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Abstract

We have grown $BiFeO_3$ bulk single crystals by a flux method and characterized the phonon spectra in detail by Raman scattering in the temperature range 4–1100 K. All the 13 Raman-active phonon modes predicted by group theory, $4A_1 + 9E$, were observed at low temperature and successfully assigned by a polarized Raman measurement. Moreover, drastic spectral changes in the Raman spectra were observed at temperatures 600–700 K and 1000–1100 K. These features are discussed from the viewpoint of phonon coupling with the magnetic ordering and the structural phase transition, respectively.

1. Introduction

For future innovative devices, there is a growing interest in multiferroic materials that show simultaneously ferromagnetic, ferroelectric and/or ferroelastic properties. $BiFeO_3$ has attracted the greatest attention in multiferroics because it shows both ferroelectric and antiferromagnetic (weak ferromagnetic) ordering at room temperature (Curie temperature $T_C \sim 1100$ K, Néel temperature $T_N \sim 640$ K) [1, 2] with a large ferroelectric polarization at 300 K in thin films [3–5].

Although Raman spectroscopy is a powerful tool with which to investigate lattice properties, magnetic ordering, structural phase transitions, etc in solids, Raman studies on multiferroics have been scarcely reported. $BiFeO_3$ is no exception: Singh *et al* first reported room-temperature phonon spectra of thin-film samples with a mode assignment [6]. More recently, Haumont *et al* observed the temperature variation of Raman spectra in a bulk crystal [7]. However, there is a large discrepancy between these results, and it is of urgent importance to present reliable phonon data to consider the basic lattice properties.
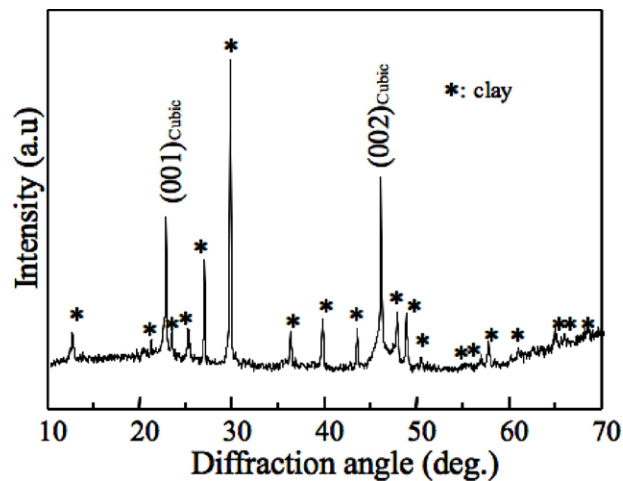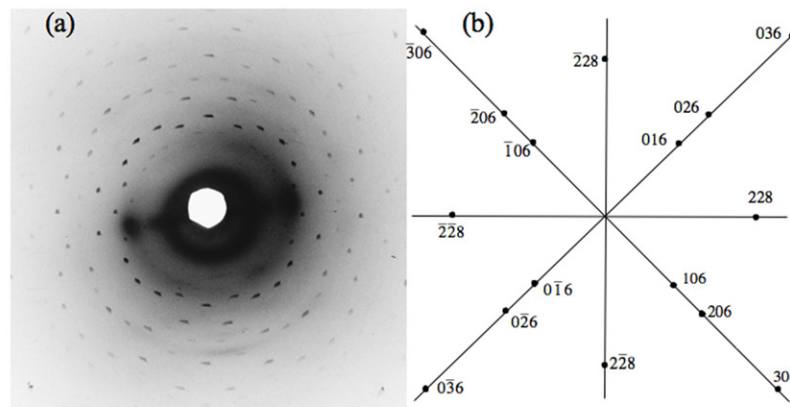
Figure 1. XRD pattern from the grown surface of $BiFeO_3$.

Here we report detailed Raman spectra of $BiFeO_3$ bulk single crystals in the temperature range 4–1100 K, and consider coupling of phonons with the magnetic ordering and the structural phase transition.

