Investigation on dependence of $BiFeO_3$ dielectric property on oxygen content*

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The influence of oxygen content on the dielectric property of $BiFeO_3$ ceramics is studied by experiment and first-principles calculation. The experimental result demonstrates that the dielectric constant of $BiFeO_3$ is strongly dependent on introduced oxygen and oxygen vacancies. By comparison with $BiFeO_3$, the introduced oxygen and oxygen vacancies can lead to a reduction in dielectric constant of $BiFeO_\delta$ at a lower frequency. The first-principles calculation also shows a similar result when photon energy is in a range of 2.0–4.1 eV. A likely explanation is that this oxygen content dependence may be ascribed to the distortion of Fe–O octahedron structure due to oxygen vacancies or excess oxygen ions in the crystal structure of $BiFeO_3$.

Keywords: $BiFeO_3$, dielectric property, oxygen content
PACC: 7780, 7720, 7870B

1. Introduction

Materials that have coupled electric, magnetic, and structural order parameters are currently gaining more and more attention due to the fact that multiferroics materials show a coexistence of electric polarization and magnetization, and have interesting physical properties related to potential technical applications, such as information storage, emerging field of spintronics, and sensors. $BiFeO_3$ (BFO) is known to be the only material that exhibits multiferroism at room temperature. It is a rhombohedrally distorted ferroelectric perovskite ($T_C \approx 1100$ K) with the space group $R3c$ and shows G-type antiferromagnetism up to 643 K (T_N).[1,2] Recently, interest in this material has increased considerably, due to the report of a large electric polarization and a nonzero magnetization in epitaxial films of $BiFeO_3$, both above room temperature.[3] Theoretically, the crystal and the electronic structures, the spontaneous polarization, and the coupling between ferroelectric and magnetic order parameters of $BiFeO_3$ have been studied by first-principles density functional theory calculations.[4−8] Experimentally, $BiFeO_3$ ceramic and thin film have been prepared by many methods. Meanwhile, the electrical and the magnetic properties, the phase transition and the phase stability, and the ferroelectric properties of these samples have been studied in detail.[9−13]

As is well known, the $BiFeO_3$ films are crystalline in a perovskite single-phase. And film crystallization is affected by oxygen partial pressure at a fixed lower deposition temperature. The XPS result has shown that $BiFeO_3$ thin film deposited at 6.666 Pa has a single phase with a Fe^{3+} valence state and a saturated hysteresis loop with a high polarization value of 71.3 μC/cm^2 and a low coercive field of 125 kV/cm. All these results imply that oxygen partial pressure in the deposition process has a significant effect on the ferroelectricity of BFO thin films.[14] Yet Ederer and Spaldin[15] investigated $BiFeO_3$ by first-principles density functional calculation and found that the electric polarization was not significantly affected by oxygen vacancies. However, the origin for the difference between these studies is currently under debate. Particularly, the influence of oxygen content on the dielectric properties of $BiFeO_3$ continues to be the focus of recent studies, experimentally and theoretically.[12−15] In the present paper, we investigate the dielectric properties of $BiFeO_3$ with different oxygen contents. In order to better understand the experimental results, we study the dependence of oxygen content on the dielectric property of polycrystalline $BiFeO_3$ by the first-principles density functional theory.

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2. Experiment and method

2.1. Experimental arrangement

The multiferroic $BiFeO_\delta$ samples with different values of oxygen content (δ) were prepared by solid state reaction method. High purity Bi_2O_3 (99.99%), Fe_2O_3(99.99%) were weighed carefully in stoichiometric proportion and thoroughly mixed in an agate mortar for about 2–3 h, with high purity isopropyl alcohol used as a medium. The samples were calcined at 650 °C for 1 h in an alumina crucible. The calcined material was once again ground thoroughly prior to heating at 810 °C for 1 h. Furnace with an accuracy of ±1 °C is used for calcinations.[16] And, nitrogen was introduced in order to eliminate the impure phase structure of $BiFeO_3$. The $BiFeO_\delta$ ceramic samples with different oxygen contents were obtained by annealing them under different temperatures and oxygen pressures. Oxygen content was measured by Potarized Zeeman Atomic Absorption Spectrophotometer (Z-5000). The structure of the $BiFeO_\delta$ sample was analysed by x-ray diffraction (XRD) with CuKα radiation. The dielectric constant and the loss tangent were measured with an HP 4294A precision impedance analyzer from 100 Hz to 1MHz at room temperature.

