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$BiFeO_3$ ceramics synthesized by spark plasma sintering

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Abstract

Phase-pure $BiFeO_3$ particles were synthesized by an improved solid state technique. High density $BiFeO_3$ ceramics were prepared using these particles by spark plasma sintering (SPS). The dielectric permittivity and loss of SPS samples were measured as functions of sintering temperature, frequency, and annealing conditions. Dielectric spectra of the ceramics annealed at 650 °C were characterized in a broad range of temperature (300–725 K) and frequency (100 Hz to 20 MHz). Two kinds of dielectric relaxation following the Arrhenius law were detected in low and high temperature ranges, respectively. The low temperature dielectric relaxation could be almost completely removed by annealing in vacuum and it should be assigned to be a valence fluctuation of Fe ions, while the high temperature dielectric relaxation was proposed to stem from the short-range motion of oxygen vacancies.

Keywords: A. Sintering; B. X-ray methods; C. Dielectric properties; C. Ferroelectric properties

1. Introduction

In recent years, there has been a large amount of research connected with the studies of multiferroic materials [1,2]. One of the most prominent examples of such materials is bismuth ferrite, $BiFeO_3$, which shows both electric polarization below $T_c \approx 1120$ K [3] and long-range magnetic ordering below $T_N \approx 640$ K [4]. Since $BiFeO_3$ belongs to a class of high T_c multiferroics, measurement under magnetic field is promising, it may give rise to an additional degree of freedom in providing an additional functionality in device designing. However, some studies have reported that a large extrinsic conductivity of these materials rendered measurement of the ferroelectric loops extremely difficult, and even made the accurate location of the Curie temperature impossible only by dielectric measurements [5]. These applications of $BiFeO_3$ could be quite limited.

For $BiFeO_3$ ceramics, its preparing process is briefness and solid-state reaction based on Bi_2O_3 and Fe_2O_3 is the most common method [6]. But there are some bottlenecks in the fabricating process. One is synthesizing pure phase materials and another is achieving high density. The synthesis of pure $BiFeO_3$ ceramics is quite subtle because it is necessary to take both kinetic and thermo-dynamic properties into account. In the solid-state route, the $BiFeO_3$ powder does not exhibit good sintering activity. From 675 °C to 830 °C, $BiFeO_3$ decomposes into $Bi_2Fe_4O_9$ slowly, above 830 °C $BiFeO_3$ separates rapidly into $Bi_2Fe_4O_9$ [7], whereas below 675 °C the density of $BiFeO_3$ ceramic sintered by a traditional solid method is very low. In view of these facts, we fabricate $BiFeO_3$ ceramics with relatively high density by a spark plasma sintering technique at different sintering temperatures.

2. *Experimental*

Phase-pure $BiFeO_3$ powders were synthesized using an improved solid-state reaction of Bi_2O_3 (Kishida, 99.9%) and Fe_2O_3 (Johnson-Matthey, 99.99%). The raw materials were mixed in stoichiometric proportions (1:1 mole ratio) carefully and ground in an agate mortar thoroughly for 15 h using isopropyl alcohol as a medium. The dried mixture was pressed into pellets at 100 MPa. The prepared pellets were sintered at 800 °C for 10 h. After calcination the pellets were ground into a fine powder and leached with 10% nitric acid twice under continuous stirring for 2 h. The leached residue was washed three times with large volumes of distilled water to neutralize the acidity. After being dried in a furnace at 300 °C for 1 h, the sample was ground to a very fine powder.

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Spark plasma sintering was carried out using a SPS furnace (Plasman, S S ALOY Co.Ltd.). The calcined powder was poured in a cylindrical graphite die of 10 mm diameter, and sintered in partial vacuum of 80 Pa for 5 min under a uniaxial pressure of 50 MPa applied throughout the sintering cycle. The sintering temperature was varied from 650 to 800 °C and the heating rate was about 100 °C/min. The samples were annealed by a siliconit tube furnace at 600 °C for 1 h under oxygen gas flow, and then some samples were annealed using an infrared image furnace (MILA-3000, ULVAC-RIKO) at 500 °C for 0.5 h in a partial vacuum of 2 Pa.

The phase identification of the calcined $BiFeO_3$ powder and the sintered ceramics was performed on an X-ray diffractometer (RINT 2000, Rigaku) using Cu-Kα radiation. The relative dielectric constant ε' and loss tangent $\tan\delta$ were measured using two inductance–capacitance–resistance (LCR) meters (HP4284A and HP4285A) over wide ranges of frequency (100 Hz to 20 MHz).

