cationic unit movements. The motions depend on three basic factors such as: (i) the symmetry of the cation; (ii) the value of the dipole moments of the cation; (iii) the structure of the anionic network surrounding the cation. The reorientation ability of the dipolar units occupying vacancies inside the anionic sublayers is determined mainly by the symmetry and size of these spatial vacancies (a reorientational disorder), while the dynamic properties of the anionic networks are limited primarily by the formation of polymeric structures. In the organic part, the dynamic properties change significantly when the temperature is being lowered since the cation mobility decreases. This process is accompanied by a significant distortion of the anionic lattice. It must be mentioned that one of the most significant features of this lattice is its flexibility and, at the same time, its facility of adaptability of symmetric cations, which is related to the effect of the electron lone pair on the Sb(III) and Bi(III) atoms. The presence of hydrogen bonds of the N–H⋯X-type in the crystal structure is significant for the lattice formation. The strength of these bonds increases proportionally to the size of atom radius of the corresponding halogen. A rearrangement of these bonds takes place during the PT, which significantly affects the dynamic properties as well as the ordering of the cations.

In the present paper, we would like to focus on the ferroelectric structures among halogenoantimonates(III) and halogenobismuthates(III), which can be found in the literature and on the correlation between their crystal structures and polar properties. For this reason, the structural analysis of the compounds with the organic cations, a description of the cationic dynamics and the deformation of the inorganic layers have been undertaken. Moreover, macroscopic dielectric properties are discussed in detail.

### 2. Structural diversity of the anionic networks of haloantimonates(III) and halobismuthates(III)

Haloantimonates(III) and halobismuthates(III) are characterized by a significant diversity of the anionic networks (from zero-, through one-, two-, and three-dimensional architectures).30–44 Taking into account the molar ratio of the amine (R) and metal (M) (Sb(III)/Bi(III)) the following four basic stoichiometries are observed.

---

**Anna Piecha-Bisiorek** was born in 1979 in Rybnik, Poland. She received her Ph.D. degree (supervisor: Prof. R. Jakubas) at the Faculty of Chemistry of the University of Wroclaw in 2008 and became an assistant professor in 2018. She took scientific internships at the Jülich Center for Neutron Science JCNS (MLZ, Garching, Germany). Her research interests cover mainly the physicochemistry of organic–inorganic hybrid materials.

---

*Inorganic Chemistry Frontiers* Review

Published on 07 April 2020. Downloaded on 7/28/2021 12:51:59 AM.
2.1. RMX₄ (R : M = 1 : 1)

The anionic sublattices observed in this group may be divided into two types: (i) polyanionic chains; (ii) isolated units.

As for type (i) three different types of polyanionic chain arrangements are observed:

- chains of the edge-sharing octahedra (with two terminal and four bridging halogen atoms) (Fig. 2(a))[^54]
- the [MX₆]⁻⁻ octahedra linked as follows: three non-equivalent M atoms possess three bridging and three terminal contacts, whereas the remaining one possesses only one terminal and five bridging contacts (Fig. 2(b))[^55]
- chains of the corner-sharing square pyramids (Fig. 2(c))[^56]

With regard to the separated units (ii) four different assemblies may be recognized.

Four octahedra linked with each other in two different ways:

- one type of central atom with three bridging and three terminal halogens (Fig. 2(d))[^57]
- two central atoms surrounded by three terminal and three bridging halogens and two others coordinated by two terminal and four bridging halogens (Fig. 2(e))[^58-60]
- face-sharing octahedra (Fig. 2(f))[^61,62]
- edge-sharing two square pyramids (Fig. 2(g))[^63-70]

2.2. R₂MX₆ (R : M = 1.5 : 1)

- infinite, one-dimensional (1D) zig-zag double chains (pleated ribbon structures) (Fig. 3(a))[^71-76]
- two-dimensional (2D) layers (honeycomb like corrugated sheets) (Fig. 3(b))[^77-89]
- discrete biotetrahedra (0D) (Fig. 3(c))[^90-94]
- four octahedral units (0D) ([M₄X₁₈]⁻⁻) (Fig. 3(d))[^95-99]

2.3. R₂MX₅ (R : M = 2 : 1)

- one-dimensional (1D) chains (cis- or trans-type) (Fig. 4(a) and (b)) respectively[^100-109]
- isolated [M₂X₁₀]⁻⁻ units (two edge-sharing octahedra) (Fig. 4(c))[^49,110,111]
tetrameric polyanion with corner-sharing octahedra (Fig. 4(d)).

2.4. \( \text{R}_2\text{M}_2\text{X}_{11} \) (\( \text{R} : \text{M} = 2.5 : 1 \))

- Corner-sharing octahedra (0D) ([M\(_2\)X\(_{11}\)]\(^{3-}\)) (Fig. 5(a)).

2.5. \( \text{R}_3\text{MX}_6 \) (\( \text{R} : \text{M} = 3 : 1 \))

- Isolated [MX\(_6\)]\(^{3-}\) octahedra (Fig. 5(b)).

