Structure of BiFeO₃ ceramics treated with hot-pressing

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BiFeO₃ ceramics synthesized at high temperature and pressure is observed to possess large spontaneous polarization and magnetism. The selected-area electron diffraction patterns indicate the coexistence of polycrystalline and nanocrystalline grains in the hot-pressed samples. Raman spectroscopic studies reveal that the Bi–O bond strain and cations (Fe³⁺) away from the oxygen octahedral center induce the polarization. The Fe–O bond strain, oxygen octahedral rotation around the [111] axis, and electromagnons build a long-range interaction between electrical polarization and magnetic moment reorientation to form an incommensurate spiral magnetic structure. This work clearly shows that the hot-pressed treatment can modify the structure and properties of BiFeO₃ ceramics.

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Multiferroic materials have attracted much attention due to their ferromagnetism (FM) and ferroelectricity (FE) properties [1–4]. BiFeO₃ (BFO) is one of the well-known multiferroic materials exhibiting the coexistence of ferroelectric and antiferromagnetic phases at room temperature. BFO ceramics has a ferroelectric–paraelectric (FE–PE) state transition at a Curie temperature of 1123 K and an antiferromagnetic-paramagnetic (AFM–PM) transition at the Neel temperature of 643 K. The materials are useful in new types of devices such as data storage, spintronics, and electro-optics [5,6]. Single phase BFO is hard to synthesize and thus its ferroelectric hysteresis loop is barely observed due to the high leakage current. Previously, some methods such as solid state reaction (rapid liquid phase sintering) were reported to prepare pure BFO ceramics [7,8] and the saturated ferroelectric hysteresis loop with a spontaneous polarization (2Pₑ) of 10 µC/cm² and coercive field (Eₑ) of 75 kV/cm was observed. Recently, various film techniques were applied to enhance the ferroelectric properties by means of epitaxial stress utilizing the mismatch between the film and substrate [1,3,5]. The (111)-oriented epitaxial BFO film on the SrTiO₃ substrate shows large spontaneous polarization (2Pₑ) of 150 µC/cm² and high coercive field (Eₑ) of 200 kV/cm. The polarization is very sensitive to the ferroelectric domain, applied external field, and mechanical stress. Large polarization in thin films was first ascribed to the effect of epitaxial strain with respect to the bulk. In addition, it has been shown that the electric polarization in BFO is intrinsic [9,10], Cazayous et al. [11], Rout et al. [12], and Haumont et al. [13] observed anomalies in the phonon spectra of the BFO in the magnetic transition (Tₐ) and ferroelectric transition (Tₑ). The results suggest that the multiferroic properties may arise from the strong phonon anomaly.

In order to investigate the ferroelectric origin, the effects of high pressure on the BFO properties and structure have been studied [14,15]. The high external pressure only affects the inter atom distances and the ferroelectric instability is known to be very sensitive to pressure. The energetic order between different phases in the materials can be notably modified by applying an external pressure. In the present work, we investigate the structural discrepancies of three BFO ceramics synthesized under different sintering conditions. The effects of high pressure on the structure of the BFO ceramics are investigated and discussed in detail.

The BFO ceramics were prepared by the sol–gel method and under high pressure. The BFO powders were first prepared by the sol–gel method. The BFO powders were annealed at 1073 K for 20 min and designated as BFO-1. BFO-1 was ground and then annealed for 20 min at 6 GPa and then annealed at 1073 K for 20 min and designated as BFO-2 (denoted as BFO-1/BFO-2/BFO-3, respectively). BFO-1 did not exhibit any ferroelectric properties. The room temperature ferroelectric (P–E) loops and magnetic hysteresis (M–H) loops of BFO-3 have been reported [16]. In contrast with BFO-3, smaller polarization and weak magnetism were observed from BFO-2. In this work, the samples were characterized by X-ray diffraction (XRD), high-resolution transmission electron microscopy (TEM, JEOL JEM-4000EX at 200 kV) equipped with
selected area electron diffraction (SAED). The low-temperature Raman spectra were acquired on a T64000 triple Raman system using the 514.4 nm line of an Ar ion laser as the excitation source (average power of ~500 mW and beam diameter of ~100 µm).

The XRD patterns of BFO-1, BFO-2, and BFO-3 are depicted in Fig. 1(a). These patterns clearly indicate the distorted rhombohedral structure of the hot-pressed BFO ceramics. Fig. 1(b) shows the magnification of the partial 2θ ranges, 31°–33°, 38°–40°, and 50°–53°. The rhombohedral characteristic peak splitting in the range of 31°–33° is clearly observed from the BFO samples. The double peaks near 32° shift and almost merge to form a broad peak as the hot-pressing temperature increases from 1098 K to 1123 K. The broadened peaks shift towards higher diffraction angles. The evolution of the diffraction peak as the annealing temperature is increased reveals structural change encompassing high rhombohedral distortion and compressive strain remnant in the hot-pressed samples. The double peaks in the range of 38°–40° are also slightly widened and obviously shift to higher diffraction angles. The peak in the range of 50°–53° shows a similar trend and broadening of the diffraction peaks implies the existence of smaller grains and remaining stress between small grains. These XRD results suggest that hot pressing affects the structure of the BFO samples.