3. *Results and discussion*

Fig. 1 shows the X-ray diffraction pattern of $BiFeO_3$ powder after leaching by dilute nitric acid and ground SPS pellets sintered at different temperatures. XRD data reveal that $BiFeO_3$ powder is obtained by improved solid-state route with a rhombohedral distorted perovskite structure with $a_{hex} = 5.5775$ Å and $c_{hex} = 13.8616$ Å. Trace of secondary phase was not observed in the acid leached $BiFeO_3$ powder. In addition, it can be seen that the SPS sample sintered at 650 °C possesses optimum properties along with phase purity and the higher sintering temperature generates an impurity phase ($Bi_2Fe_4O_9$). The density of SPS samples was above 90% of the theoretical density, and the relative density of the SPS sample sintered at 800 °C was about 96% [8]. It is higher than that of ceramic samples fabricated by traditional solid-state method.

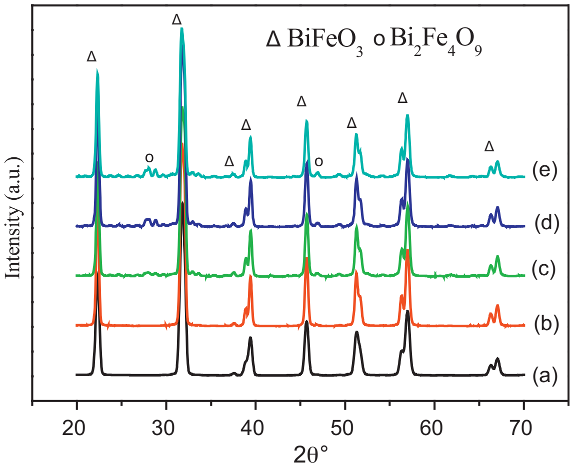

Fig. 1. X-ray diffraction patterns of (a) $BiFeO_3$ powder after leaching by HNO_3 and ground SPS pellets after sintering at (b) 650 °C, (c) 700 °C, (d) 750 °C, and (e) 800 °C.

The frequency dependence of relative dielectric constant (ε') and loss ($\tan\delta$) for $BiFeO_3$ samples synthesized by SPS at different temperatures are presented in Fig. 2. The value of ε' decreased with the increase of frequency. The sample sintered at 650 °C without oxygen annealing possesses a stable and low ε' in the whole frequency range. Its dielectric constant decreases

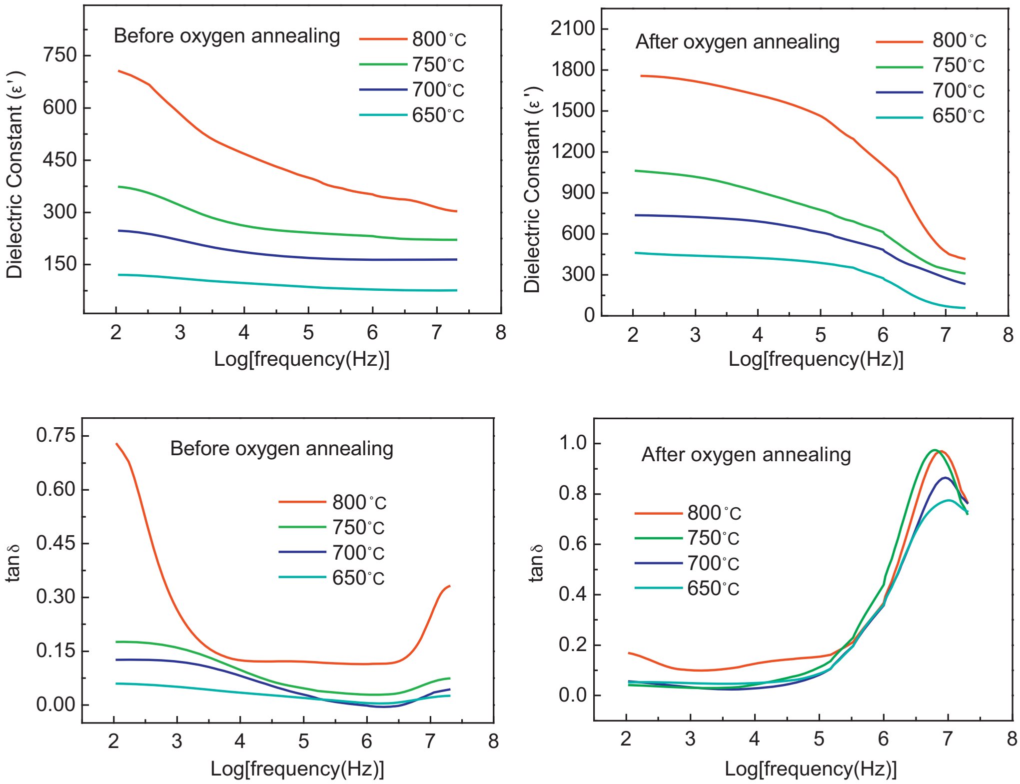

Fig. 2. Dielectric constant and loss vs. frequency for SPS samples before and after oxygen annealing.

slowly from 128.6 to 74.2 when the frequency increase from 100 Hz to 20 MHz, and its tan δ is lower than 0.13. In whole frequencies, ε' increases with the increase of SPS sintering temperatures, and the dielectric loss have the same regularity.