2.6. Different modifications of the anionic substructures

The richness of the anionic structures among halobismuthates (\( \text{III} \)) and haloantimonates(\( \text{III} \)) is related also to the more exotic type of stoichiometry\(^{134,136} \) (see Fig. 6), e.g. \( \text{RM}_2\text{X}_7 \),\(^{137,138} \)

3. Ferroelectricity among haloantimonates(\( \text{III} \)) and halobismuthates(\( \text{III} \))

The ferroelectricity among halobismuthates(\( \text{III} \)) and haloantimonates(\( \text{III} \)) is limited only to four different types of chemical
compositions: \( \text{RMX}_4 \), \( \text{R}_3 \text{M}_2 \text{X}_9 \), \( \text{R}_2 \text{MX}_5 \) and \( \text{R}_5 \text{M}_2 \text{X}_{11} \). Below, the analysis of the physical properties is presented and a correlation between the crystal structure and the origin of their polarity (ferroelectricity) is discussed. In our review we focus on pure organic–inorganic hybrids based on Bi(III) and Sb(III) (mixed anionic networks were not analyzed); however, due to the discovery of the first ferroelectric among halobismuthates \( (\text{R} \, \text{R}^\prime \, \text{M} \, \text{X}_6) \) a single exception has been made.

### 3.1. \( \text{RMX}_4 \) type compounds

Ferroelectricity in the \( \text{RMX}_4 \) type compounds is a unique feature. Based on the literature, only two examples of ferroelectrics, characterized by the 1D polymeric anionic structure, are known: \((4\text{-aminopyridinium})[\text{SbCl}_4]^{51-53}\) \((4\text{-NH}_2\text{C}_5\text{H}_4\text{NH})[\text{SbCl}_4], \text{4-APCA})\) and \((\text{trimethylamino-N-methyl stilbazolium})[\text{Bi}_2\text{Cl}_8]^{54}\) \((\text{C}_{17}\text{H}_{24}\text{N}_2)[\text{Bi}_2\text{Cl}_8], \text{TAMS}[\text{Bi}_2\text{Cl}_8]\)\). The detailed X-ray structure analysis indicates that in both compounds, the ferroelectricity is related mainly to a strong deformation of the \([\text{MX}_4]^{2-}\) type of substructure (see Fig. 2(a) and Table 2).

The crystal structure of 4-APCA is built up of the polyanionic chains of \([\text{SbCl}_4]^{-}\) forming a tunnel-like structure and disordered 4-aminopyridinium cations connected via weak hydrogen bonds. Phase situation is complex and characterized by rich polymorphism in the solid state (see Scheme 1). The ac calorimetry studies have shown that the high temperature PT at 304 K is of the ‘order – disorder’ type and leads to a inco-

---

**Fig. 5** (a) Structure of the isolated \([\text{M}_2\text{X}_{11}]^{2-}\) anions; (b) isolated \([\text{MX}_6]^{2-}\) octahedra.

**Fig. 6** Atypical anionic structures among haloantimonates(III) and halobismuthates(III). ((a and b) labels correspond to the different organization of the inorganic structures) \( \text{RM}_2\text{X}_7 \) polyanionic 1D chains; \( \text{R}_4\text{M}_6\text{X}_{22} \) 0D units; \( \text{RM}_3\text{X}_{10} \) infinite (1D) polyoctahedral chains; \( \text{R}_4\text{M}_8\text{X}_{28}, \text{R}_3\text{M}_5\text{X}_{18}, \text{R}_6\text{M}_8\text{X}_{30} \) isolated (0D) units.137–145

**Table 2** Phase diagram of \( \text{RMX}_4 \) stoichiometry

<table>
<thead>
<tr>
<th>Stochiometry</th>
<th>245 K, 1st</th>
<th>250 K, 2nd</th>
<th>271 K, 2nd</th>
<th>304 K, 2nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>((4\text{-NH}_2\text{C}_5\text{H}_4\text{NH})[\text{SbCl}_4])</td>
<td>V: P2(/c)</td>
<td>V: I(\beta)C</td>
<td>III: Cc</td>
<td>II: C2/c</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Stochiometry</th>
<th>245 K, 1st</th>
<th>250 K, 2nd</th>
<th>271 K, 2nd</th>
<th>304 K, 2nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{C}_{17}\text{H}_24\text{N}_2)[\text{Bi}_2\text{Cl}_8])</td>
<td>I: Pn(\alpha)2(\alpha)</td>
<td>I: Pn(\alpha)2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1st-first order PT; 2nd-second order PT

- **Red** ferroelectric phase
- **Green** paraelectric phase
mensurate modulated phase (II). At 270.5 K (II → III) a ‘lock-in’ transition to a commensurate modulated phase is observed, which, in turn, becomes a ferroelectric one. The anomaly at 248 K leads to the next polar, but modulated incommensurate phase, while below 240 K the crystal becomes nonpolar again. The ferroelectric transformation at 270.5 K is characterized by a ‘displacive’ type of mechanism related to the displacement of the organic cations in relation to the anionic chains. Dielectric dispersion measurements carried out in the radio-frequency region around $T_c$ (270.5 K) revealed a critical slowing-down assigned mainly to the domain-like wall motion of the incommensurate phase (Fig. 7(a)). The relaxation process was found to be nearly monodispersive, which is rare among incommensurate ferroelectrics. The polar properties of 4-APCA were confirmed by the switchable $P_s$ of about 0.35 μC cm$^{-2}$ at 265 K. One should note that among halogenobismuthates(III) and halogenoantimonates(III), 4-APCA was the first example of a ferroelectric compound characterized by the molecular mechanism of a ‘displacive’-type assigned to the ferroelectric PT.

