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Dielectric and ferroelectric properties of $BiFeO_3$ ceramics sintered in different atmospheres

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Abstract

Pure $BiFeO_3$ powders were successfully synthesized by microwave-hydrothermal processing, and the pellets were sintered in different atmospheres. The properties of $BiFeO_3$ ceramic samples were characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), dielectric measurements (LCR) and polarization-field hysteresis loop. The effects of different atmospheres (including air, N_2, O_2 and H_2) on ferroelectric properties of $BiFeO_3$ ceramics were studied in this paper. The results show that the $BiFeO_3$ ceramics sintered in H_2 and N_2 atmosphere have a single-phase rhombohedra distorted perovskite structure with no trace of other impurity phases. The dielectric properties of $BiFeO_3$ ceramics were greatly influenced by O_2 and H_2 atmospheres. The samples sintered in H_2 atmosphere have the highest dielectric constant. Polarization-field hysteresis loops measured at room temperature indicated the samples sintered in H_2 and N_2 atmospheres have higher spontaneous polarization and lower breakdown field, but the ferroelectric properties of samples sintered in O_2 atmospheres were poor.

Keywords: A. Microwave processing; C. Dielectric properties; C. Ferroelectric properties

1. Introduction

$BiFeO_3$ is a good candidate, with the crystallographic space group R3c, allows the existence of both antiferromagnetic and ferroelectric orders with very high transition temperatures [1]. It may give rise to an additional degree of freedom in providing an additional functionality in device designing [2]. So $BiFeO_3$ has been extensively investigated in the forms of bulk ceramics, single crystal and thin film owing to its high phase transition temperature and good multiferroic properties [3,4]. As for $BiFeO_3$ ceramics, their commercial applications are not yet successful due to difficulties in restricting the formation of impurity phase and pores as well as mitigating the serious leakage current-induced dielectric breakdown [5]. In order to improve the purity and electrical properties, some researchers attempt to use sol–gel method and spark plasma sintering to synthesis purity phase $BiFeO_3$ ceramics [6,7]. Recently it has been shown that rapid liquid phase sintering of $BiFeO_3$ can result in a high resistivity and polarization values of $BiFeO_3$ [8], but can also lead to high dielectric loss and more defects. Several research groups adopted the strategy of doping $BiFeO_3$ with different trivalent ions on A, B or both A and B site [9–11]. The doping has resulted in the reduction of the leakage current density and in the improvement of the ferroelectric properties to some extent, but it is still far from the practical applications. It is possible that the sintering atmosphere was a key parameter to improve the leakage current and structural inhomogenity.

Therefore, we aim in this work to prepare poreless, low-resistive single-phase multiferroic $BiFeO_3$ ceramics and study the effect of different atmospheres (including air, N_2, O_2, H_2) on the density and electric properties of $BiFeO_3$ ceramics, the optimal sintering atmosphere was determined by the analysis of density and electric properties of $BiFeO_3$ ceramics.

2. Experimental procedures

Analytical grade chemical bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$) ($\geq 99.5\%$) and iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) ($\geq 99.5\%$) were used as raw materials. Sodium hydroxide, NaOH, was used as alkaline mineralizer. Equi-molar

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mixtures of bismuth nitrate and iron nitrate were dissolved in distilled water. NaOH was added dropwise to the above solution until pH = 13. The resultant solution was poured into double-walled digestion vessels, microwave hydrothermal experiments were conducted in a temperature-controlled oven. The powder produced was washed thoroughly with distilled water and dried at 80 °C, and then heat-treated at 600 °C for 2 h. The $BiFeO_3$ ceramics were prepared using a conventional ceramic processing. The microwave hydrothermally synthesized $BiFeO_3$ powders were ball-milled with 1 wt% PVA and then dried. Pellets of 11 mm in diameter and 0.9 mm in thickness were uniaxially pressed at 60 MPa. The pellets were sintered in different atmospheres (including air, N_2, O_2 and H_2) at 800 °C.