The representative SAED patterns of BFO-3 are shown in Fig. 2. Patterns (b) and (c) are taken from the selected locations in (a) labeled as 1 and 2. As shown in Fig. 2(b), the two sets of discrete diffraction spots and two diffraction rings indicate that BFO-3 consists of many polycrystalline grains with different sizes and orientations. Fig. 2(c) also reveals that BFO-3 consists of some crystalline grains. In conjunction with the aforementioned XRD data, it can be inferred that some grains unfreeze and consolidate during the hot-pressing process. The nanocrystalline and polycrystalline structures are observed to coexist in BFO-3.

The temperature-dependent Raman spectra in the range of 10 to 650 cm⁻¹ taken from BFO-3 are shown in Fig. 3(a). With decreasing measurement temperature (from bottom to top), the signal peaks become sharper and gradually shift to higher frequencies. Finally, there are 18 Raman modes at 80 K. By dividing the Raman spectra, modes at 17.2, 24.4, 58.2, 74.3, 145.7, 174.6, 222.3, 263.3, 278.0, 302.1, 349.0, 372.5, 437.3, 473.6, 522.2, 529.0, 555.0, 610.1 cm⁻¹ can be discerned. Fig. 3(b) is the corresponding Gaussian fit in the range of 250–650 cm⁻¹ for the Raman spectra obtained at 80 K. These modes can be assigned by comparing to previous results [11–13,17,18]. The four sharp modes at 145.7, 174.6, 222.3, and 522.4 cm⁻¹ are assigned as the A₁ modes. The three modes at 17.4, 24.7, 58.0 cm⁻¹ are the magnons in the hot-pressed samples, which are in agreement with the observations by Singh et al. [19] and Cazyous et al. [20]. The 17.4 and 24.7 cm⁻¹ peaks assigned as σ and γ magnons are considered to
Another noticeable mode at near 522 cm$^{-1}$ in the spectra is assigned as A$_{1}$-4 [23,24] which is in agreement with the observation of Lobo et al. [25]. Fitting with the Gaussian function, we obtain the peak at 522.2 cm$^{-1}$ with FWHM of 6.9 cm$^{-1}$ from BFO-3, 523.9 cm$^{-1}$ with FWHM of 16.8 cm$^{-1}$ from BFO-2, and 524.7 cm$^{-1}$ with FWHM of 17.5 cm$^{-1}$ from BFO-1. As reported early, the A$_{1}$-4 mode reveals Fe–O bond stretching or strain along the [111] axis and the E$_{8}$-mode is related to the Fe$^{3+}$O$_{6}$ octahedral rotation around the [111]-axis. Sharpening of the A$_{1}$-4 mode is induced by the long range interaction.

The EMs may affect the binding state of the Fe–O bond in the Fe$^{3+}$O$_{6}$ octahedral and magnetic moment orientation of the Fe$^{3+}$ ions. The EMs combined with the ferroelectricity and magnetic modes induce an incommensurate spiral magnetic structure [4,20] which is the origin of the enhanced magnetism. Meanwhile, modifications of the E-1 and 4A$_{1}$ modes are associated with the enhanced polarization. The EM activity is crucial to the multiferroic properties.

By considering the XRD and SAED patterns together, the structural discrepancies can be attributed to different sample preparation techniques or heating conditions that may impact the crystalline structure. The high pressure affects the inter-atomic distances and high temperature controls the phase. The high temperature and high pressure act in concert to form the complex phase in BFO-3. The branches of the EMs build long-range electric and magnetic interactions forming an incommensurate spiral magnetic structure in BFO. The EMs also modify polarization and the long-range electric and magnetic interactions constitute the origin of the multiferroic properties.

In summary, our measurements show structural discrepancies in BFO samples produced by hot-pressing sintering. Some polycrystalline and nanocrystalline grains coexist in the hot-pressed BFO samples. The 4A$_{1}$-mode in the Raman spectra shifts and are enhanced. The evolution of the E-1 mode corresponds to the shifts in the Bi$^{3+}$ and Fe$^{3+}$ ions from their “ideal” positions due to Bi–O and Fe–O bond strain and stress, related structural distortion, and polarization. The EMs provide long-range interactions between electrical polarization and the magnetic moment. Owing to the coexistence of EMs and enhanced A$_{1}$-4, E-4, E-5, and E-8 modes, an incommensurate spiral magnetic structure is formed in the hot-pressed samples in which the magnetism is modified. The long-range interaction associated with electrical polarization and magnetization is the key to the multiferroic properties of the BFO samples. This work indicates that a high pressure can modify the materials structure to get polycrystalline grains with special properties and it is a very useful synthesis method.

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