With regard to (TAMS)[Bi$_2$Cl$_8$], it belongs to room temperature (RT) ferroelectrics, but the Curie temperature was not achieved on heating due to the earlier decomposition of the compound. (TAMS)[Bi$_2$Cl$_8$] crystallizes in an acentric orthorhombic space group (Pna$_2$1), and consists of a framework of infinitive [Bi$_2$Cl$_8$$^{2-}$] inorganic chains, separated by [TAMS]$^{2+}$ cations. The non-centrosymmetric crystal structure and polar alignment of the organic species contribute to the $P_s$ value, which is of the order of 0.08 μC cm$^{-2}$ at 453 K. 4-APCA was the first example of a ferroelectric compound characterized by the molecular mechanism of a ‘displacive’-type assigned to the ferroelectric PT.

3.2. **R$_3$M$_2$X$_9$ type compounds**

Within the chemical stoichiometry R$_3$M$_2$X$_9$ the ferroelectricity is limited to two types of anionic sublayers among four possible ones (Fig. 3); 2D (two-dimensional layers) (Fig. 3(b)) and 0D-discrete bioctahedral units (Fig. 3(c)). The 2D structure is usually characteristic of the chloride and bromide ferroelectrics containing only small alkylammonium moieties (methyl-, dimethyl and trimethyl-ammonium) or non-substituted rings (e.g. pyrrolidinium cations) (Table 3). The bulky organic cations due to the steric effects cannot occupy small vacancies within the layers. On the other hand all known iodide ferroelectrics possess the 0D anionic network (Table 4) thus the restriction with respect to the size and symmetry of the organic moieties is not so obvious.

![Scheme 1](image.png)  
**Scheme 1** Phase diagram of 4-APCA.$^{51–53}$

![Fig. 7](image.png)  
**Fig. 7** Temperature dependence of the real part of the complex dielectric permittivity for: (a) 4-APCA.$^{51}$ (b) (TAMS)[Bi$_2$Cl$_8$].$^{54}$
The characteristic feature of the paraelectric phase in 2D 
R$_3$M$_2$X$_9$ ferroelectrics is the presence of two crystallographically 
dependent alkylammonium cations in the crystal structure 
(N(1) and N(2)). The cation N(1) is located in voids inside 
the polyanionic layers, whereas the N(2) one between the layers 
(Fig. 8). All cations are connected to the anionic sublattice by 
N–H⋯X hydrogen bonds. Both types of cations are highly dis- 
ordered in the paraelectric phase.

The disorder of N(1) is usually described by a two-site 
model with an occupancy factor of the N(1) atom, equal to 0.5.

The other cation N(2) is also split between two positions, N(21) 
and N(22), however, with different occupancy factors, which 
change with temperature. Since the N(2) cation is in the 
general position of the crystal structure, this change does not 
lead to any changes in the lattice symmetry in contrast to the 
N(1) cation dynamics. The paraelectric–ferroelectric transitions 
lead to the distortion of the anionic network, which results in 
the loss of the symmetry center. Thus the N(1) cations now 
occupy a single position in a ferroelectric domain and their 
long-range order is responsible for an appearance of $P_s$. In the

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Phase diagram of R$_3$M$_2$X$_9$ with a 2D anionic architecture</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH$_3$NH$_3$)$_3$[Bi$_2$Br$_9$]</td>
<td>145 K, 1st</td>
</tr>
<tr>
<td>$P_s$ = 7.96 $\mu$C/cm$^2$, $\varepsilon_{\text{max}}$ = 52</td>
<td></td>
</tr>
<tr>
<td>(C$_6$H$_5$NH$_3$)$_3$[Bi$_2$Br$_9$]</td>
<td>322 K, 1st</td>
</tr>
<tr>
<td>$P_s$ = 7.6 $\mu$C/cm$^2$, $\varepsilon_{\text{max}}$ = 450</td>
<td></td>
</tr>
<tr>
<td>(C$_6$H$_5$NH$_3$)$_3$[Sb$_2$Br$_9$]</td>
<td>323 K, 1st</td>
</tr>
<tr>
<td>$P_s$ = 5.2 $\mu$C/cm$^2$, $\varepsilon_{\text{max}}$ = 290</td>
<td></td>
</tr>
<tr>
<td>$P_s$ = 0.04 $\mu$C/cm$^2$, $\varepsilon_{\text{max}}$ = 22</td>
<td></td>
</tr>
<tr>
<td>(NH$_4$CHNH$_2$)$_3$[Bi$_2$Br$_9$]</td>
<td>176.9 K, 2nd</td>
</tr>
<tr>
<td>$P_s$ = 0.005 $\mu$C/cm$^2$, $\varepsilon_{\text{max}}$ = 18</td>
<td></td>
</tr>
<tr>
<td>(NH$_4$CHNH$_2$)$_3$[Sb$_2$Br$_9$]</td>
<td>152 K, 1st</td>
</tr>
<tr>
<td>$P_s$ = 7, $\varepsilon_{\text{max}}$ = 7</td>
<td></td>
</tr>
</tbody>
</table>