For the samples annealed in oxygen at 600 °C for 1 h, a decrease of dielectric constant was observed from 1 MHz to 10 MHz. The dielectric constant of the samples annealed in oxygen is higher than that of the samples without oxygen annealing. There are dielectric loss peaks of the oxygen annealed samples near the frequency of 10 MHz. From 100 Hz to 100 kHz, the tan δ of $BiFeO_3$ samples annealed in oxygen are lower than that of the samples without oxygen annealing. But from 100 kHz to 20 MHz, the tan δ of the samples annealed in oxygen is higher than that of the samples without oxygen annealing.

Literatures reported that the deviation from oxygen stoichiometry leads to valence fluctuation of Fe ions from Fe^{+3} to Fe^{+2} state in $BiFeO_3$, resulting in high conductivity [9]. Some oxygen vacancies in $BiFeO_3$ would compensate for the bismuth vacancies that can be present due to bismuth volatilization. In the process of oxygen annealing for our samples, Fe^{2+} ions were oxidized to Fe^{3+} ions and Fe^{3+} ions were oxidized into Fe^{4+} ions [10], as Eqs. (1) and (2) described. A large increase of dielectric constant of the $BiFeO_3$ ceramics annealed in oxygen may be attributed to the lower leakage current densities, which stem from the ion valence change of Fe. The annealing treatment in oxygen at 600 °C should produce more oxygen vacancies (V_O^{2-}) for bismuth volatilization. At low frequencies the vacancies (V_O^{2-} and V_{bi}^{3-}) are able to follow f, but at high frequencies the vacancies could not follow f, resulting in a decrease of dielectric constant.

$$2Fe^{2+} + V_O^{2+} + 0.5O_2 \Rightarrow 2Fe^{3+} + O^{2-} \tag{1}$$

$$2Fe^{3+} + V_O^{2+} + 0.5O_2 \Rightarrow 2Fe^{4+} + O^{2-} \tag{2}$$

Fig. 3 shows the variation in dielectric constant and loss with temperature of the samples annealed in oxygen and in vacuum at 75 kHz, 120 kHz, 300 kHz, 1 MHz, 3 MHz, and 10 MHz. The data in Fig. 3(a) show strong dispersion in the real dielectric constant across a temperature range of 360–725 K and a wide dielectric constant peak from 600 to 700 K. Meanwhile, two sets of dielectric relaxations (part α and part β) are detected in the $BiFeO_3$ ceramics with O_2 annealing. For the SPS sample annealed in vacuum, as shown in Fig. 3(b), a dielectric anomaly is observed at around 670 K, which is attributed to the antiferromagnetic transition [11]. Moreover, the dielectric relaxation at low temperatures disappeared, and only a relaxation of loss at temperatures above 500 K is observed, which is consistent with the dielectric relaxation of part β in Fig. 3(a).

For the two sets of dielectric relaxations, we have investigated the variation of the relaxation temperature with the frequency. As shown in Fig. 4, the variation relations obey the Arrhenius law,

$$f = f_0 \exp\left(\frac{-E_a}{kT}\right) \tag{3}$$

where f_0 is the preexponential term, E_a is the activation energy, and k is Boltzmann's constant. The fitting parameters have been obtained $E_a = 0.45$ eV for the dielectric relaxation of part α,

