Phonon Spectroscopy Near Phase Transition Temperatures in Multiferroic BiFeO₃ Epitaxial Thin Films

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We report a Raman scattering investigation of multiferroic bismuth ferrite (BiFeO₃) epitaxial (c-axis oriented) thin films from -192 to 1000°C. Phonon anomalies have been observed in three temperature regions: in the γ-phase from 930°C to 950°C; at ~ 370°C, Néel temperature ($T_N$), and at ~ -123°C, due to a phase transition of unknown type (magnetic or structural). An attempt has been made to understand the origin of the weak phonon-magnon coupling and the dynamics of the phase sequence. The disappearance of several Raman modes at ~ 820°C ($T_C$) is compatible with the known structural phase transition and the Pbnm orthoferrite space group assigned by Arnold et al. [1]. The spectra also revealed a non-cubic β-phase from 820-930°C and the same non-cubic phase extends through the γ-phase between 930-950°C, in agreement with Arnold et al. [2], and an evidence of a cubic δ-phase around 1000°C in thin films that is not stable in powder and bulk. Such a cubic phase has been theoretically predicted in [3]. Micro-Raman scattering and X-ray diffraction showed no structural decomposition in thin films during the thermal cycling from 22-1000°C.

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I. INTRODUCTION

Multiferroics are the materials which display a coexistence of at least two of the switchable states: polarization, magnetization or strain in the same phase [4]. In addition, they may also exhibit a magnetoelectric (ME) effect: magnetization induced by an electric field and electric polarization by means of magnetic field [5]. The current interest in multiferroics is largely based on engineered epitaxial and heterostructured thin films, because their physical properties are as good as bulk and permit technological applications in data storage, magnetic recording, spintronics, quantum electromagnets, and sensors [6–8]. Devices made up of multiferroic materials can perform more than one task and facilitate device miniaturization. A weak ME effect has been observed in most multiferroics, generally showing a small change in their spontaneous polarization under applied magnetic field [5–10]. However, the complete switching of ferroelectric domains by applied magnetic fields has rarely been observed. Why and under what circumstances a large coupling should exist and how to control the coupling are still open questions. Understanding the physics of the different possible interactions between magnetic and electric order parameters i.e. giving rise to magnetoelectric (ME) coupling would be very useful.

Magnetism and ferroelectricity are involved with local spin ordering and off-center structural distortions, respectively [11]. These are quite complementary phenomena that coexist in certain multiferroic materials. Currently, BiFeO₃ (BFO) is one of the most widely studied multiferroics because it is one of only two or three single-phase multiferroics at room temperature i.e. an antiferromagnetic (AFM) incommensurate phase with cycloidal modulation ($\lambda \approx 60$ nm) below $\approx 370$ °C [12, 13], ferroelectric up to $\approx 820$ °C [14], and ferroelastic between 820-930°C [15]. Bulk BFO crystallizes in a rhombohedral ($a = 5.58$ Å and $\alpha = 89.5^\circ$) structure at room temperature (RT) with space group R3c (C$\text{6}_3$) and antiferromagnetism of G-type [15, 16]. The structure and properties of bulk BFO have been studied extensively [13, 15, 16, 17, 18] and although early values of polarization were low ($P_t = 6.1$ μC/cm$^2$) due to sample quality, $P_t = 40-100$ μC/cm$^2$ was recently found in bulk by several different groups [15, 19]. The epitaxially grown thin films of BFO on SrTiO$_3$ (STO) substrates show very high values of $P_t (~ 100$ μC/cm$^2$) [6] compared to the best known ferroelectrics such as PbZrTiO$_3$ (~ 70μC/cm$^2$) and BaSrTiO$_3$ (~ 30μC/cm$^2$). This makes BFO a potential material for novel device applications.

