Journal of Ceramic Processing Research. Vol. 19, No. 2, pp. 101~104 (2018)

J O U R N A L O F
Ceramic Processing Research

Effect of sintering atmosphere on ferroelectric properties of SBT ferroelectric ceramics

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The effect of sintering atmosphere on the properties of SBT ferroelectric ceramics was studied by sol-gel method and interlayer annealing process. It was found that the sintered samples in oxygen atmosphere had more a-axis-oriented grains and more grains which are perpendicular to the plane than those in air atmosphere. The Curie temperature of the samples obtained by sintering in oxygen and air atmosphere is Tc = 273 °C and Tc = 265 °C, and the conductivating energy Ea = 0.94 eV and Ea = 0.66 eV, respectively. The residual polarization intensity of the samples sintered in air atmosphere is 2Pr = 15.3 μC/cm^2, the corresponding coercive field is Ec = 51 kV/cm; the residual polarization intensity of the sample sintered in oxygen atmosphere is 2Pr = 16.6 μC/cm^2, and the corresponding coercive field is about Ec = 45 kV/cm. That is because the samples sintered in the oxygen atmosphere has larger lattice distortion, lower oxygen vacancy concentration and larger a-axis oriented grains, which are favorable for the increase of the remnant polarization and reduction of the coercive field.

Key words: Sintering atmosphere, SBT, Ferroelectric properties, Activation energy.

Intrucduction

Research on lead-free ferroelectric materials is a hot spot in the field of ferroelectric materials . In many fields, there are few studies on functional devices of bismuth layered perovskite structure. This is mainly due to the composition and the crystal structure are complex of the perovskite structure material, so different functional devices with perovskite structure have different properties and applications. So bismuth layered perovskite structure material is still an important system [1]. Bismuth layered structure ferroelectric (BLSF), also known as the Aurivillius phase [2-4], is made from the Bi6s and O2p orbitals. It has a reduced symmetry in structure and forms a dipole, which exhibits excellent ferroelectric, piezoelectric, and nonlinear optics [5]. The chemical formula of Aurivillius phase is $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^2$, which generally presenting a special layered structure. The perovskite-like block $(A_{m-1}B_mO_{3m+1})^{2-}$ is interleaved with fluorite-like layer $(Bi_2O_2)^{2+}$. The subscript m represents the number of perovskite layers. The TiO_6 quasi octahedral vertex contribute to the formation of perovskite layer, $(Bi_2O_2)^{2+}$ layer occurs once every m $(A_{m-1}B_mO_{3m+1})^{2-}$ layer [6-8]. The bismuth layered perovskite structure material shows obvious anisotropy, which means the residual polarization intensity will not be the same in different directions. The polarization intensity is obvious in the a/b direction, however, the polarization intensity is small or even zero in the c direction [9]. $Sr_2Bi_4Ti_5O_{18}$ (SBT) is a typical bismuth layered perovskite structure ferroelectric material with m = 5, and has fatigue-free properties on Pt electrode. Although its inversion voltage is relatively small, but its residual polarization intensity and the Curie temperature can't meet the actual requirements, so its application has been limited [10]. In order to clarify SBT's performance mechanism, the influence of sintering atmosphere on SBT was studied in this paper.

Experimental Method

The nanoscale, porous and well dispersed powders were prepared by self-propagating sintering. The prepared powders were firstly calcined at 800 °C for 2 hours, and then were put into an isostatic tool with a diameter of 10 mm to be molded under the pressure of 160 Mpa. Remove the compressed billets and cut them into samples with the thickness of 0.5-1 mm. The samples were sintered at 1100-1150 °C in air atmosphere and oxygen atmosphere respectively. Keep the sintering temperature for 2-4 hours and then cool the samples naturally to room temperature. An electrode was prepared on ceramic samples to conduct related electrical performance tests. X-ray diffraction (XRD; D8-Advance) with Cu-Kα radiation was used for phase structure analysis. The surface microstructure of sintered ceramic samples were examined by scan electron microscopy (SEM; Fei Nova NanoSEM). The dielectric properties were analyzed by Broadband Dielectric Spectrometer

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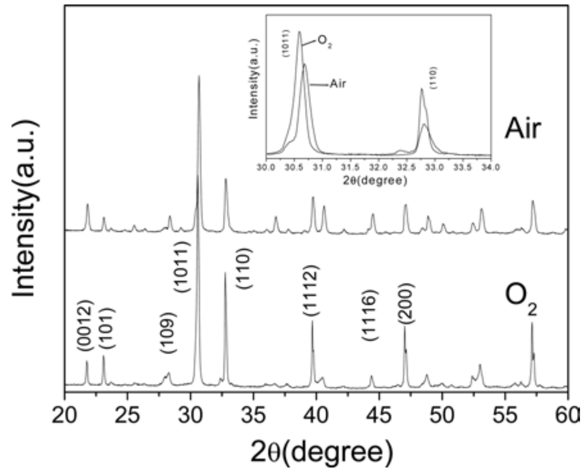

Fig. 1. XRD of the SBT ferroelectric ceramics in various atmospheres.

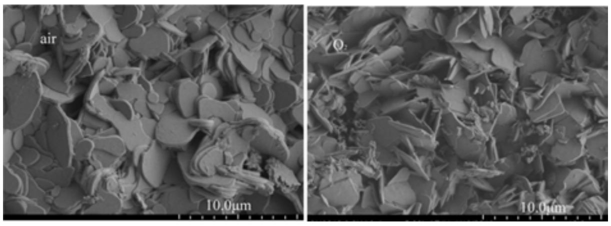

Fig. 2. Surface morphologies of the SBT ferroelectric ceramics in various atmospheres.

