INTERATOMIC INTERACTIONS AND ZONE CENTRE PHONONS IN MULTIFERROIC BiFeO_3 CERAMICS

M. M. SINHA

Department of Physics
Sant Longowal Institute of Engineering and Technology, Longowal, Sangrur (Punjab)-148106, India
mm_sinha@rediffmail.com

RUBY

Department of Physics
Sant Longowal Institute of Engineering and Technology, Longowal, Sangrur (Punjab)-148106, India
gr_rby@yahoo.com

H. C. GUPTA

Department of Physics
Indian Institute of Technology, Delhi, Hauz Khas, New Delhi-110016, India
hcgupta@physics.iitd.ac.in

The existence of an epitaxially stabilized tetragonal-like (“T-like”) monoclinic phase in BiFeO_3 thin films with high levels of compressive strain has been reported recently. While their structural and ferroelectric properties are different from those of rhombohedral-like (“R-like”) films with lower levels of strain, little information exists on magnetic properties. In this study we have applied a short range force constant model by using normal coordinates to investigate the Raman and the infrared wavenumbers in tetragonal BiFeO_3 having space group $P4mm$ (C_{4v}^1). The calculation of zone center phonons has been made by using three stretching and six bending force constants. The calculated Raman and infrared wavenumbers are in very good agreement with the observed ones. The potential energy distribution has also been investigated for determining the significance of contribution from each force constant toward the Raman and the infrared wavenumbers.

Keyword: Raman spectra, infrared spectra, zone centre phonons, multiferroic materials

1. Introduction

The multiferroic ceramic BiFeO_3 (BFO) has attracted much attention in recent times not only because they possess ferroelectric and ferromagnetic properties, but also because the coupling between the magnetic and electric ordering leads to additional functionalities¹. In magnetoelectric multiferroics, a magnetic field may control the electric polarization or an applied electric field may control the magnetic phase, which leads to an application of electric-field-controlled magnetic data storage.^{2,3} The lead-free multiferroic BFO⁴ related materials have generated great interest for applications because of their superior thin-film ferroelectric and ferromagnetic properties, which are comparable to those of the

tetragonal Ti- rich lead zirconate titanate (PZT) system. The lead zirconate titanate $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) related materials have served an important role for such applications up until now⁵. A critical drawback of these materials is the presence of lead and the concern about the toxicity of lead-containing devices. BFO is also currently widely investigated as it offers room-temperature multi-functionality after very high polarization values were reported in 2003 for films grown on SrTiO_3 (STO) substrates⁴. However, it can be argued that the rhombohedral R3c structure of BFO-R possess significant difficulties and challenges. For example, the ferroelectric polarization of BFO-R is directed along the (111) direction giving rise to eight possible polarization orientations. As a result, ferroelectric switching is complicated and very hard to control for any meaningful multi-functionality. Therefore, BFO phase of different symmetry, which in principle could address these issues, is desired. This interest increased after recently it was predicted theoretically and confirmed experimentally that the structure and properties of BiFeO_3 films under a large, biaxial compressive strain could deviate significantly from the bulk material into a "super-tetragonal" structure with an extremely high c/a ratio.⁶⁻¹¹ This phase, in some sense, appears incommensurable to its rhombohedral counterpart and requires a thorough investigation much along the lines that bulk BFO has received.

