

# **Aurivillius Ceramics: Focus on Symmetry**

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## **Abstract**

Structure—physical properties relationships for Aurivillius ceramics are discussed, with emphasis in symmetry considerations. Single-crystal materials and polycrystal ceramics are analysed. Electric and magnetic coupling properties are considered. Colour Symmetry Groups and Texture Analysis tools are employed. Symmetry conditions for polarisation vectors and inverse pole figures related to Aurivillius phases are given.

**Keywords:** Aurivillius; symmetry; Neumann principle; texture.

## **INTRODUCTION**

Symmetry plays a decisive role in the structure—physical properties relationship of ferroelectric materials. In the case of Aurivillius ceramics, the application of symmetry considerations to structural and technical characterisation is not yet fully systematised. The present paper tends to contribute some useful elements in the indicated direction. Firstly, the proper connection between crystal symmetry and electric polarisation is remarked. Secondly, colour symmetry treatment of magnetic coupling properties is suggested. Finally, the application of symmetry and texture analysis tools to the description of Aurivillius polycrystal samples is illustrated.

## **SINGLE CRYSTALS**

### **Crystal Space Group and Electric Polarisation**

Table I resumes the crystallographic characteristics of some representative Aurivillius phases. A wide diversity of crystal-symmetry groups is evident.

**TABLE I** Crystallographic data of representative Aurivillius phases and related materials

<i>n</i>	Formula and references	Crystal system	Space group	Point group	Spontaneous polarisation
1	Bi <sub>2</sub> WO <sub>6</sub> [1]	O	P2 <sub>1</sub> ab	2 mm	P    a
	Sb <sub>2</sub> (W,V)O <sub>6-x</sub> [2]	M	P2 <sub>1</sub> /a	2/m	P = 0
	Abi <sub>2</sub> Nb <sub>2</sub> O <sub>9</sub> (A = Sr, Ca) [3]	O	A2 <sub>1</sub> am	2 mm	P    a
2	BaBi <sub>2</sub> Nb <sub>2</sub> O <sub>9</sub> [3]	T	I4/mmm	4/mmm	P = 0
	Bi <sub>3</sub> TiNbO <sub>9</sub> [4]	O	A2 <sub>1</sub> am	2 mm	P    a
	Bi <sub>2</sub> W <sub>2</sub> O <sub>9</sub> [5]	O	P2 <sub>1</sub> an	2 mm	P    a
3	Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub> [4]	M	B1a1	m	P ⊥ b
	α-Bi <sub>4</sub> V <sub>2</sub> O <sub>11</sub> [6]	M	C2/m	2/m	P = 0
	Bi <sub>5</sub> Ti <sub>3</sub> FeO <sub>15</sub> [7]/[8]	O	F2mm/A2 <sub>1</sub> am	2 mm	P    a
5	Ba <sub>2</sub> Bi <sub>4</sub> Ti <sub>5</sub> O <sub>18</sub> [9]	O	B2ab	2 mm	P    a
6	Bi <sub>7</sub> Ti <sub>4</sub> NbO <sub>21</sub> [10]	O	I2cm	2 mm	P    a

M: Monoclinic; O: Orthorhombic; T: Tetragonal.

The last column presents the conditions that are obligatory for the electric dipole moment, in correspondence with the point group that is associated with the reported space group.

The theoretical basis for the electric dipole column of Table I resides in the Neumann Principle (NP): The symmetry group of any physical property, in a given object, contains the structure point group as a subgroup. The NP leads to important consequences in relation to the physical properties of Aurivillius phases.

– For crystals belonging to centric point groups the occurrence of spontaneous polarisation is impossible. These crystals are not allowed to exhibit pyro- ferro- or piezoelectricity.

– For crystals associated with group 2 mm, the spontaneous polarisation vector P points necessarily parallel to the rotation axis (“a”). Components of P non-parallel to a are impossible in this type of crystals.

The application of the NP to the analysis of Aurivillius phases’ crystal

structures would lead to the improvement of a number of determinations, for example, of those reported in [3, 6, and 9].