The crystalline phase of the sintered samples was identified using an automated diffractmeter (D/max-$_{22}$00PC, RIGAKU, Japan). A scanning electron microscope (JSM-6460) was used to investigate the microstructure of $BiFeO_3$ ceramic sintered in different atmospheres. The dielectric data of $BiFeO_3$ ceramics were collected using the LCR meter (Agilent 4980A). Room temperature ferroelectric measurements were carried out using ferroelectric hysteresis loop tracer (Model:610E).

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of $BiFeO_3$ ceramics. The XRD patterns reveal that the $BiFeO_3$ ceramics sintered in N_2 and H_2 atmospheres have a single-phase rhombohedra distorted perovskite structure. But trace of secondary phase was observed when samples sintered in O_2 atmospheres. Bernardo [12] has reported that $BiFeO_3$ was a metastable product, it seems to initiate its decomposition at the temperature above 800 °C and trace amounts of $Bi_2Fe_4O_9$ mullite-type phase can be observed at this temperature. Fig. 1 indicated that microwave hydrothermal synthesis was an effective method to synthesis pure $BiFeO_3$ powder and sintering in N_2 and H_2 atmospheres have no effect on the purity. The O_2 atmosphere has an influence on the purity, which is in good agreement with Bernardo's experimental results [12]. It indicated that sintering in O_2 atmosphere was favorable for the decomposition of $BiFeO_3$.

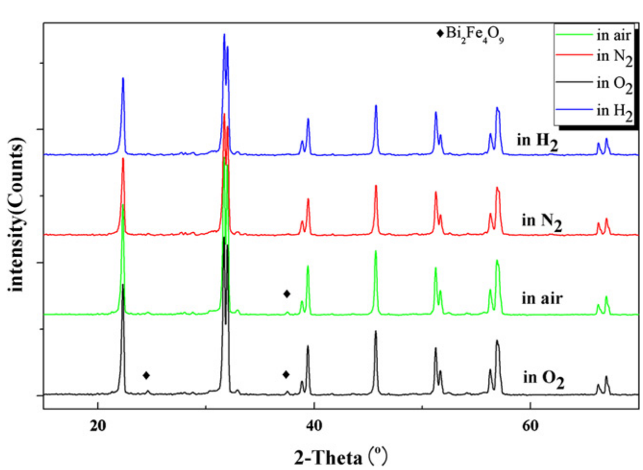

Fig. 1. X-ray diffraction pattern of $BiFeO_3$ ceramics sintered in different atmospheres.

Fig. 2 shows the SEM micrographs of the as-sintered surface of $BiFeO_3$ ceramics. It can be seen that all grain samples were irregular in shape. The samples sintered in N_2 and H_2 atmospheres have a high densification, whereas, the densification was obviously poor when sintered in O_2 atmospheres, some distinct pores existed in the grain and grain boundary and several tiny whitish spots were observed immersed in a matrix of light gray grains. We thought that the tiny whitish spots were $Bi_2Fe_4O_9$ mullite-type phase. It indicates that the N_2 and H_2 atmospheres were beneficial to the sintering densification of $BiFeO_3$ ceramic, which could be explained that the concentration of oxygen vacancies, which was important for the transfer of mass and energy between reactants during sintering, was increased when sintered in N_2 and H_2 atmospheres, which resulted in the diffusion of ions was improved in sintering process.

However, the production of oxygen vacancies was inhibited when sintering in O_2 atmospheres, thus inhibiting the diffusion of ions, which led to the lower densification and the formation of secondary phase.

Fig. 3 shows the dielectric constant of the samples sintered in different atmospheres as a function of frequency at room temperatures. The dielectric loss for all samples are low at low frequencies up to 10 kHz and then show a rising trend above 10 kHz, the maximum value of dielectric loss is reached at the frequency of 1 MHz. Usually in $BiFeO_3$, oxygen deficiency is an inherent problem and space charge polarization is always present [4]. The high values of dielectric constant at lower frequency are explained on the basis of dipolar and space charge polarization due to the presence of inhomogeneities in the dielectric structure. However, at high frequencies the electronic polarization is effective and dipolar contribution becomes insignificant. The decrease in dielectric constant with increased frequency could be explained on the basis of dipole relaxation phenomenon, the inability of the electric dipoles to be in pace with the frequency of applied electric field at high frequency.