2. Experiment

In the ferroelectric phase, $BiFeO_3$ bulk crystal belongs to the rhombohedral system with space group $R3c$. It has lattice parameters $a = 5.61$ Å and $\alpha = 89.28°$ and the unit cell contains two distorted perovskite-like units [8]. The spontaneous polarization is oriented to the diagonal direction of this pseudo-cubic lattice $\langle 111 \rangle_{Cubic}$. Group-theoretical analysis predicts 13 Raman-active phonon modes at the Γ point; $\Gamma = 4A_1 + 9E$. If polarized Raman scattering is observed by back-scattering from the $(111)_{Cubic}$ plane, the A_1 modes can be observed by parallel polarization, while the E modes can be observed by both parallel and crossed polarization. Here, parallel and crossed polarization mean detection of scattered light intensity with polarization parallel and vertical to that of the incident light, respectively.

The present sample of $BiFeO_3$ single crystal was grown by a flux method using a Bi_2O_3/Fe_2O_3 source [9]. The flux mixture was placed in a platinum crucible sealed in an evacuated quartz tube, and small plate-shaped crystals with a typical dimension of $1 \times 1 \times 0.5$ mm^3 were obtained by a slow cooling process to room temperature. Figure 1 shows a typical x-ray diffraction (XRD) pattern of the sample embedded in clay with the grown surface facing outside. Although clay signals are overlapped, this pattern clearly shows that the grown surface has the $BiFeO_3(001)_{Cubic}$ plane, and no secondary or 'parasitic' phases like $Bi_2Fe_4O_9$ [9] are included. In figure 2(a) we show a Laue pattern of the grown surface of the sample, and its major spots are re-plotted in figure 2(b) with Miller indices of each reflection. This pattern indicates that the sample is a single crystal with grown surface $(001)_{Cubic}$. As described below, Raman spectra were observed in back-scattering geometry from the $(111)_{Cubic}$ and $(001)_{Cubic}$ planes. For back-scattering measurement from the $(111)_{Cubic}$ plane, the plate-shaped crystal was embedded in a resin and mechanically polished to expose the $(111)_{Cubic}$ plane. During the polishing process, the crystal orientation was checked by polarized microscopic observation using a crossed Nicol prism configuration.

**Figure 2.** Laue pattern of the grown surface of BiFeO$_3$ (a) and its major spots with Miller indices (b).
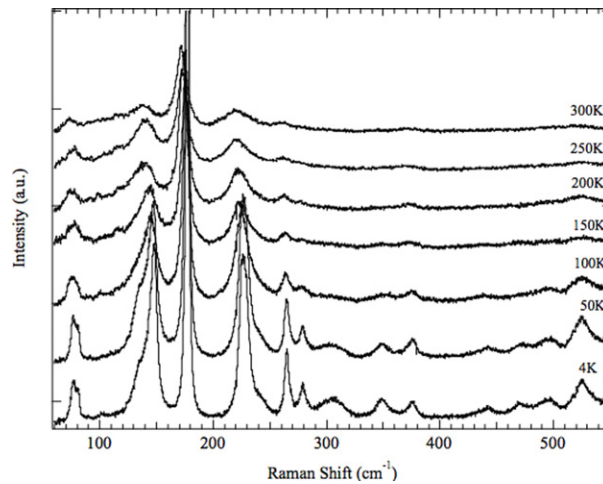
Figure 3. Raman spectra of the BiFeO$_3$(111)$_{Cubic}$ plane at 4–300 K by parallel polarization.