1st-first order PT, 2nd-second order PT

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Phase diagram of R$_3$M$_2$X$_9$ with a 0D anionic architecture</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH$_3$NH$_3$)$_3$[Bi$_2$Br$_9$]</td>
<td>145 K, 1st</td>
</tr>
<tr>
<td>$P_s$ = 7.96 $\mu$C/cm$^2$, DFT calculation, $\varepsilon_{\text{max}}$ = 52</td>
<td></td>
</tr>
<tr>
<td>(C$_6$H$_5$NH$_3$)$_3$[Sb$_2$Br$_9$]</td>
<td>322 K, 1st</td>
</tr>
<tr>
<td>$P_s$ = 7.6 $\mu$C/cm$^2$, $\varepsilon_{\text{max}}$ = 450</td>
<td></td>
</tr>
<tr>
<td>(C$_6$H$_5$NH$_3$)$_3$[Sb$_2$Cl$_9$]</td>
<td>323 K, 1st</td>
</tr>
<tr>
<td>$P_s$ = 5.2 $\mu$C/cm$^2$, $\varepsilon_{\text{max}}$ = 290</td>
<td></td>
</tr>
<tr>
<td>$P_s$ = 0.04 $\mu$C/cm$^2$, $\varepsilon_{\text{max}}$ = 22</td>
<td></td>
</tr>
<tr>
<td>(NH$_4$CHNH$_2$)$_3$[Bi$_2$Br$_9$]</td>
<td>176.9 K, 2nd</td>
</tr>
<tr>
<td>$P_s$ = 0.005 $\mu$C/cm$^2$, $\varepsilon_{\text{max}}$ = 18</td>
<td></td>
</tr>
<tr>
<td>(NH$_4$CHNH$_2$)$_3$[Sb$_2$Br$_9$]</td>
<td>152 K, 1st</td>
</tr>
<tr>
<td>$P_s$ = 7, $\varepsilon_{\text{max}}$ = 7</td>
<td></td>
</tr>
</tbody>
</table>

1st-first order PT, 2nd-second order PT
case of the 2D ferroelectrics the polar direction is maintained within the corrugated layer structure. This means that the layers enhanced the polarizability of the system, which is coupled with the dynamics of the N(1) type cations.

An enhanced value of the electric permittivity close to $T_c$ is observed for the 2D ferroelectrics, because easily polarizable anionic layers favor the long-range order of the dipole–dipole interactions (Fig. 9).

In spite of the structural similarities of the 2D type ferroelectrics their dielectric responses, character of PTs and phase situations are quite diverse. The dielectric response of the majority of the 2D analogs shows a critical slowing down of the macroscopic relaxation time, which indicates an ‘order–disorder’ mechanism of ferroelectric transition (Fig. 9(a)). In turn in the case of MABB the dielectric response ($\varepsilon(T)$) is characteristic of ‘improper’ ferroelectrics ($1^{st}$ order PT)

Fig. 8 Comparison of the crystal structures of DMACA in the paraelectric and ferroelectric phases (ref.88).

Fig. 9 Temperature dependence of the real part of the dielectric permittivity ($\varepsilon'$) for (a) $(\text{NH}_2\text{CH}_3)_3[\text{Sb}_2\text{Cl}_9]$ (DMACA)$^{131}$ (b) $(\text{CH}_3\text{NH}_3)_3[\text{Bi}_2\text{Br}_9]$ (MABB)$^{84,85}$ (c) $(\text{CH}_3\text{NH})_3[\text{Sb}_2\text{Cl}_9]$ (TMACA)$^{131}$ around $T_c$. 
(Fig. 9(b)), while for the TMACA the dielectric results indicate the existence of a narrow-range intermediate metastable phase (incommensurate) between the ferroelectric and paraelectric phases (Fig. 9(c)).

The only parameter that correlates well with the temperature scope of the ferroelectric phases is the cation size (Tables 3 and 4). It is clearly seen that an increase of the cations size leads to the shift of the Curie point towards high temperatures. The large cations usually have less freedom of movement in the anion layer (N(1)-type) gaps, which is why they are easier to freeze at higher temperatures in cooling cycles in comparison with the ferroelectrics with the small cations.

Haloantimonates(III) and halobismuthates(III), characterized by the 2D anionic structure, usually possess a smaller value of \( P_s \) in contrast to that for the 0D analogs, in spite of the fact that the organic cations of the presented crystals have a larger value of dipole moments, \( \mu \). Nevertheless it should be noted that in the formamidinium analogs the cations possess a quite small value of \( \mu = 0.23 \) D and the dielectric anomalies are rather intermediate. It seems that the relationship between structural parameters of the crystals and the macroscopic properties \( (P_s \text{ and } \varepsilon) \) is rather complex and its recognition requires further studies on \( R_2MX_5 \)-type compounds. It is interesting that most 0D ferroelectrics possess polar properties above room temperature, except for \( (NH_2CHNH_2)_3[Bi_2I_9] \) and \( (NH_2CHNH_2)_3[Sb_2I_9] \). The paraelectric phase exhibits usually high symmetry (trigonal or hexagonal), which proves a high dynamic disorder of the cationic networks. Generally, the mechanism of ferroelectric phase transitions for the 0D compounds is quite complex because the ‘order–disorder’ and ‘displacive’ contributions are possible.

