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$BiFeO_3$: Synchrotron radiation structure refinement and magnetoelectric geometry

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Abstract

Presently $BiFeO_3$ focuses attention due to its multiferroic nature. This phase shows a highly distorted perovskite crystal structure, with $R3c$ crystal symmetry. Details of the crystallographic structure are required input for a detailed explanation of its remarkable magnetoelectric properties. Present report contributes a high-resolution synchrotron radiation diffraction analysis of the $BiFeO_3$ crystal structure. Single-phased sample was obtained by conventional solid-state reaction under bismuth atmosphere. XRD experiment was performed on beamline 2-1, Stanford Synchrotron Radiation Laboratory, with 12 keV X-rays. For data Rietveld processing, Fullprof software package was applied. Obtained cell parameters (in Å, hexagonal system description) were $a = 5.57414(4)$; $c = 13.85882(12)$. Group-theoretical analysis of $BiFeO_3$ linear magnetoelectric tensor is presented. Only transverse effect is allowed by symmetry. Axial-symmetry polycrystal ceramics cannot show linear magnetoelectric coupling.

Keywords: X-ray methods; Ferroelectric properties; Magnetic properties; Magnetoelectricity; Perovskites

1. Introduction

$BiFeO_3$, the prototype single-phase magnetoelectric, is very popular nowadays.[1] Mentioned phase is rhombohedral (space group $R3c$)[2] ferroelectric (Curie temperature 769.85 °C)[3] and antiferromagnetic (Neel temperature 373.85 °C).[4] Its crystallographic and magnetic structures have been – and continue to be – studied by a variety of techniques,[5–7] including neutron diffraction.[8] Detailed knowledge of this phase's symmetry group, lattice parameters and atomic positions are required to perform comprehensive investigation of it's structure–properties relationships.[9]

In this scenario, present communication contributes an independent determination of $BiFeO_3$ crystallographic parameters, obtained by powder synchrotron radiation diffraction measurements. Powder diffractometry projects the three-dimensional reciprocal lattice into a one-dimensional reciprocal space. The one-dimensional nature of powder diffraction practically eliminates the influence of zero-shift and other systematic errors in the detection of very small lattice spacing *differences*. The mentioned advantage of powder diffraction grows up when we include the consideration of high-resolution synchrotron present-day powder diffractometers.

In general, magnetoelectric materials show linear and/or higher-order effects. Specifically, $BiFeO_3$ is well known for exhibiting quadratic effect.[10] Notwithstanding adverse conditions due to incommensurable magnetic ordering,[5] linear magnetoelectric effect in $BiFeO_3$ has been reported by Wang et al.,[11] Zvezdin et al.,[12] and Popov et al.[13] This phenomenon is characterized by means of the so-called magnetoelectric linear coupling tensor $\alpha_{ij} = \Delta E_i/\Delta H_j$. E_i and H_j represent, respectively, the electric and magnetic fields. The second part of the paper contains some basic geometrical considerations, leading to suggestions for successful experimental determination of α_{ij} in $BiFeO_3$. Axial nature of the analyzed tensor, and symmetry groups representation tools are taken into account.

2. Experimental

Polycrystalline $BiFeO_3$ was prepared by a conventional ceramic procedure. Stoichiometric quantities of Bi_2O_3 (Riedel-de Haen, 99.5%) and Fe_2O_3 (Merck, >99%) were homogenised for 3 h in a ZrO_2 planetary mill. After drying and sieving, the intimately mixed materials were heated in air at 850 °C for 2 h. The formation of a single-phase oxide was confirmed by conventional powder XRD. The room temperature [$T_{\text{sample}} = 25 \pm 1\,^\circ\text{C}$]

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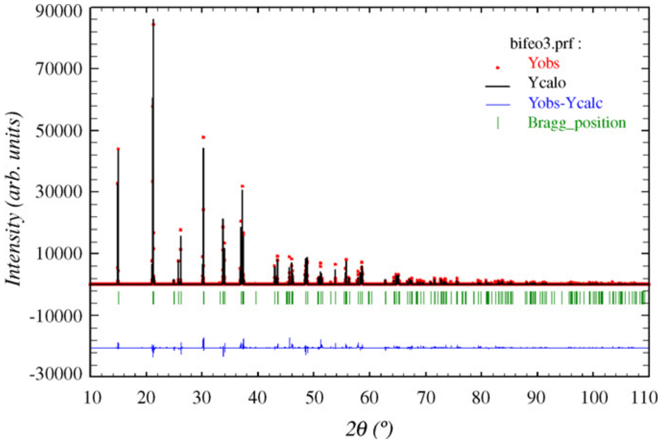

Fig. 1. Observed and calculated diffraction patterns for $BiFeO_3$.

Table 1
The crystal structure of $BiFeO_3$

Space group	*R*3*c* (hexagonal system description)
Cell parameters (Å)	$a = 5.57414(4)$; $c = 13.8588(1)$
Atomic parameters	
x	Bi: 0.00000; Fe: 0.00000; O: 0.895(1)
y	Bi: 0.00000; Fe: 0.00000; O: 0.206(1)
z	Bi: 0.00000; Fe: 0.7207(3); O: 0.628(1)
B (Å^2)	Bi: 1.00(2); Fe: 0.68(7); O: 0.2(2)
Occup.	Bi: 6.000; Fe: 6.000; O: 18.000
Mult.	Bi: 6; Fe: 6; O: 18
Bragg *R*-factor	9.5 Vol(Å^3): 372.918(5).

structure of the obtained material was investigated by means of high-resolution synchrotron X-ray powder diffraction. At beamline 2-1, Stanford Synchrotron Radiation Laboratory, the sample was mounted on a zero background holder and data was collected in reflection geometry at 12 keV ($\lambda = 1.03265$ Å) from 10° to 110° in 2θ. The scanning step was 0.01° in 2θ. Fig. 1 shows the experimental and calculated diffraction patterns.