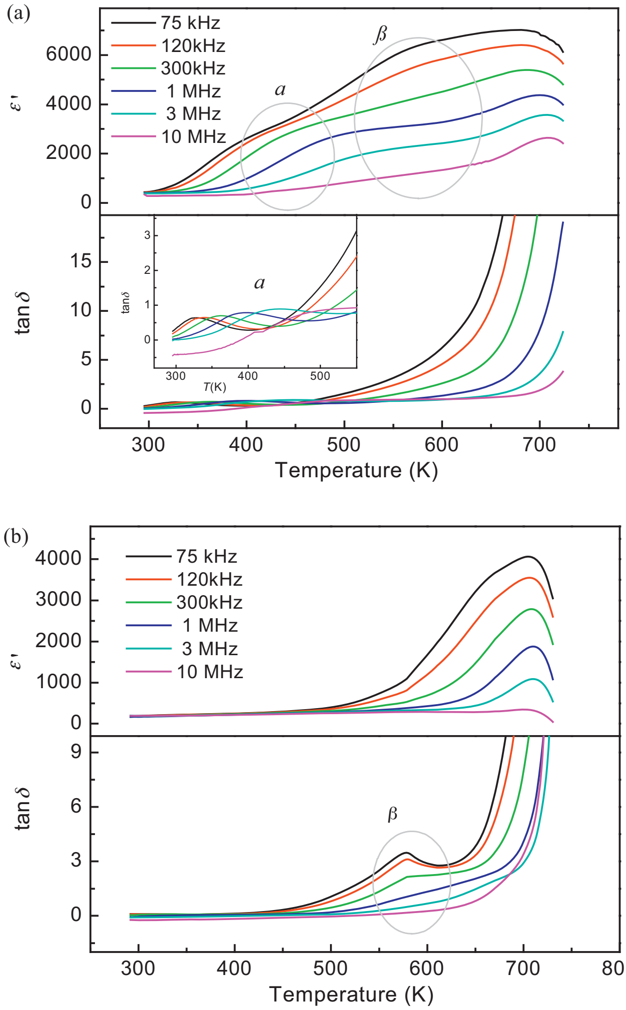

Fig. 3. Temperature dependence of the dielectric constant and loss for SPS samples sintered at 650 °C: (a) after oxygen annealing and (b) annealed in vacuum.

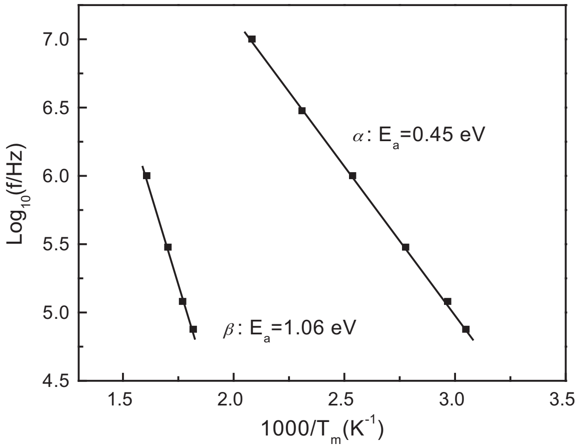

Fig. 4. Arrhenius plots of the measured frequency f and the peak temperature T_m of dielectric loss in $BiFeO_3$ ceramics.

$E_a = 1.06$ eV for the dielectric relaxation of part β and $f_0 = 3.5 \times 10^{10}$ Hz. It should be noted that $E_a = 0.45$ eV is comparable to 0.53 eV which is the activation energy of a similar dielectric relaxation of our former result [8]. The dielectric relaxation behavior of part α is ascribed to the valence fluctuation of Fe ions (between Fe^{3+} and Fe^{4+}). The dielectric relaxation is also a thermal activated process. This relaxation behavior at low temperatures (part α) is not an intrinsic one since it can be removed by annealing in vacuum. Just as observed in Fig. 3(b), the real dielectric permittivity of the sample annealed in vacuum exhibits no dispersion below the temperature of 500 K.

On the other hand, the dielectric relaxation behavior at high temperatures (above 500 K) might be contributed from the defect dipole. It was reported by Waser et al. [12] that the oxygen vacancies can move due to thermal activation in the temperature range of 500–800 K. Waser et al. reported that the activation energy of oxygen vacancy is 1.005–1.09 eV at 513 K. This is in good agreement with the experimental result of the activation energy (1.06 eV) obtained from the dielectric relaxation in the present paper. So the dielectric relaxation occurring in the temperature range above 500 K for $BiFeO_3$ samples could be related to the movement of the oxygen vacancies under the external testing electric field. The short-range hopping of oxygen vacancies, similar to the reorientation of the dipole, leads to a dielectric relaxation, part β.

4. *Conclusions*

In conclusion, dense $BiFeO_3$ ceramics have been prepared by SPS technique at temperatures range from 650 to 800 °C. $BiFeO_3$ ceramic with excellent phase properties was synthesized at low sintering temperature successfully. The dielectric behaviors of the SPS samples annealed in oxygen and in vacuum were investigated in a broad range of temperature and frequency. Two sets of dielectric relaxation with frequency dispersion are found on the samples annealed in oxygen. The low temperature one is a thermal activated process, which can be removed by vacuum annealing. The dielectric relaxation at high temperatures is attributed to the short-range motion of oxygen vacancies and cannot be removed by vacuum annealing.

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