For low-temperature microscopic measurements at 4–300 K, the (111)$_{Cubic}$ plane sample was placed in a flow-type liquid-helium cryostat (Oxford Instruments), while for high-temperature measurements at 300–1100 K, as-grown samples with (001)$_{Cubic}$ surface were placed in an electric furnace (Linkam Scientific Instruments) placed on the stage of a Raman microscope. An argon-ion laser at 514.5 nm was used as an excitation source for Raman scattering. The laser beam was linearly polarized and focused by an objective lens to a diameter ~1 μm at the sample surface. The scattered light was collected by the same objective lens, fed to a double monochromator of focal length 85 cm for dispersion, and the spectra were detected by a liquid-nitrogen-cooled charge-coupled-device (CCD) camera.

3. Results and discussion

First, we observed phonon spectra of BiFeO$_3$ in detail at low temperatures. Figure 3 shows observed Raman spectra from the BiFeO$_3$(111)$_{Cubic}$ plane at 4–300 K by parallel polarization. Although 13 phonon modes (4A$_1$ + 9E) are expected by group theory, as described above, the

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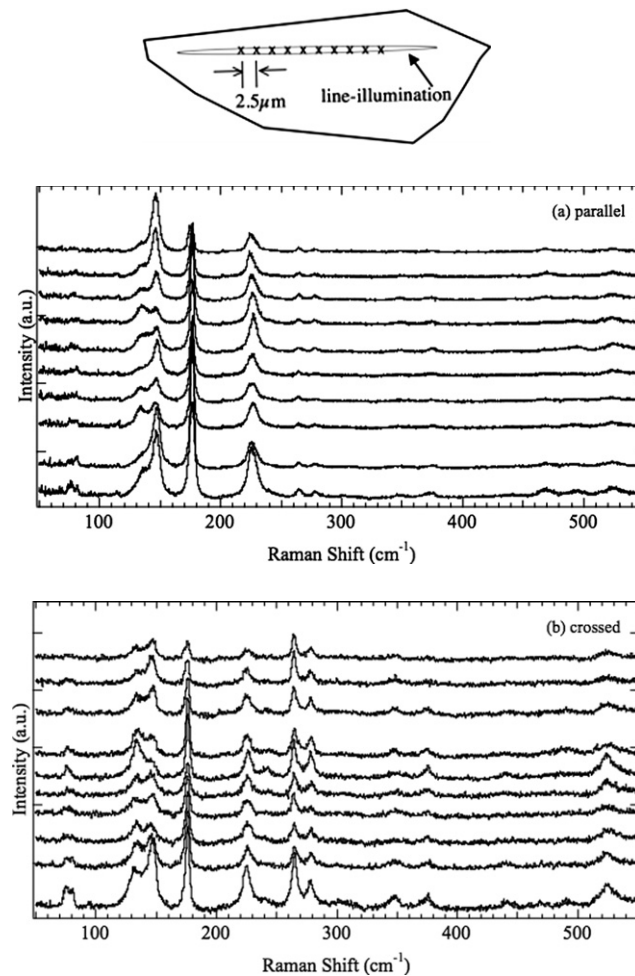
Figure 4. Polarized Raman spectra observed at different points of BiFeO$_3$ at 4 K: (a) parallel polarization (b) crossed polarization. The top figure illustrates the line-illumination scheme for serial detection.

number of clear features at 300 K is much less than this. However, with decreasing temperature (from top to bottom), the signal peaks become sharp, shifting to higher frequency, and we finally recognized 13 phonon modes at 4 K. Since we find no apparent or drastic spectral variation due to a structural phase transition in this temperature range, the sample is expected to remain in the rhombohedral structure down to 4 K.

Next, we classified the observed 13 phonon signals to A$_1$ and E modes as follows, with careful consideration of the domain structure [9]. Observation of the as-grown sample with (001)$_{Cubic}$ face by a polarized microscope with crossed Nicol prisms showed that the sample consisted of small domains with typical dimensions of a few to several tens of micrometres. The domain had different orientations of $\langle 111 \rangle_{Cubic}$, or permanent dipole direction, overlapping each other by 90° rotation of the crystal. Thus, the probed region may contain domains with $\langle 111 \rangle_{Cubic}$ direction different from the normal of the surface, and this leads to complicated Raman spectra. To overcome this difficulty, we used a line-illumination technique to select only expected domains with the $\langle 111 \rangle_{Cubic}$ direction exactly normal to the surface. As