The motivation for the present study is manifold. The first objective is to test the recent space group determination of the γ-phase reported by Arnold et al. [1] as being orthorhombic. Their definitive neutron study showed that the γ-phase is indeed stable (which in itself had been controversial), and that it has the same orthorhombic Pbnm orthoferrite symmetry as does the β-phase. A cubic Pn3m perovskite structure was definitely ruled out, although a body-centered orthorhombic space group was indistinguishable from the primitive Pbnm. A main aim of our Raman study is to test the orthorhombic crystal class for the γ-phase and see whether we can further distinguish between primitive and body-centered orthorhombic structures.

II. EXPERIMENTAL DETAILS

We investigated 300 nm (001) BFO thin films on STO (100) substrates with ~ 25 nm thick SrRuO₃ (SRO)
buffer layer by pulsed laser deposition (PLD). A Jovin Yvon T64000 micro-Raman microprobe system with Ar ion laser ($\lambda = 514.5\ nm$) in backscattering geometry was used for polarized and temperature dependent Raman scattering. Sample deposition and experimental details are given in [15].

The X-ray diffraction (XRD) pattern (see Fig. 2a) of the BFO films taken using CuK$_\alpha$ (1.5406Å) radiation show c-axis (pseudo-cubic <001> direction perpendicular to the substrate) orientation with a high degree of crystallinity. The c-axis length was found to be $3.95\ \AA$, which implies epitaxial strain is quite relaxed. This agrees with the reported values ($c = 3.997\ \AA$) [31].

The comparison of the unpolarized (perpendicular to the <001> of the substrate) Raman spectrum of BFO thin film with STO and SRO/STO spectra (cf. Fig. 2a in [15]) precludes any Raman contribution from the substrate and bottom electrode; to the contrary, we observed a dip, rather than a peak, at the STO strongest peak position. As is evident from the intensity comparison, all of these peaks are due to the BFO normal modes of vibrations and none of them arose from the substrate. We verified our results using target materials, single crystals, and also by growing (001) BFO films on different substrates.

III. RESULTS AND DISCUSSION

A. Phonons in the $\gamma$-phase

Fig. 1 shows the temperature dependent Raman spectra of (001)BFO film (300nm thick) on SrTiO$_3$ substrates with SrRuO$_3$ buffer layer (25nm thick). As can be seen from Fig 1a, four phonon features marked with arrows persist into the $\gamma$-phase from 930-950$^\circ$C. Therefore this confirms an existence of non-cubic $\gamma$-phase. No first-order Raman scattering from phonons is allowed for cubic Pm3n (because each ion is at an inversion center, all phonons are odd-parity). This is in agreement with the observation of an orthorhombic symmetry for the $\gamma$-phase by Arnold et al. [1]. Although the Raman lines are broad and weak at these temperatures, they exhibit no significant frequency shift at the $\beta$-$\gamma$ transition at 930$^\circ$C; nor are there additional lines above or below 930$^\circ$C. Therefore it is very likely that the structure is Pbmn in both $\beta$ and $\gamma$ phases and that no primitive-to-body-centered phase change occurs. Note that Fig 1 is for a thin film. Therefore we conclude that the films do not differ from single crystals and powders previously studied with regard to the $\gamma$-phase.

There is renewed interest in this $\beta$-$\gamma$ transition because of the earlier discovery of a metal-insulator transition at 931$^\circ$C where the orthorhombic-cubic transition takes place in bulk [13] and that the same transition may occur at 47 GPa at RT. Earlier Mössbauer studies established that at this pressure the magnetization also disappears [21]. Although Gavriluk et al. [21] concluded that this is a rhombohedral-rhombohedral symmetry-preserving Mott transition, that seems quite unlikely, because Haumont et al. [22] have found several phase transitions at lower pressure. Thus the symmetry of BiFeO$_3$ is not rhombohedral on either side of the high-pressure metal-insulator transition. Whether the transition is a Mott transition or a band transition is unresolved. Various theoretical models disagree: Vasquez et al. [3] get an ab initio Mott transition; Clark et al. [23] got a band transition to a semimetal from a screened exchange model.