It can be seen in Fig. 3 that the samples sintered in O_2 atmosphere show higher dielectric constant and dielectric loss below the frequency of 0.1 MHz, but the dielectric constant and dielectric loss are the lowest above the frequency of 0.2 MHz. The samples sintered in H_2 atmosphere show the highest dielectric constant and dielectric loss values over the entire frequency range examined. The microstructures and impurity phases in $BiFeO_3$ samples sintered in O_2 atmosphere are some of the main reasons for dielectric properties of $BiFeO_3$ ceramic, the lower densification and the formation of secondary phase resulted in larger number of grain boundaries and the improvement of inhomogeneity, which act as scattering center for flow of

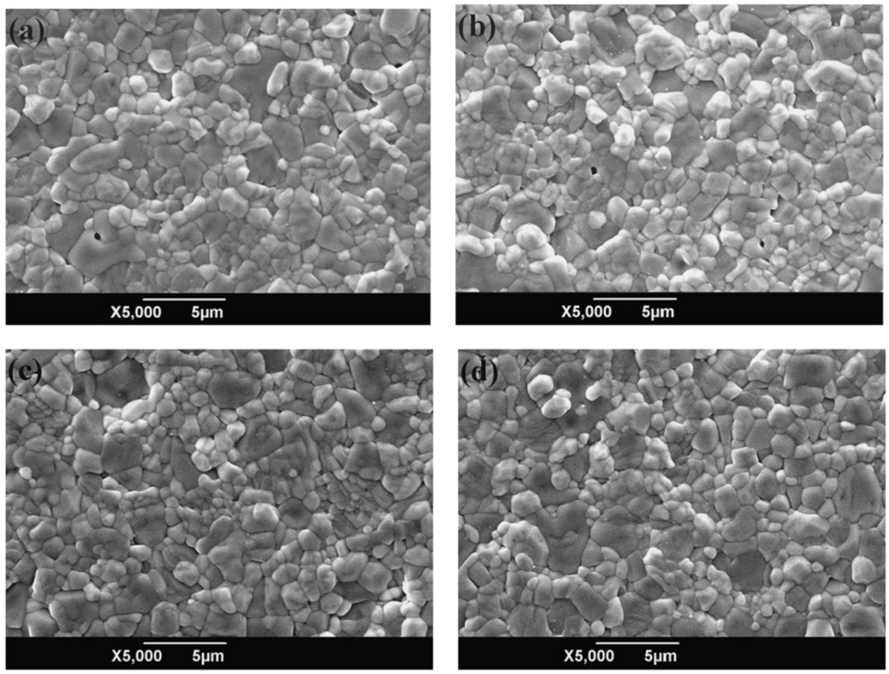

Fig. 2. SEM micrograph of $BiFeO_3$ ceramics sintered in different atmospheres: (a) in air; (b) in O_2; (c) in N_2 and (d) in H_2.

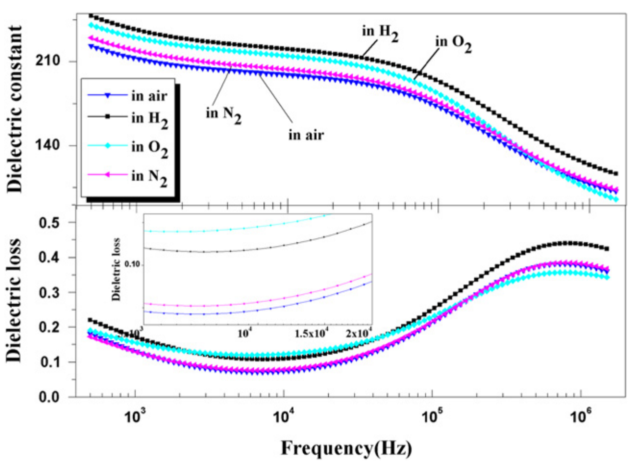

Fig. 3. Frequency dependence of dielectric properties for $BiFeO_3$ ceramic sintering in different atmospheres.