2.2. Details of first-principle calculation

First-principles plane-wave pseudo potential density functional theory as implemented in the CASTEP code was employed.[17] The generalized gradient approximation (GGA) PW91 functional was used. Spin polarization was considered in calculation. For a small error expected, an ultra soft pseudo potential was used for optimizing the geometry and a norm-conserving pseudo potential was used for investigating dielectric properties. For all structures we relaxed the ionic positions while keeping the lattice vectors fixed until the Hellman–Feynman forces were less than 10^{-2} eV/ Å. All results were obtained by using projector-augmented plane-wave method through explicitly treating 15 valence electrons for Bi (5d106s26p3), 14 for Fe (3p63d64s2), and 6 for O (2s2sp4). Brillouin zone integrations were performed with a Gaussian broadening of 0.1 eV during all relaxations. These calculations were performed with a 4×4×4 Monkhorst–Pack k-point mesh centred at Γ and a 450 eV plane-wave cutoff, both of which result in good convergence of the computed ground-state properties. During the calculation, we used the crystal structure obtained by optimizing the atomic positions within the experimentally observed $R3c$ symmetry. Our calculated structural parameters were identical to those given in Ref. [2]. To investigate the influence of oxygen content on the dielectric property of $BiFeO_3$ we performed calculations for a unit cell doubled along one of the rhombohedral lattice vectors (so that it contains four formula units), in which we introduced one oxygen atom corresponding to $\delta = 3.25$, removed one oxygen atom corresponding to $\delta = 2.75$, two oxygen atoms corresponding to $\delta = 2.50$, and three oxygen atoms corresponding to $\delta = 2.25$. In all cases, the dielectric properties were investigated after relaxing all ionic positions in the supercell.

3. Results and discussion

Figure 1 shows the XRD patterns of the $BiFeO_\delta$ samples annealed at different temperatures and oxygen pressures. The pure phase structures of $BiFeO_3$ for these samples are unchanged since high intense peaks are evidently observed and no other peaks of impure phase structure appear in Fig. 1.

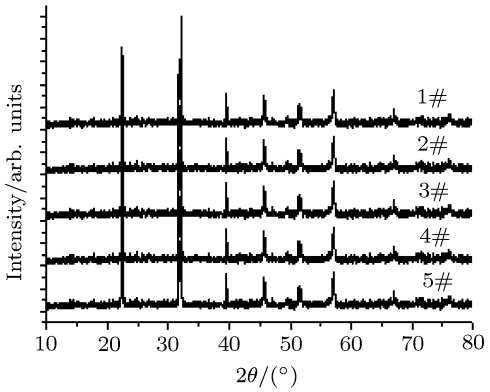


Fig. 1. XRD patterns for $BiFeO_\delta$ samples with $\delta = 2.66$, 2.71, 2.99, 3.41 and 3.49 corresponding to 1#, 2#, 3#, 4# and 5# samples, respectively.

Figure 2 depicts the dielectric constants of the $BiFeO_3$ samples with different values of oxygen content δ as a function of frequency at room temperature. The dielectric constants for all the samples decrease with frequency increasing, which can be expected from a conventional dielectric relaxation process. Since fewer experimental data of the dielectric constants are available for samples with different oxygen contents in earlier studies, it is difficult for us to compare our experimental results with existing ones. Fortunately, the value of the dielectric constant of $BiFeO_3$ in this work accords well with that reported by Mahesh and

Palkar.[16] Dissimilarly, the dip observed at 105 kHz in Ref. [16] is absent in our data. For other samples with different oxygen contents, we all obtained a smooth curve.