Figs. 1b and b show the temperature variation (from RT up to 1000$^\circ$C) of unpolarized Raman spectra of a BFO (001) thin film. A closer observation near the phase transitions reveals two noticeable changes in the signature of the Raman spectra: the disappearance of several higher-order modes at $\sim 820^\circ$C and the complete disappearance of all the modes above 900$^\circ$C. This temperature behavior implies that BFO maintains its room temperature structure up to $\sim 820^\circ$C, indicating the structural (ferroelectric) phase transition, in agreement with the earlier investigations on BFO bulk single crystal and polycrystalline samples [24]. Note that thin films of BFO show first order phase transitions as in bulk, whereas STO and PbTiO$_3$ PTO are known to be first order in bulk but second order in thin films [24, 26].

The presence of the four peaks ($\sim 213, 272, 820$ and $918\ cm^{-1}$) above $820^\circ$C up to $\sim 950^\circ$C (Fig. 1b) shows that the intermediate beta-phase is not cubic (Pm3n) as reported by Haumont et al [24]. In fact, the phase diagram of BFO [27] and its most recent revised versions [15], show that BFO possesses a non-cubic $\beta$-phase between 820 to 933$^\circ$C before it goes to the $\gamma$-phase, and the $\beta$-phase was recently shown to be orthorhombic by using high temperature X-ray diffraction and domain structures [15] and neutron diffraction [4]. The complete disappearance of peaks at above 950$^\circ$C – not at 930$^\circ$C – indicates that the $\gamma$ high temperature phase also cannot be cubic (Pm3n), for which any first-order Raman scattering is forbidden.

Fig. 2a shows the room-temperature XRD patterns of an as-grown film and film after it underwent 1000$^\circ$C thermal cycle. As can be seen, the as-grown film is highly epitaxial showing only (00l) peaks and became polycrystalline after thermal cycling. In principle it is possible that the specimen would melt at high temperatures and then recrystallize in the specimen holder (bottom of the Pt crucible). However, we monitored the sample surface continuously with an optical microscope and no thermal decomposition was observed up to 1000$^\circ$C.

The Raman spectra (Fig. 2b) before and after heating show exactly same number of phonon modes, indicating either no decomposition up to 1000$^\circ$C or complete recrystallization, contrary to earlier studies [17], which could be due to the reduced surface/volume ratio, minimal surface imperfections and defects, and increased stabilization from the substrate. Note that the possibilities of subtle structural changes (small changes on angles and/or in-plane lattice parameters) cannot be completely
ruled out. However, the Raman frequencies before and after thermal cycling remain unchanged makes this unlikely. This fact favors films over bulk or powder samples for very high temperature studies in the future. Reaching the tetragonal and cubic phases extrapolated from the powder study of Arnold et al. [2] does not seem impossible with thin films.

B. Phonon anomalies near $T_N$:

There are discrepancies in the literature regarding both the crystal structure of (001) BFO thin films e.g. with several reports claiming tetragonal [6, 28], rhombohedral [29, 30], and monoclinic [31, 32] structure, and its phonons. Of particular interest regarding phonon-magnon coupling in BFO was the report [24] of a very
In general, the change in phonon frequency band and width with temperature can be caused by several factors, such as anharmonic scattering, spin-phonon coupling, lattice expansion and/or contraction due to anharmonicity and/or magnetostriction effects, and phonon renormalization resulting from electron-phonon coupling [33]. The latter one is not applicable here as BFO is a highly resistive material, and the carrier concentration is low. The change in ionic binding energies with temperature also affects the change in phonon bandwidth in ionic compounds. However, this is not applicable here as BFO is insulating. Figs. 1b and d reveal the fluctuation of phonon frequency and full-width at half maxima (FWHM) around 370°C (onset could be ∼360°C), which happens to be the $T_N$ of BFO. Near $T_N$ we see small (1 or 2 cm$^{-1}$) changes in both peak frequency and linewidth for three phonon modes at 72, 140, and 171 cm$^{-1}$. These satisfy the non-mean-field predictions of Nugroho et al [33]. This behavior could be the manifestation of phonon-magnon interaction that vanishes above $T_N$, 370°C. This weak interaction can be explained with the fact that the magnetic phase transition is not accompanied by a structural phase change. The observation of a rather weak phonon-magnon interaction is also consistent with the theoretical prediction of weak magnetization and ME coupling in BFO thin film by Ederer et al [35].