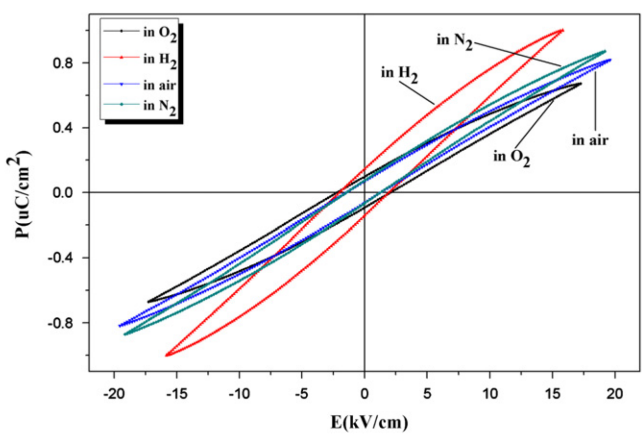

Fig. 4. Polarization hysteresis loops of $BiFeO_3$ samples sintered in different atmospheres.

electrons, so the space charge polarization is very effective at low frequencies. But space charge polarization is not able to establish at high frequency, meanwhile, the production of oxygen vacancies is inhibited when sintering in O_2 atmospheres; dipolar contribution is insignificant, and it led to the poor dielectric properties at high frequency. The improvement of dielectric properties in samples sintered in N_2 atmosphere is insignificant, but samples sintered in H_2 atmosphere have the highest dielectric constant and dielectric loss values over the entire frequency range examined as compared with the samples sintered in air, which is consistent with a combined response of orientational relaxation of dipoles and the high leakage current densities, the concentration of oxygen vacancies is higher when samples sintered in H_2 atmospheres, lead to higher leakage current densities due to the ions valence change of Fe, as:

$$2Fe^{3+} + O^{2-} + H_2 \rightarrow 2[Fe^{3+} \bullet e] + V_O^{\bullet\bullet} + H_2O \quad (1)$$

which led to the high dielectric constant and dielectric loss values.

Polarization hysteresis loops of these samples were measured and shown in Fig. 4. For the samples sintered in different atmosphere at 800 °C, the saturated polarization hysteresis loops were observed at room temperature. We can see from Fig. 4 that the samples sintered in H_2 atmospheres showed higher spontaneous polarization and lower breakdown field, but the spontaneous polarization of samples sintered in O_2 atmospheres was very low. The spontaneous polarization of the samples sintered in air, N_2, O_2 and H_2 are 0.814, 0.870, 0.671 and 1.02 uC/cm^2

respectively. It can be attributed to the formation of impurity phase and the high porosity of samples sintered in air and O_2 atmospheres. The sample sintered in a reducing atmosphere have a higher spontaneous polarization may contribute to the high density and high conductivity due to valence fluctuation of Fe ions in $BiFeO_3$ ceramics.

4. Conclusions

$BiFeO_3$ ceramics sintered in different atmospheres were prepared by using microwave hydrothermal processing. Sintering atmosphere had a great influence on the properties of $BiFeO_3$ ceramics. The samples sintered in N_2 and H_2 atmosphere were of single-phase rhombohedral distorted perovskite structure, but those samples sintered in O_2 atmospheres were favorable to the decomposition of $BiFeO_3$ and a trace of impurity phase was observed in $BiFeO_3$ ceramic. The densification of $BiFeO_3$ ceramic was significantly improved when the samples were sintered in reducing atmospheres, and the highest dielectric constant and dielectric loss was obtained when samples were sintered in H_2 atmospheres. The samples sintered in H_2 and N_2 atmospheres have higher spontaneous polarization and lower breakdown field, while the ferroelectric properties of samples sintered in O_2 atmospheres were poor.

Acknowledgments

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