### 3.3. \( R_2MX_5 \) type compounds

A Cambridge Structural Database survey (version 5.40 March 2019) permits us to predict the probability of the appearance of acentric/ferroelectric compounds within \( R_2MX_5 \)-type stoichiometry. 192 entries, adopting either polymeric (1D) or isolated (0D) anionic substructures, have been found.

The results presented in Tables 5 and 6 confirm that the ferroelectricity in the \( R_2MX_5 \)-type compounds is adopted in the 1D anionic network. The ferroelectricity does not depend on the symmetry and size of the organic cations (heteroaro-
matic, heterocyclic aliphatic) but is strongly affected by the dipole moment values.

A characteristic feature of this subclass is the construction of the anionic lattice, which is created by 1D infinite chains of different configurations (cis- or trans-mode), however, the cis-conformation (and its modifications) is very common in the analyzed subgroup. Generally, one can state that the distortion of the anionic chains through the PT is a driving force, which contributes mainly to the $P_s$ value. This effect is coupled with the dynamics of the polar organic cations, which are usually disordered in the paraelectric phase to varying degrees. Distortion of the anionic substructure is treated as a ‘displacive’ contribution to the molecular mechanism of the ferroelectric transition, whereas a change in the dynamics of the organic moieties is an ‘order–disorder’ contribution (Fig. 10).

The molecular mechanism of the paraelectric-ferroelectric transformation varies from ‘displacive’ through mixed up to purely ‘order–disorder’, however, which of these mechanisms is dominant depends strongly on the subtle differences in the development of the polyanionic chains. In the case of the ‘displacive’ $R_2MX_5$ subclass we should take into account the $ns^2$ electron lone pair effect (5s$^2$-Sb and 6s$^2$-Bi), which seems to play a key role in the distortion of the MX$_6$ octahedron. The derivatives, characterized by trans-connected octahedra containing bulky organic methylviologen MV$^+$ amine: (MV)$[\text{BiBr}_5]^{157}$, (MV)$[\text{Bi}_5\text{Cl}_3]$, are an example of such a distorted structure. The MV$^{2+}$ cations have stabilized unprecedented regular [BiBr$_5^{2−}$]$_\infty$ chains of trans-connected octahedra.

Through PT, the trans Bi–Br bonds differentiate markedly and the result is the chain polarity. Moreover, the electronic lone pair is stereochemically activated below 243 K leading to an acentric polar phase. The mixed-halide analog, (MV)$[\text{Bi}_5\text{Cl}_3]$, reaches one of the highest room-temperature $P_s$ values (>15 $\mu$C cm$^{-2}$ at 298 K) in the field of organic–inorganic hybrid ferroelectrics. It should be added that trans-connected isomers are much rarer than cis-connected ones. It is difficult to indicate a different correlation between the crystal structure and dynamics and the scope of polar phases in this group of compounds.

Compared to $R_3M_2X_9$ connections, the organic cations in $R_2MX_5$ show less freedom of movement in the paraelectric phases (usually a two-site model) thus the compounds adopt

<table>
<thead>
<tr>
<th>Anionic substructure</th>
<th>All compounds</th>
<th>Piezoelectric</th>
<th>Ferroelectric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isolated pyramids [MX$_5$]$^{2−}$</td>
<td>35</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>Isolated bioctahedra [M$<em>4$X$</em>{10}$]$^{4−}$</td>
<td>81</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Isolated tetrameric forms [M$<em>4$X$</em>{30}$]$^{8−}$</td>
<td>4</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Infinite chains [MX$_5$]$^\infty$</td>
<td>72</td>
<td>30</td>
<td>9</td>
</tr>
<tr>
<td>Summary</td>
<td>192</td>
<td>41</td>
<td>9</td>
</tr>
</tbody>
</table>

Fig. 10 Comparison of the crystal structures of (NH$_2$(CH$_2$)$_3$NHCH$_3$)[BiCl$_5$]$^{155}$ in the paraelectric and ferroelectric phases.
lower symmetry (mainly orthorhombic). Thus most of the paraelectric-ferroelectric transitions in the $\text{R}_2\text{MX}_5$-subclass is described by the $\text{mmmFmm}_2$ Aizu relationship (non ferroelastic transitions), in turn methylviologen analogs characterized by trans-connected-modes of the anionic chains exhibit also non-ferroelastic transition between monoclinic phases described by $2/mFm$ or $2/mF2$ species (Fig. 11).

As it is presented (Table 5) for the hybrids based on very similar organic cations ($N$-methyl-$1,3$-diaminopropane) and ($N$, $N$-dimethyl-$1,3$-diaminopropane) the inexistence of $T_c$ the differences in the $T_c$ values (existence of polar phases) reach about $230$ K ($376$ and $143$ K, respectively), however, the values of $P_s$ are comparable ($2.38$ and $1.36 \mu C m^{-2}$, respectively). In turn, the organic–inorganic compounds based on the ethylammonium cation indicate similar values of $T_c$ ($190$ and $160$ K), while $P_s$ differs almost by three orders. In conclusion, within $\text{R}_2\text{MX}_5$-type ferroelectrics the amount of the deformation of the anionic chains is crucial, when it comes to the value of $P_s$ and a character of the dielectric response close to $T_c$ (Fig. 12).