There are several reports on the Raman spectra of BiFeO_3 obtained from single crystal^{12,13} polycrystalline samples^{14,15} and thin films on SrTiO_3 substrates^{16,17}. These spectra are similar with respect to the frequencies of the observed Raman lines and their assignment is based on the rhombohedral R3c structure. As an exception, Singh et al.¹⁶ have assumed that the BFO/STO thin film they studied has tetragonal P4mm structure, which seems not to be correct¹⁸. Indeed, the spectra of Singh et al.¹⁶ are practically identical to those from strain-free rhombohedral BiFeO_3 ¹²⁻¹⁵ and, in addition, the type of substrate (SrTiO_3) and the film thickness (600 nm) presuppose rhombohedral-like structure¹¹. It is, thus, important to undertake a fresh and complete theoretical investigation of the phonon modes for the single-crystal phase of tetragonal BFO. Many authors have made attempt to observe phonon modes experimentally in tetragonal phase of bismuth ferrite by using different methods. Iliev et al.¹⁸ have reported the polarized Raman spectra of true tetragonal -like BiFeO_3 by using polarized Raman spectroscopy. Mazumdar et al.¹⁹ have also reported the polarized Raman spectra for rhombohedral and tetragonal Bismuth ferrite. Raman scattering study of nearly tetragonal bismuth ferrite (BFO-T) thin films has been done by Choi et al.²⁰ BFO-T has also been studied theoretically by Tutuncu et al.²¹ using first principle calculations based on the plane-wave pseudopotential method. Singh et al.¹⁶ has observed three A_1 modes and three E modes in tetragonal BiFeO_3 thin films by employing a novel side-view backscattering geometry. They have also calculated the zone center phonon modes using short range force constant model by fitting their observed values which do not agree well with the values recently observed by others¹⁸⁻²⁰. It is, thus, important to undertake a fresh theoretical investigation of the phonon properties for the single-crystal phase of tetragonal BFO. We have

revisited the result by considering new set of observed phonon frequencies reported recently^{18, 19} by applying a short range force constant model.

2. Structure

In bulk form BiFeO_3 has rhombohedral structure with space group $R3c$ and for the thin-film phase, it is to be considered as tetragonal structure with space group $P4mm$ (C_{4v}^1)⁴. It was experimentally confirmed that under large, biaxial compressive strain the properties and structure of bismuth ferrite could change from bulk (rhombohedral) to supertetragonal structure with high c/a ratio⁷. Group theoretical calculations for BiFeO_3 in the tetragonal phase (SG: $P4mm$) predict 15 vibrational Raman modes at the BZ centre i.e

$$\Gamma = 4A_1 + B_1 + 5E$$

Out of these $3A_1$, $4E$ (E mode is doubly degenerate) are Raman active as well as infrared active modes, B_1 is only Raman active mode and $1A_1$, $1E$ are acoustical modes. Structure of tetragonal unit cell is shown in figure 1.

Fig. 1: Unit cell of tetragonal BiFeO_3

The primitive cell contains one formula unit i.e in primitive cell of tetragonal BFO there is one Bi ion, One Fe, one axial O1 ion and two equatorial O2 ions. Unit cell parameters used for BFO-T are: $a = 3.67 \text{ \AA}$, $c = 4.64 \text{ \AA}$ and position coordinates of Bi, Fe, O1 and O2 atoms are taken from reference²² and are given in Table 1.

3. Theory

The determination of the frequency of normal vibrations involves the kinetic and potential energies of the system. It is necessary to solve the secular equation to determine the normal vibrations frequency. Wilson developed the GF matrix method to solve the

secular equation for calculating the normal frequencies which is also known as normal coordinate analysis. The normal coordinate analysis is based on the Wilson–GF matrix method and makes use of Cartesian symmetry coordinates²³. The Eigen value equation is given by

$$\det \left| FG - E\lambda \right| = 0$$

Where F is a matrix of force constants and thus brings the potential energies of vibrations into the equation, G is a matrix that involves the masses and certain spatial relationships of the atoms and thus brings the kinetic energies into the equation, E is a unit matrix and λ which brings the frequency ν into the equation is defined by

$$\lambda = 4\pi^2 c^2 \nu^2$$

The matrix F was constructed by using short-range force constant model (SRFCM). The short-range forces are the forces that are effective up to certain neighbours only. Their magnitude diminishes generally after the second-neighbour inter-atomic interactions. The stretching forces between two atoms were assumed to be obeying the Hooke’s law. The stretching forces alone are not adequate to account for transverse vibrations in the lattice and therefore bending forces were included in the calculation. In this model bending forces are considered to arise from the resistance to the deformation of the angles of the triangles formed by atoms with its two neighbours. To evaluate the changes in the angles of a triangle, a comparison is made between the triangle in the equilibrium position and the projection of the deformed triangle onto the equilibrium plane.