C. Phonon anomalies near 140-150K:

In order to study the cryogenic behavior of BFO thin films, we carried out scattering measurements (Fig. 3a) down to 81 K; no significant change in Raman spectra has been observed, indicating the RT structure remained unchanged down to 81K. However, a close observation shows phonon anomalies around 150K (Figs. 3b and c). This agrees with the observation of change in magnetic order at 150K by Pradhan et al [36], but the nature of this phase transition remains moot.

Figs. 3b and c show small anomalies in the frequency and linewidth of two phonon branches at 140 and 171 cm$^{-1}$ near 140K, a temperature at which anomalies have previously been reported. Although the changes are small and the data sparse, they are highly reproducible. We are aware of similar observations on single crystals by Brahim Dkhil [37], and we thank him for preprints of his work. The present data merely show that the same effects are present in thin films.

The nature of the phase transition at 140K remains unknown. There are anomalies in magnon scattering cross-sections [38, 39] and linewidth [40, 41], in mechanical loss tangent [38, 42] and 140K is the end-point in Almeida-Thouless data plots [40, 41]. However, the earlier sugges-
tion by our group \[43\] that 140K is a spin-reorientation transition temperature is not confirmed by very recent neutron scattering studies \[44\] and spin-glass effects \[45\] have also been suggested but are unproven.

D. Weak phonon-magnon coupling:

In our Raman spectra (Figs. 1- and d) we observed small (1 or 2 cm\(^{-1}\)) increases or decreases in phonon frequencies near \(T_N\). Note that this is observed for several different phonon symmetries. The symmetry-independent of the phonon-magnon coupling implies an interaction of form \(P^2M^2\) (where \(P\) and \(M\) are the polarization and magnetization, respectively) in the free energy, as first suggested for magnetoelectrics by Smolenaski and Chupis \[13\]. In general the coupling of phonons and magnons can occur through several different microscopic physical models: The Torrance-Slonczewski model \[40\] involves modulation of the crystal field at the spin site by the optical phonon and is significant for ions with unquenched orbital angular momenta, such as Cs\(^{3+}\) or Fe\(^{3+}\); the model of Buyers et al. \[47\] is an angular momentum coupling of spins in octahedra where the optical phonon eigenvector is rotation-like as viewed from the magnetic ion. However, such models do not give frequency anomalies near \(T_N\) like those we observed in BiFeO\(_3\). A rather detailed model of magneto-capacitance was given by Fox et al. \[48\] for BaMnF\(_4\) near \(T_N\), and related models by Scott \[49\] and by Glass et al. \[50\] for the BaMF\(_4\) family near T(2D), the two-dimensional spin ordering temperature [typically ca. 375 in that family].

The free energy of Fox et al. can be defined as:

\[
G = f(L^2, L_z^2) + BM^2 + (b_0 + b_1P + b_2P^2)M_xL_x + ... ,
\]

where \(P\) is the spin magnetization direction and \(L\) is (1/2)\(g\mu S^{1/2} (S+1)^{1/2}\) [ \(\sum (S_j \text{up} - S_j \text{down})\) ]; \(M\) is the weak magnetization \(M = g\mu S^{1/2} (S+1)^{1/2}\) [ \(\sum (S_j \text{up} + S_j \text{down})\) ]. Note that \(P\) is not the total polarization \(P\) but only the part induced by the magnetoelectric coupling: \(P = P_t + \hat{p}\) and it was carried out to second order in polarization \(P\), sublattice magnetization \(M\), and weak ferromagnetization \(L\), with the result that the magnetocapacitance varies with temperature as \((b_0 - b_1b_2)L_2(T)\), where \(b_0\), \(b_1\), and \(b_2\) are respectively the coefficients of magneto-electric free energy terms independent of, linear in, and quadratic in polarization \(P\). The authors noted that the mean-field theory, although generally not satisfactory for magnetic transitions, works very well for weakly damped ferromagnets because the expansion parameter \(L\) is small at all temperatures. Note that the sign of the magnetocapacitance term can be positive or negative depending upon the magnitude of \((b_0 - b_1b_2)\). Because they used mean field theory, their work neglected the small term near \(T_N\) due to fluctuations considered below.