3.4. $\text{R}_3\text{M}_2\text{X}_{11}$ type compounds

Complexes of $\text{R}_3\text{M}_2\text{X}_{11}$ stoichiometry are unique in crystalchemistry of haloantimonates($\text{m}$) and halobismuthates($\text{m}$). Currently, scientific literature gives only seven examples of the compounds marked by this type of chemical composition and all of them exhibit ferroelectric properties (see Table 7). A typical trait of the compounds in question is the presence of

![Fig. 11](image1) Comparison of the crystal structures of ($\text{C}_{13}H_{14}N_2$)$[\text{BiBr}_5]$\textsuperscript{157} in the paraelectric and ferroelectric phases.

![Fig. 12](image2) Temperature dependence of the real part of the complex dielectric permittivity for: (a) ($\text{C}_3\text{H}_7\text{N}_2)_2[\text{SbCl}_5]$\textsuperscript{158} (b) ($\text{C}_{12}H_{14}N_2$)$[\text{BiBr}_3]$\textsuperscript{157}
discrete biocahedral units, $[M_2X_{11}]^{5-}$ in their crystal structure, in which two octahedra are connected with each other by one bridging halogen atom (see Fig. 13).

A cationic subnetwork consists in turn of four kinds of nonequivalent types of organic species marked by varied dynamic disorder. Phase situation for all $R_5M_2X_{11}$-ferroelectrics is presented in Table 7.

A detailed analysis of the phase diagrams and structural data shows that the size of the organic cation and its shape and symmetry, have a significant influence on PTs’ sequence, on the symmetry of each phase, on the polar properties of compounds as well as on the temperature range of the existence of the polar (ferroelectric) phases. Thus, this group may be divided into two subgroups: the first one created by the hybrids based on the aliphatic cations, e.g. $(CH_3NH_3)_5[Bi_2Br_{11}]$,$^{116-118}$ $(CH_3NH_3)_5[Bi_2Cl_{11}]$$^{119-122}$ and $(NH_2CHNH_2)_5[Sb_2Br_{11}]$,$^{163}$ (abbreviated as aliphatic analogs) and the second one formed by aromatic counterions: 

### Table 7  Phase diagram of $R_5M_2X_{11}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(CH_3NH_3)<em>5[Bi_2Br</em>{11}]$</td>
<td>116–118</td>
</tr>
<tr>
<td>$(CH_3NH_3)<em>5[Bi_2Cl</em>{11}]$</td>
<td>119–122</td>
</tr>
<tr>
<td>$(NH_2CHNH_2)<em>5[Sb_2Br</em>{11}]$</td>
<td>163</td>
</tr>
<tr>
<td>$(C_6H_{12})<em>5[Bi_2Cl</em>{11}]$</td>
<td>113</td>
</tr>
<tr>
<td>$(C_6H_{12})<em>5[Bi_2Br</em>{11}]$</td>
<td>114</td>
</tr>
<tr>
<td>$(C_6H_{12})<em>5[Sb_2Br</em>{11}]$</td>
<td>123</td>
</tr>
<tr>
<td>$(C_6H_{12}NH)<em>5[Bi_2Br</em>{11}]$</td>
<td>115</td>
</tr>
</tbody>
</table>

1st-first order PT, 2nd-second order PT  
| ferroelectric phase | paraelectric phase |

1. Independent parts of the unit cell of $[C_3N_2H_5_5]_5[Bi_2Br_{11}]$ in the paraelectric and ferroelectric phases ($M = Bi(III)/Sb(III), X = Cl, Br, I$).$^{113,114}$
ferroelectrics are much stronger than those in the aromatic 
R5M2X11 type: 

\[ \text{dipole interaction} \]

it is shifted by almost 150–180 \( \text{K} \) towards the low temperatures. Despite obvious structural 
differences between these two subgroups (aliphatic/aromatic), 
the following elements are common for the compounds of the 
R5M2X11 type:

- PTs are continuous in nature;
- PTs are classified as an ‘order–disorder’ type;
- Close to \( T_c \), a critical slowing down of the macroscopic 
relaxation time is observed;
- Molecular mechanism of the ferroelectric PT is dominated 
by the dynamics of the organic cations.

In the paraelectric phase, two out of five cations, being in a 
general position, are ordered, while the remaining three, 
located at special positions, reveal an orientational disorder 
two-site model, \( 180^\circ \) reorientation). In the ferroelectric phase, 
all cations are ordered, however, the key input to \( P_s \) is given 
only by three out of five organic cations.

Another element that distinguishes the analyzed materials 
is the long-range dipole–dipole interaction. It determines both 
the values of \( P_s \) and the electric permittivity close to \( T_c \). 
Methylammonium ferroelectrics mark themselves out by the 
higher values of \( P_s \) in the range of 2–3 \( \mu \text{C cm}^{-2} \) and \( \varepsilon_{\text{max}} \geq 1 \times 10^4 \), 
than those for the aromatic analogs. The value of \( P_s \) for 
the latter compounds is by almost one order, and for \( \varepsilon' \) almost 
by 1.5 order, lower than that for the former ones. This means 
that the long-range dipole–dipole interactions in the aliphatic 
ferroelectrics are much stronger than those in the aromatic 
one. This in turn has an impact on the values of the PT temper-
atures. The stronger the dipole–dipole interaction the higher 
the values of \( T_c \) (Fig. 14).