Potential energies include short range valence forces between nearest neighbors Fe-O1, Fe-O2 and Bi-O2 and bending forces between O2-F-O2, O1-F-O2, Bi-O1-F, Bi-O2-F, O1-Bi-O1 and O1-F-O1. The input parameters used for the calculation are the lattice parameter, masses of the atoms, symmetry coordinates²⁴ and the available Raman and infrared wavenumbers. The obtained inter-atomic force constants thus obtained are presented in Table 2.

4. Results and Discussion

In the present calculation we have used three stretching force constants (Ki) and six bending force constants (Hi) along with lattice parameters, position coordinates of the atoms, masses of the atoms and the symmetry co ordinates. All the optical phonon modes

Table 1. Position coordinates of BiFeO3 (BFO-T) in P4mm structure

Atom	x	y	Z
Bi	0	0	0
Fe	0.5	0.5	0.439
O1	0.5	0.5	-0.164
O2 ₁	0.5	0	0.308
O2 ₂	0	0.5	0.308

Table 2. Interatomic force constants for BFO-T

Force constants	Between atoms	Distance(Å)/Angles(°) (for BFO-T)	Force constant (N/cm)
K1	Fe-O1	1.842	1.610
K2	Fe-O2	1.933	1.500
K3	Bi-O2	2.33	0.400
H1	O2-F-O2	84.32	0.160
H2	O1-F-O2	71.67	0.09
H3	Bi-O1-F	106.33	0.05
H4	Bi-O2-F	101.13	0.01
H5	O1-Bi-O1	85.46	0.01
H6	O1-F-O1	180	0.418

are calculated at the zone centre and are given in table 3 along with other observed values¹⁸⁻²⁰. A very good agreement has been obtained between the present calculated phonon modes and the available observed wave numbers. Singh et al.¹⁶ have observed three A₁ modes and three B₁ modes. They have also calculated zone center phonon modes corresponding to their observed results using short range force constant model. But their observed higher A₁ phonon modes are not in agreement with the phonon wavenumbers reported by a number of authors¹⁸⁻²⁰. In present investigation, the calculated results for A₁ and B₁ mode shows very good agreement with the observed phonon modes by Iliev et al.¹⁸, Mazumdar et al.¹⁹ and Choi et al.²⁰. To the best of our knowledge no experimental values are available for E mode and therefore no comparison is made for this mode. E mode calculated in present calculations matches well with other theoretically calculated values of E mode as reported by Tutuncu et al.²¹.

Table 3. Theoretical and experimental zone centre frequencies (cm⁻¹) in case of BiFeO₃

Modes	Observed by Mazumdar et al.[19]	Observed by choi et al.[20]	Observed by Iliev et al.[18]	Present calculations	Calculated by Tutuncu et al.[21]
A ₁	693	690	691	693	662
	365	365	367	350	427
	147	---	147	126	237
B ₁	269	275	271	299	332
E	---	---	---	614	612
	---	---	---	360	357
	---	---	---	212	207
	---	---	---	96	91
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The potential energy distributions (PED) for each mode are also investigated to determine the contribution of different force constants to various frequencies. It was observed from PED calculation that for higher energy modes mainly affected by internal vibrations of FeO₆ octahedra. These higher frequencies are contributed by stretching force constant Fe-O and bending force constant O-F-O. This observation is also in agreement with result of Choi et al.²⁰.

In the lower frequencies of A_1 and E mode, the force constant Bi-O play very significant role. The information available for E mode wavenumbers in literature is not sufficient and therefore, a precise determination of E mode wavenumbers is required for the comparison of the present investigation. An overall agreement is obtained from the present investigation with the available experiments.

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