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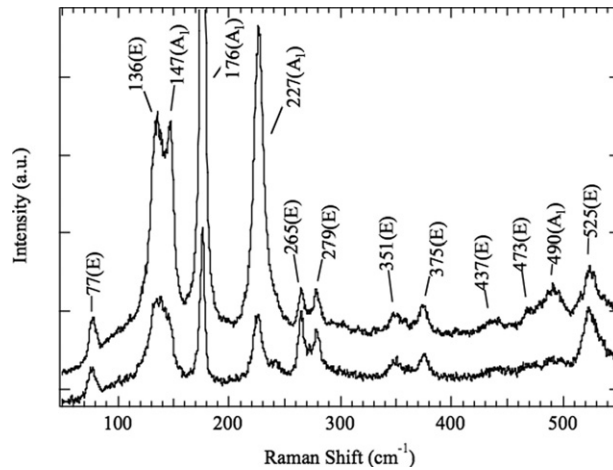
Figure 5. Raman spectra of BiFeO$_3$ at 4 K; (upper) parallel polarization, and (lower) crossed polarization.

drawn schematically in the top of figure 4, the sample surface was illuminated by a linearly prolonged laser beam with dimension 1 μm $\times$ 40 μm using a cylindrical lens placed before the microscope, and polarized Raman spectra were observed at ten different points separated by 2.5 μm. The results obtained at 4 K are shown in figures 4(a) and (b) for parallel and crossed polarization, respectively. In each figure, the spectrum (from top to bottom) derives from the left-hand end to the right-hand end points in the illuminated area. The signal intensity ratio changes depending on the position as expected if multiple domains are included in the probed area. We can clearly find here, however, that the dominant feature is the enhancement of four peaks at 147, 176, 227 and 490 cm^{-1} by parallel polarization, and the other seven peaks at 77, 136, 265, 279, 351, 375, 437, 473, and 525 cm^{-1} by crossed polarization, which is shown typically in figure 5. They correspond, respectively, to the A$_1$ and E phonon modes. The strong, low-frequency A$_1$ modes were not completely eliminated by crossed polarization, probably because 90° rotated domains still existed in the depth direction at the probed point, or the polished surface was slightly tilted from the correct (111)$_{Cubic}$ plane.

Our result is compared with that of Singh *et al* [6]. Recalling that Singh *et al* [6] used thin films grown on SrTiO$_3$(111) and there is a great difference in the sample preparation technique from ours, the agreement is very good for the three strong A$_1$ modes in the low-frequency region (our value; 147, 176 and 227 cm^{-1}), but not good for the others. Since Singh *et al* measured a thin-film sample at 300 K, the signals are generally much more obscure than ours and, furthermore, strong substrate signals overlap the spectra, making it very difficult to identify the film signal. Compared with our spectra and those of Singh *et al*, which have common features, the spectra of Haumont *et al* in a recent paper [7] are entirely different. They observed 11 Raman-active modes at 50–550 cm^{-1} (accurate frequencies are not given in their paper). However, they did not make mode assignment from their polarized Raman study, nor did they present any data such as XRD to identify the grown products. Thus, further comparison is not possible.