From Fig. 2, we can also see that the dielectric constants of all samples increase with oxygen content increasing when δ is less than 2.99. After reaching the maximum corresponding to $\delta = 2.99$, dielectric constant has a drop trend when oxygen content is further increased. As an example, the dielectric constant measured at 1 kHz reaches a maximum value of 90 when $\delta = 2.99$, one and a half times bigger than that for $BiFeO_{2.66}$. That is to say, by comparison with $BiFeO_3$, the introducing oxygen and oxygen vacancies can lead to a reduction in dielectric constant of $BiFeO_\delta$.

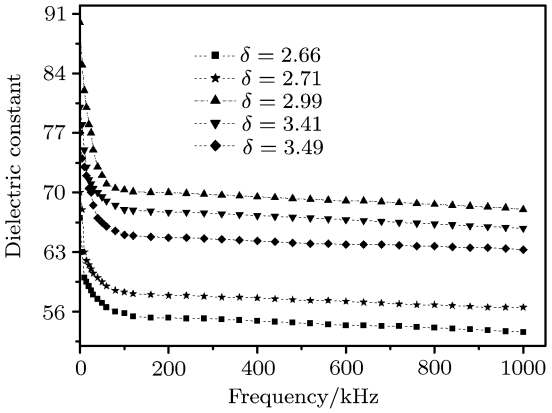


Fig. 2. Frequency dependences of dielectric constant of $BiFeO_3$ ceramic samples with different oxygen contents.

As is well known, bismuth ferrite crystallizes into a rhombohedrally distorted perovskite structure with space group $R3c$, where all ions are displaced along the [111] direction relative to the ideal centrosymmetric positions, and the oxygen octahedron surrounding the transition metal cations (Fe) rotates around this axis, alternately clockwise and counterclockwise. The polarization of $BiFeO_3$ is strongly dependent on oxygen content due to the stable ionic configuration in $BiFeO_3$. The high stability of the ferroelectric configuration also leads to a negligible dependence of the electric polarization on oxygen vacancy concentration. We find that the ferroelectricity of $BiFeO_3$ is affected by the presence of oxygen content, and dependent on the exact position of the oxygen vacancy. The presence of oxygen vacancies for all cases leads to the formation of Fe^{2+} ions, which can be identified unequivocally in the partial densities of states although the actual differences in charge among Fe sites are very small.[12] There exist always some oxygen vacancies in $BiFeO_\delta$, which results in a relatively high conductivity and small dielectric constant.[18] The free volume available for the displacement of Fe^{3+} ions in the Fe–O oxygen octahedron is distorted, thereby leading to a reduction in dielectric polarization.

Figure 3 shows the frequency dependences of dielectric loss in $BiFeO_\delta$ ceramic samples for different values of δ. Similar to the dielectric constant, the dielectric loss also decreases smoothly with frequency increasing. This is consistent with the results reported in Ref. [16]. Once again, the dip in the dielectric loss reported in Ref. [16] is not present here, either. For all samples except the sample with δ=2.99, each has a smaller dielectric loss than that of pure $BiFeO_3$. Different from the dielectric constant data presented in Fig 2 the dielectric losses for all the samples increase with the increase of oxygen content δ and the dielectric loss in $BiFeO_\delta$ ceramics has a maximum at $\delta = 3.49$. In general, a larger dielectric constant always corresponds to a higher conductivity for an ordinary dielectric material. For example, a peak value will appear on the frequency dependent curve of dielectric loss when the dielectric constant of material is reduced. While for our results, it is entirely contrary to this universal rule. A further study is necessary to confirm and understand the mechanism in detail.

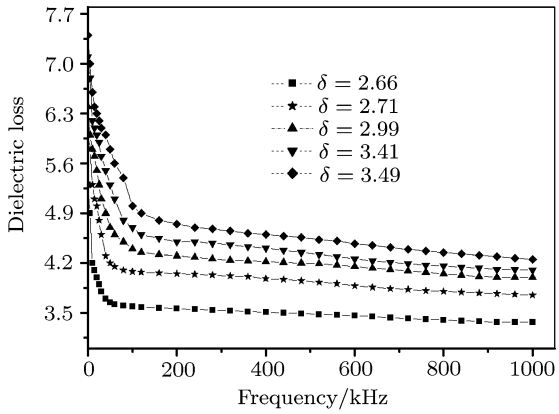


Fig. 3. Frequency dependences of dielectric loss of $BiFeO_3$ ceramic samples with different oxygen contents.