### Magnetic Coupling Effects and Colour-Symmetry Point Groups

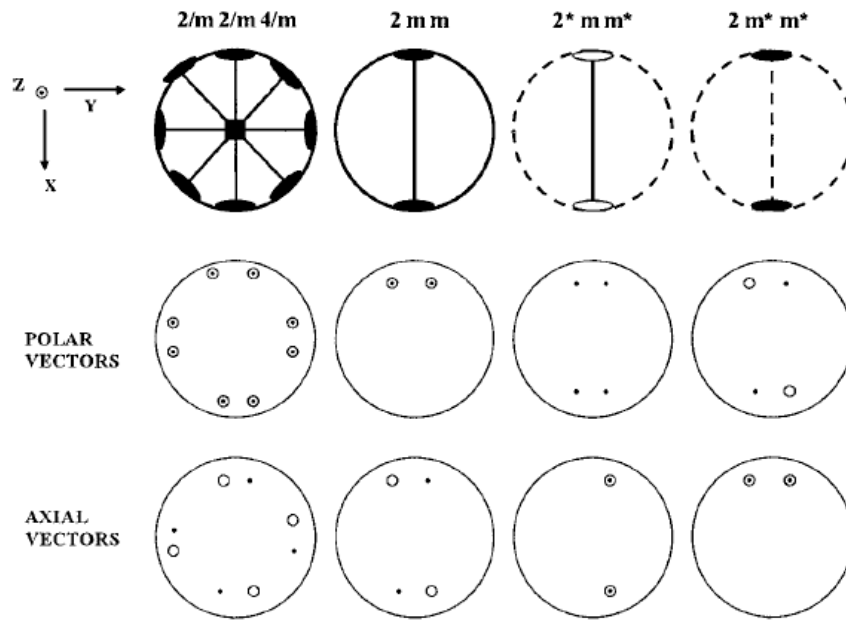
The potential occurrence of pyromagnetic ( $dB_j = i_j d\theta$ ), magnetoelectric ( $B_i = m_{ij} E_j$ ) and piezomagnetic ( $B_i = b_{ijk} T_{jk}$ ) effects in Fe-containing Aurivillius crystals motivates at present basic and technological interest. Just written symbols have the following meaning:  $B_j$ : magnetic induction vector,  $i_j$ : pyromagnetic coupling vector;  $\theta$ : temperature;  $b_{ijk}$ : piezomagnetic tensor;  $T_{jk}$ : mechanical stress;  $m_{ij}$ : magnetoelectric tensor;  $E_j$ : electric field intensity.

Experimental investigations on this subject are in their initial stages. The following is a brief mention of symmetry considerations to be taken into account in the study of the mentioned physical effects.

The magnetic coupling factors  $i_j$ ,  $m_{ij}$  and  $b_{ijk}$  are, respectively, first-, second- and third-rank axial tensors. The behaviour of axial vectors and tensors under symmetry operations shows interesting differentiating characteristics. An axial vector does not invert itself under the inversion operation. While a polar vector is always parallel to a normal symmetry plane, an axial vector is normal to such a plane.

Symmetry investigations of magnetic phenomena must include colour symmetry categories and rules.

Figure 1 represents, by means of stereographic projections, diagrams that show the symmetry behaviour of polar and axial vectors for the



**Figure 1.** Polar- and axial-vectors symmetry. Selected tetragonal and orthorhombic colour point groups.

Colour-symmetry groups that are possible in Aurivillius 2 mm crystals. The first row describes the colour symmetry elements, as follows. Filled square: fourth-order symmetry axis; filled boat; second-order symmetry axis; void boat: anti-symmetry second-order axis; continuous gross line or circumference: mirror; discontinuous line: anti-mirror. The second and third rows present the directions that are generated by the considered colour symmetry operations. Points show orientations towards the North hemisphere while empty circles denote South oriented ones.