Finally, we analysed the Raman spectra of BiFeO$_3$ at high temperatures from the viewpoint of coupling between phonons and phase transitions. Figure 6 shows back-scattered Raman spectra from BiFeO$_3$(001)$_{Cubic}$ plane at 300–1100 K. On increasing the temperature (from bottom to top with 100 K step), all signal peaks shift to a lower frequency and broaden because of lattice anharmonic effects [10]. Here, in addition, we can easily find the following anomalies:
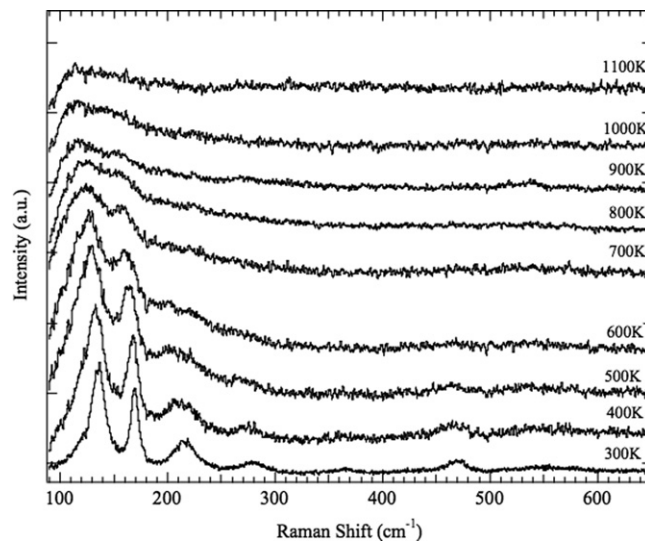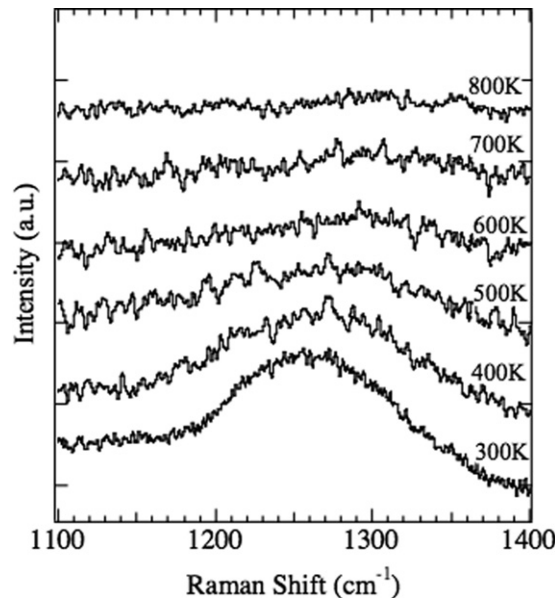
Figure 6. Raman spectra of $BiFeO_3$ at 300–1100 K.

Figure 7. Raman spectra of $BiFeO_3$ at 300–800 K.

(a) the low-frequency peaks significantly broaden and merge into a broad peak at 600–700 K, and (b) the signals disappear almost completely around 1000–1100 K. Since bulk $BiFeO_3$ shows phase transitions of magnetic ordering at $T_N \sim 640$ K, (a) may suggest coupling between phonons and the spin system. If $BiFeO_3$ enters the undistorted cubic perovskite phase at above $T_C \sim 1100$ K, then (b) is not surprising since there is no Raman-active phonon mode due to its high symmetry. Previous papers on similar compounds like $YMnO_3$ [11], $LaMnO_3$ [12], and $RFeO_3$ (R = Tb, Dy, Ho, Er, Tm) [13] reported that important first-order phonon signals

appeared up to $\sim$600 cm^{-1}. In the present experiment, we actually observed the range of 50–1400 cm^{-1}, and confirmed that no important features appeared beyond 600 cm^{-1} except for a peculiar broad signal at $\sim$1250 cm^{-1} as shown in figure 7. This may be due to higher-order phonons, or, since it suddenly disappears at 600–700 K, the mode may have some origin of magnetic ordering. Further studies on magnetic ordering/phonon-spin coupling are now in progress.

4. Conclusion

We investigated BiFeO$_3$ bulk single crystals by Raman scattering in the temperature range 4–1100 K. We have successfully observed all the allowed phonon modes at 4 K with a tentative mode assignment based on a polarized Raman study. Drastic changes in Raman spectra were observed at 600–700 K and 1000–1100 K, and discussed in combination with the magnetic ordering and the structural phase transition, respectively.

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