3. Results of structure refinement

Table 1 shows the results of the performed structural analysis. Numbers in parentheses are standard deviations. The absence of parentheses means that the considered quantity remained fixed. Highly symmetric Bi sites were taken as reference coordinates.

Fig. 2 represents a unit cell of the investigated crystal and Fig. 3 shows some characteristic Fe–O interatomic distances in a perovskite octahedron.

4. Magnetoelectric geometry

One interesting aspect of linear magnetoelectric coupling is the axial nature of the characteristic tensor α_{ij}. As the magnetic field intensity H_j is a pseudo-vector (it does *not* invert under inversion symmetry), so α_{ij} also behaves interestingly under inversion and mirror symmetries. The systematic treatment of structure–properties relationships, with symmetry considerations taken into account, is by application of group-theoretical tools. Specifically, the Neumann Principle (*any macroscopic property's symmetry group necessarily includes the structure point group as a sub-group*) leads to the following criterion: For a physical property (polar or axial) tensor to be non-null, the

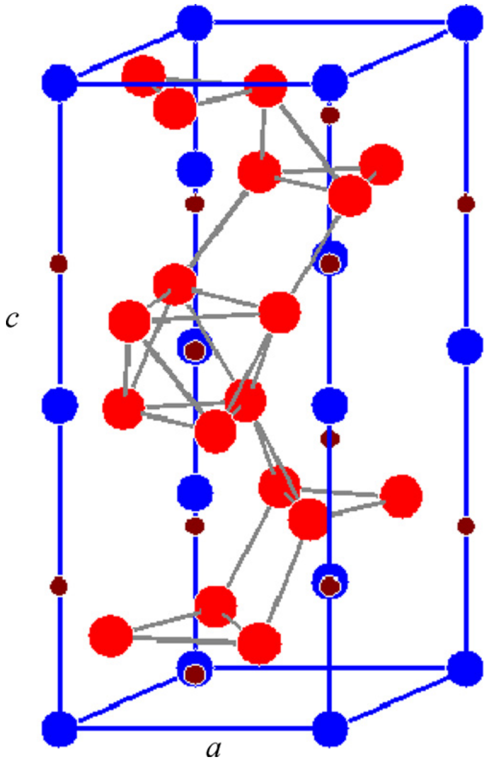

Fig. 2. $BiFeO_3$ (hexagonal) unit cell. Blue atoms are Bi, red ones are O and small brown are Fe. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

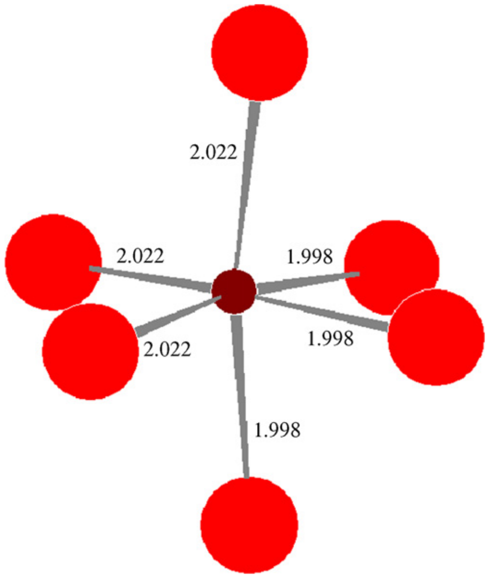

Fig. 3. Characteristic interatomic distances in a Fe–O octahedron. Errors affect the third decimal place.

Table 2
Irreducible representations of crystal point group $C_{3v} = 3m$

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	−1	R_z
E	2	−1	0	(y, x); $(R_x, -R_y)$

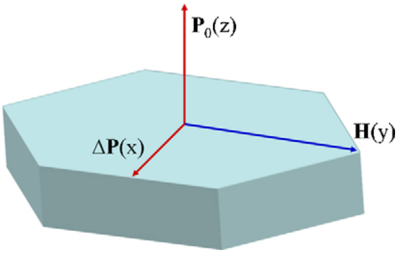

Fig. 4. Measuring transverse magnetoelectric coupling in $BiFeO_3$.

symmetry coordinates of the related (action-effect) quantities must belong to the same irreducible representation.

Table 2 shows the irreducible representations of the $C_{3v} = 3m$ point group, to which $BiFeO_3$ belongs.

In Table 2: x, y and z represent polar vectors' symmetry coordinates. R_x, R_y and R_z correspond to pseudo-vectors. It is seen that z and R_z belong to different representations, so $\alpha_{33} = 0$. On the other hand, the pairs (y, x) and $(R_x, -R_y)$ are matched with each other, both belonging to the degenerate irreducible representation E. From the given considerations it follows that the linear magnetoelectric coupling tensor for $BiFeO_3$ shows the following structure:

$$\alpha = \begin{bmatrix} 0 & \alpha_{12} & 0 \\ -\alpha_{12} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Linear longitudinal magnetoelectric coefficient for $BiFeO_3$ is always zero. Fig. 4 shows a suitable geometrical arrangement for measuring transverse α_{12} in a single crystal. For a polycrystal to exhibit linear (transverse) magnetoelectric coupling, a sharp texture resembling Fig. 4 is required. Axial-symmetry polycrystal ceramics do *not* show linear magnetoelectric coupling.

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