In order to better understand the experimental results, we turn to first-principles calculations of dependence of oxygen content on dielectric property of polycrystalline $BiFeO_3$. The first-principles plane-wave pseudopotential density functional theory as implemented in the CASTEP code was used. By calculation, the real parts of dielectric functions of polycrystalline $BiFeO_3$ samples for five different oxygen contents are plotted in Fig. 4.

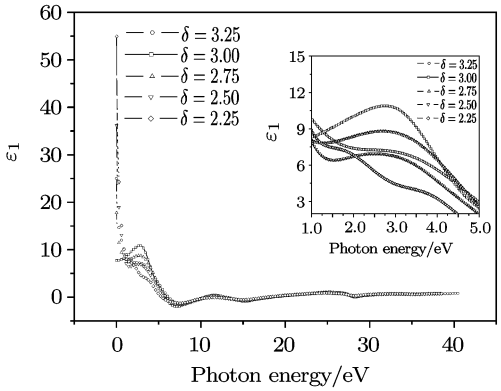


Fig. 4. Curves for real part of the dielectric function (ε_1) of polycrystalline $BiFeO_3$ with different oxygen contents versus photon energy, calculated by first principle method. The inset in the figure clearly shows the variations of the dielectric function of $BiFeO_\delta$ at low photon energy in a range of 1.0–5.0 eV.

The values of static real part of dielectric constant ε_1, are about 7.5 for $\delta = 3.00$, which is smaller than 18 for $\delta = 2.75$, 25 for $\delta = 3.25$, 36 for $\delta = 2.50$, and 55 for $\delta = 2.25$. With the number of oxygen vacancies increasing, the value of ε_1 increases rapidly. In order to show the influence of oxygen content clearly, the curves for ε_1 versus photon energy for five different oxygen contents are plotted in Fig. 4. It can be seen that the dielectric constant of $BiFeO_3$ with pure phase has the largest value when photon energy is in a range of 2.1–4.0 eV. That is to say, the introducing oxygen and oxygen vacancies can lead to a reduction in dielectric constant of $BiFeO_3$. Obviously, this is consistent well with our experimental result at a lower frequency. Unlike earlier results, our calculated results are found to be in good agreement with experimental values especially in the case of lower photon energy. The agreement between the calculated result and our experimental data further demonstrates that the free volume available for the displacement of Fe^{3+} ions in the Fe–O oxygen octahedron is distorted when some oxygen vacancies are introduced into $BiFeO_3$ ceramics, which will bring on a reduction in dielectric polarization, resulting in relatively high conductivity and small dielectric constant.

4. Conclusions

In summary, multiferroic $BiFeO_3$ ceramic samples with different values of oxygen content (δ) are prepared by the solid state reaction method. The x-ray diffraction analysis illustrates that for all multiferroic $BiFeO_3$ ceramic samples with different oxygen contents, each possesses a pure phase $BiFeO_3$ structure. The measurements of dielectric property demonstrate that both dielectric constant and dielectric loss of $BiFeO_\delta$ ceramics decrease with frequency increasing in a range of 100 Hz–1 MHz. The studies of dependence of dielectric property on oxygen content show that introducing oxygen and oxygen vacancies can lead to a reduction in dielectric constant of $BiFeO_\delta$ at a lower frequency compared with $BiFeO_3$. Our first-principles calculation is also very similar to experimental result when photon energy is in a range of 2.0–4.1 eV. These results imply that the dielectric property of $BiFeO_3$ is significantly affected by introducing oxygen and oxygen vacancies. The observation for our experiment may give an important inspiration to the practical applications of this material.

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