Focusing attention on (typical of Aurivillius phases) 2 mm and m point groups, it may be demonstrated that magnetoelectric and piezomagnetic effects are possible for crystals belonging to both groups. Pyromagnetism is possible only for m point group.

## POLYCRYSTALLINE CERAMICS

### Texture and Polarisation Description

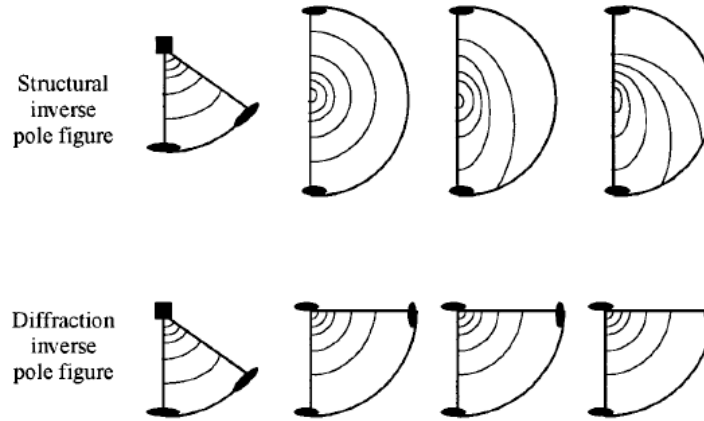
Analytical tools of Texture Analysis are suggested as appropriate instruments for characterisation of polarisation processes in ferroelectric polycrystals [11]. Figure 2 represents, by means of inverse pole figures (IPF), the symmetry changes that take place in a textured Aurivillius ceramic during a poling procedure. The considered hypothetical sample has been obtained by hot forging. It shows fibre (0, 0, and 1) texture. Sample direction for all IPFs is parallel to the direction of pressure application. Polarising field is also applied in this direction.

The starting condition is at a temperature above the Curie point,  $T > T_c$ . The inverse pole figure irreducible region that is shown corresponds to point group  $4/mmm$  ( $2/m2/m4/m$ ). The constant-density lines indicate higher population densities in the vicinity of crystal direction (0, 0, 1).

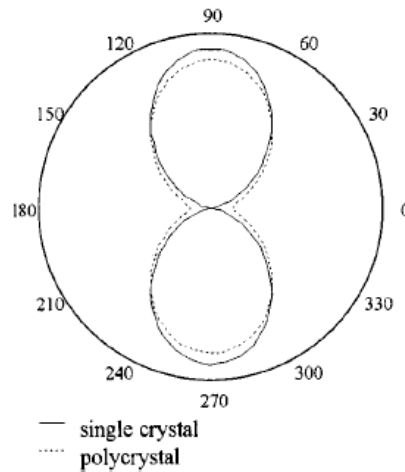
By cooling the sample,  $T < T_c$ , the structural IPF irreversible region enlarges itself as corresponds to  $2mm$  point group. Due to Friedel's law, the diffraction IPF shows  $mmm$  ( $2/m2/m2/m$ ) symmetry. In the virgin ferroelectric condition, the statistical symmetry of all the IPF coincides with that of the paraelectric structure ( $4/mmm$ ).

On poling, the structural IPF experiences a break-down of the statistical  $mmm$  symmetry. Favourably oriented domains grow by expanding their borders into non-favourably oriented regions. Diffraction is not sensitive to this phenomenon, so diffraction IPF remains invariant during poling.

Physical condition	a) paraelectric	b) virgin ferroelectric	c) poling	d) saturation
Temperature	$T > T_c$	$T < T_c$		
Crystal point group	2/m 2/m 4/m	2 m m		
Laue class		m m m		



**Figure 2.** Texture description of polarization process. Hot forged Aurivillius ceramic.



**Figure 3.** Dielectric constant surface representations. Single crystal and textured polycrystal ceramic of  $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$ .

## Macroscopic Physical Properties

IPF plays the role of weight function for physical properties average calculations. Figure 3 shows an example of texture-modulated dielectric constant for an Aurivillius polycrystal [11].

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