Although the second-order theory of Fox et al. \[48\] was satisfactory for describing all the data in BaMnF\(_4\) near \(T_N\), it is not sufficient for phonon behavior in BiFeO\(_3\). In this case it is necessary to go to fourth order in \(L\). The reasons are explained by Nugroho et al. \[33\] in their work on YbMnO\(_3\). In this case the key term in the free energy is of the form \(gP^2L^2\), which for weak coupling gives an explicit interaction of electric field to \(L\) that results in a magnetocapacitance of

\[
(g^2P^2/kT) \int [<L^2(x)L^2(0)> - <L^2>^2] dx.
\]

Although this fourth-order term is higher order than the term in g<\(L^2\) considered by Fox et al. \[48\], it is singular at \(T_N\), because it is proportional to the cube of the correlation length (\(\eta\)) that diverges at \(T_N\).

The result is that the phonons in Raman effect in BiFeO\(_3\) of any symmetry will be expected to have small anomalies in their frequencies at \(T_N\). These small dips or jumps will be proportional to temperature \(t(\alpha - 1)\) \[33\], where \(t\) is reduced temperature, \(t = [T_N - T]/T_N\) and \(\alpha\) is the critical exponent describing divergence of the specific heat \[52\]. Since the \(\alpha\) is typically small, the phonon frequencies should vary approximately as \(T_N/[T_N - T]\) near \(T_N\) and in principle could be used to evaluate critical exponent \(\alpha\). However, in the present work the data are too imprecise for this chore, and even higher resolution would be insufficient due to phonon damping. The bump in phonon frequencies and linewidth are qualitatively predicted from the non-mean field theory of Nugroho et al. \[33\]. However, their model does not predict magnitudes for the height (increase in frequency) or width (how near the transition the increase occurs) of the bump. No anomaly at all is predicted by the mean-field theory of Fox et al. \[48\], which does not consider terms in the free energy introduced by Nugroho et al. \[33\]. A similar behavior has been observed at 150 K (Figs. 3b and c) that could be due to the change in magnetic ordering \[36\]. As matter of coincidence the bottom electrode SRO has a ferromagnetic phase transition at 150 K. Note that none of these peaks is related to SRO and a modulated effect is highly unlikely, but not impossible.

In summary, our Raman frequencies near \(T_N\) and 150 K show small peaks or dips for all phonon modes that are qualitatively similar to those predicted by Nugroho et al. \[33\], implying a general interaction of form \(gP^2L^2\), and the need for a fluctuation term neglected in the mean-field, weak ferromagnetism model of Fox et al. \[48\].

IV. CONCLUSION

In conclusion, high quality epitaxial (001)BFO films have been grown on (100) STO substrates using PLD. The XRD studies showed that films are c-axis oriented with high degree of crystallinity. The RT polarized Raman scattering of (001)BFO films showed pseudooctohombic monoclinic crystal structure contrary to the rhombohedral and tetragonal symmetries reported earlier. We observed the ferroelectric phase transition...
at around 820°C and no softening of Raman modes was observed at low frequencies, as in BFO single crystals. The AFM-PM phase transition at around 370°C caused some small changes in the phonon frequencies, linewidth, and/or intensities of several low frequency modes, indicating ME coupling in the material. A non-cubic $\gamma$-BiFeO$_3$ phase was observed between 931-950°C in the BFO thin films, in agreement with the accepted BiFeO$_3$ phase diagram. The spectra also revealed an evidence of a cubic $\delta$-phase around 1000°C in thin films that is not stable in powder and bulk.

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