The other property, which deserves to be compared, is the 
dynamic property of ferroelectrics, analyzed using the dielec-
tric relaxation data. All R5M2X11 ferroelectrics indicate the criti-
cal slowing down of the macroscopic relaxation time around 
\( T_c \), a phenomenon typical only of the ferroelectrics with an 
‘order–disorder’ mechanism of PT. What matters for these 
crystals is a difference in the values of the macroscopic dielec-
tric relaxation time. The dielectric dispersion in a case of the 
aromatic analogs is limited to the kilohertz frequencies (\( 10^3\)– 
\( 10^4 \) Hz), while in the aliphatic ones it is shifted to the micro-
wave range (\( 10^8\)–\( 10^{10} \) Hz). One of the reasons for such a 
difference may be the size of the inertia moments of the 
organic dipoles as well as the way, in which the cations are 
bound through the hydrogen bound networks. The imida-
zolium cations have much higher inertia moments than methyl-
ammonium and formamidinium.

The most mysterious phenomenon in the R5M2X11 ferro-
electric group is the molecular mechanism of PT. In this 
regard, two possible contributions must be taken into account:

(i) ‘order–disorder’
(ii) ‘displacive’

The first contribution (i) is related to the dynamics of the 
organic cations, i.e. orientational disorder. The typical feature 
of the ferroelectrics with a continuous PT is the critical 
slowing down of the macroscopic relaxation time and a signifi-
cant entropy effect (\( \Delta S > R \ln 2 \)) indicating the mechanism of 
type (i).

The other contribution, of the ‘displacive’ type (ii), is not 
proved by experimental methods; however, based on the struc-
tural data, there are reasons to believe that the distortion of 
the discrete biotahedral units is likely to appear and, there-
fore, should be taken into account. This effect is well visible 
among the aliphatic ferroelectrics but it is marginal in aromatic 
one. The distortion of the biotahedra units causes a
change in the negative charge distribution in the crystal structures, related to the halogen atoms; this subsequently leads to a change of the P₆ values. There is one more factor necessary to analyze, namely, the electron lone pair effect. This effect should be attributed to the presence of the 6s² electrons of Bi (III) atom, which is less polarizable than 5x² electrons of Sb (III) atoms. All that leads to the conclusion that the anionic sublattice plays an important role in the generation of ferroelectricity in the R₂M₂X₁₁ type hybrids. Flexibility of the biotahedral units (corner-sharing octahedra) may be a decisive parameter in the origin of spontaneous polarization.

3.5. R₃MX₄ type compounds and their modification (e.g. R’′R’ R₂ MX₆)

Recently a first halobismuthate(III) compound characterized by mixed organic networks has been reported by Wang et al. The cationic substructure consists of two different molecules: one methylammonium (R’′) and two benzylammonium (R’′) ones as well as by an isolated octahedral unit [BiBr₆]⁻.%(CH₃)₂NH₂(C₆H₅CH₂NH₂)₂BiBr₆ appears to be a RT multiaxial ferroelectric with Pₑ = 1.0 μC cm⁻². The symmetry-breaking paraelectric–ferroelectric transformation is regarded in the Aizu notation as 3mfm at 386 K. The molecular mechanism of the ferroelectric PT is assigned to the change in dynamics of the organic cations thus the transition is classified as an ‘order−disorder’ type. The discovery of a new type of connection of halobismuthates(III) with a mixed anionic substructure creates a new path to design molecular multiaxial ferroelectrics.

Although R₃MX₄ type compounds seem to be the ‘poorest’ with regard to their ferroelectricity, an interesting phenomenon, related to the imidazolium based hybrid, has been detected. The most spectacular result was the preparation of a new crystalline ferroelectric material [(C₃H₅N₂)₅[Sb₂Br₁₁]] using an in situ solid-state chemical reaction, where the starting substrate was (C₃H₅N₂)₅[SbBr₆]₂H₂O.

4. Conclusions

In this review we present the attempts to find a correlation between crystal structures and polar/ferroelectric properties of hАОntimonates(III) and halobismuthates(III). The materials under consideration are characterized by a rich diversity of the anionic sublattice (more than 40 types), nevertheless, the ferroelectric properties are limited only to four specific compositions: RMX₄, R₂MₓX₉, R₃MX₅, R₃M₂X₁₁. Of importance is that within the mentioned stoichiometry, the anionic network dimensions are also changed. One should note that so far already 31 ferroelectrics have been synthesized and fully characterized from the above mentioned family, which put them on one line with a well-known family of perovskite-type ferroelectric crystals [ABX₃, A₂BX₆].

The RMX₄ type ferroelectrics (2 examples) indicate a 1D anionic structure, while the PTs are classified as a ‘displacive’ one. In the case of R₃MₓX₉ hybrids the ferroelectric ordering is observed only in the 0D (face-sharing biotahedral species) and 2D inorganic lattice (corrugated layer structure and small organic cations). The molecular mechanism of the paraelectric–ferroelectric PTs for the 2D ferroelectrics is of the ‘order−disorder’ type. In turn for the 0D compounds the mechanism is quite complex because the ‘order−disorder’ and ‘displacive’ contributions are possible. Moreover, in the case of the R₃MₓX₉ complexes of the 2D-type the ferroelastic structure in both paraelectric and ferroelectric phases is observed (possible biferroics), however, the coupling between the corresponding order parameters, polarization and deformation, is very weak.

With regard to R₂MₓX₆ complexes, the ferroelectricity is conditioned by the presence of the 1D anionic structures with different modifications and the majority of PTs is of the ‘displacive’-type with a minor ‘order−disorder’ contribution.

The R₃M₂X₁₁ hybrids are the most attractive from the viewpoint of polar properties. In this subclass, the inorganic part is created by the discrete anionic structures of the corner-sharing octahedra (0D-type). All of the R₃M₂X₁₁ crystals reveal ferroelectric properties. The molecular mechanism of the paraelectric–ferroelectric PT is not well recognized yet, however, the ‘order−disorder’ contribution, related to the dynamics of the organic cations, seems to play a key role. On the other hand the strong distortion of the anionic units as a result of the electron lone-pair effect (5s² (Sb) and 6s² (Bi)) influences additionally the total polarization of the material. Of great importance is that aliphatic analogs, e.g. (CH₃NH₃)₅[Bi₂Cl₁₁], (CH₃NH₃)₅[Bi₂Br₁₁] and (NH₂CHNH₂)₅[Sb₂Br₁₁] indicate dielectric properties similar to the well-known TGS (triglycine sulphate) family and thus make them the most promising materials for applications.

It appears that not all stoichiometries have been analysed in terms of possible ferroelectric properties and R’′R’′BiBr₆ is the best example. It should be also added that the complexes of iodobismuthates(III), both with the organic cations (e.g. methylammonium) and with the monovalent metals (mixed cationic sublattice), are the most advantageous in the case of absorbing materials in solar cells. We anticipate that the broadening group of molecular–ionic ferroelectrics will help to develop rational structure–property relationships, leading to materials with precisely tunable characteristics.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The paper is a result of the realization of the project no. UMO-2016/21/B/ST3/0046/2017 financed by the National Science Centre, Poland (Prof. G. Bator).

References

1 G. Rijnders, S. Currás, M. Huijben, D. H. A. Blank and H. Rogalla, Influence of Substrate-Film Interface


30 S. A. Adonin, I. D. Gorokh, D. G. Samsonenko, I. V. Koriol’kov, M. N. Sokolov and V. P. Fedin, Crystal Structures of Binuclear Bi(III) Chloride and Bromide...
Inorganic Chemistry Frontiers

Review


55 A. Lipka, Preparation and Crystal structures of 2,2’ Bipyridinium Pentachloroantimonate (C10H8N2H2)SbCl5.
and of the Metastable Modification of 4,4′-bipyridinium pentachloroantimonate (C_{10}H_{14}N_{2}H_{2})SbCl_{5}, Z. Naturforsch., 1983, **38b**, 1615.


65. S. Pohl, W. Saak, R. Lotz and D. Haase, On the Existence of Weak Interactions between Sb(m) and Phenyl Groups: SbBr₄(SbPh₃)₂, Sb₂Br₆(SePh₃)₂·2CH₂Cl₂, Sb₂Br₆(SPMMePh)₄, and (Ph₃P)₃Sb₂Br₆·CH₃CN, Z. Naturforsch., 1990, **45b**, 1355.


89 A. Kallel and J. W. Bats, Tris(Trimethylammonium) Nonachlorodiantimonate(III), \([NH(CH₃)₂]_3SbCl₉\), Acta Crystallogr., 1983, C41, 1022.
91 C. R. Hubbard and R. A. Jacobson, Molecular Bromine Bridging of \(Sb^{III} \cdot \cdot \cdot Sb^{III}\)–Anions and the Crystal Structure of Tetramethylammonium Nonabromoantimonate(III)-Dibromine, Inorg. Chem., 1972, 11, 2247.
92 M. Hall, M. Nunn, M. J. Begley and D. B. Sowerby, Nonahalogenodiantimon(III)ates; their preparation and the crystal structures of \([Hpy]_3[Sb₂Cl₉]_0\), \([nMe₃]_3[Sb₂Br₉]_0\), and \([nMe₃]_3[Sb₂Br₅Cl₉]_0\), J. Chem. Soc., Dalton Trans., 1986, 1231.
94 P. Sklarz, R. Jakubas, A. Piecha-Bisierek, G. Bator, M. Chański, W. Medycki and J. Wuttke, Organic-Inorganic Hybrid Crystals, \((2,4,6-CH₃PyH)₃Sb₂Cl₉\) and \((2,4,6-CH₃PyH)₂Bi₂Cl₆\), Crystal Structure Characterization and Tunneling of CH₃ Groups Studied by \(^1H\) NMR and Neutron Spectroscopy, Polyhedron, 2018, 139, 249.


118 M. Polomska and R. Jakubas, Dynamics of Ferroelectric Domains in (C6H4NH3)2Bi2Br11 Studied by Liquid Crystal Decoration Technique, *Ferroelectrics*, 1990, 106, 57.


131 M. Chański, A. Bielonska, R. Jakubas and A. Piecha-Bisioerek, Structural Characterization and Properties of Bis(1,4-H2-1,2,4-Triazolium) Pentachlorobismuthate (III) and Cocrystal of Ammonium Chloride with Tris(1,4-H2-1,2,4-Triazolium) Hexachlorobismuthate (III), *Polyhedron*, 2014, 71, 69.