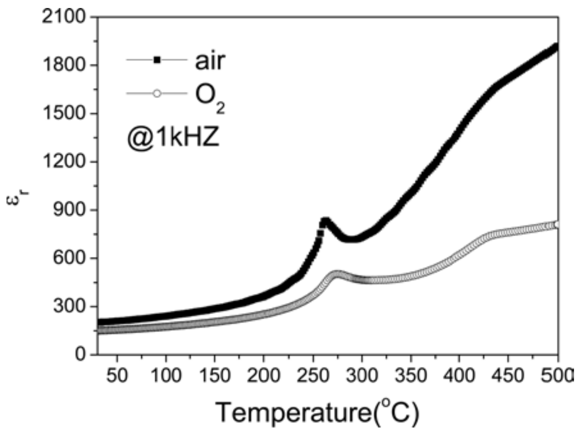

Fig. 3. Temperature dependence of dielectric permittivity of the SBT ferroelectric ceramics at various atmospheres.

(Novocontrol). Ferroelectric hysteresis (P-E) loops were measured by a ferroelectric analyzer (Radiant Precision Workstation).

Results and Discussion

Fig. 1 shows the XRD patterns of SBT ceramics sintered in different atmospheres. According to the picture, we can see that the bismuth layered perovskite structure have been formed. The diffraction peak strength of the samples obtained by sintering in oxygen atmosphere is higher than that obtained in air atmosphere. The diffraction peak of I (200)/(1011) and I(110)/(1011) for samples sintered in oxygen atmosphere are larger than those sintered in air atmosphere, which indicates that there are more grains in a-axis orientation in the samples obtained in oxygen atmosphere. Because the polarization axis of bismuth layered perovskite structure ferroelectric materials is a-axis direction, so more grains in a-axis orientation are favorable to the ferroelectric properties of the samples [11]. It can be seen from Fig. 1, the diffraction peak of the sintered samples in the oxygen atmosphere shifted to a small angle compared to that in the air atmosphere. For samples obtained in oxygen atmosphere, the Ti ion offset from the center of the oxygen octahedral increased, so the intensity of spontaneous polarization increased as well. Then the unit cell needs more energy to break the original equilibrium state of spontaneous polarization, resulting in the increasing of the Curie temperature.

Fig. 2 is the surface of SBT ferroelectric ceramic samples sintered in oxygen atmosphere and air atmosphere, respectively. It can be seen from the figure that the bismuth layered perovskite structure have been formed, and there are more grains which are perpendicular to the plane, indicating that there are more a-axis orientation grains [12], which is consistent with the XRD analysis.

Fig. 3 shows the relationship between the dielectric constant and the temperature of the SBT ferroelectric ceramic samples sintered in oxygen atmosphere and air atmosphere. The test frequency of the dielectric constant is 1 kHz. The Curie temperature Tc of the sample obtained by sintering in an air atmosphere is 265 ºC, which is slightly lower than that in oxygen atmosphere (273 ºC). A similar phenomenon was found in Li-doped $K_{0.5}Na_{0.5}NbO_3$-based piezoelectric ceramics by Long [13]. The concentration of oxygen vacancy has a greater effect on the Curie temperature of the sample. The more oxygen vacancies there are, the more intense ferroelectric domain pinning is, and therefore the more energy is needed to convert the ferroelectric phase into a cis phase. Therefore the Curie temperature of the samples sintered in the air atmosphere is higher. However, it was found from the XRD that the Curie temperature of the sintered samples sintered in oxygen atmosphere was higher. Because the grain size, crystal structure and heterogeneous phase can change the Curie temperature [14-19], Curie temperature changes are the result of these factors together, the specific reasons should be studied further.

In order to understand the effect of sintering atmospheres on the conductance, the AC conductance of SBT ferroelectric ceramic samples at different temperatures was tested. Fig. 4 shows the AC conductance of SBT ferroelectric samples sintered in different atmospheres at different temperatures. According to the Arrhenius formula $f_p = f_0 \exp{-E_a/(kT)}$ the conductance activation energy was obtained by fitting and calculation

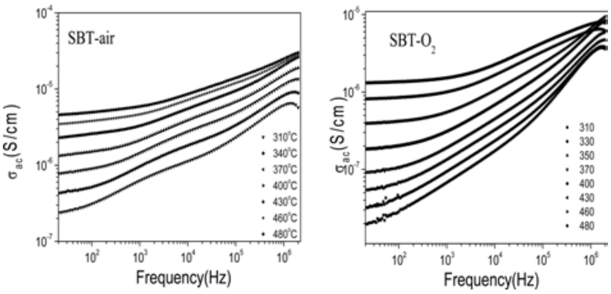

Fig. 4. Frequency dependence of σ_{ac} conductivity for SBT ferroelectric ceramics under different temperatures.

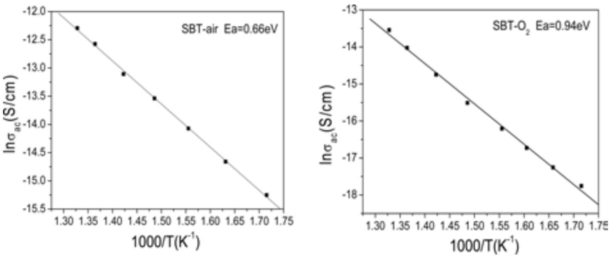

Fig. 5. Temperature dependence of σ_{ac} conductivity for SBT ferroelectric ceramics.

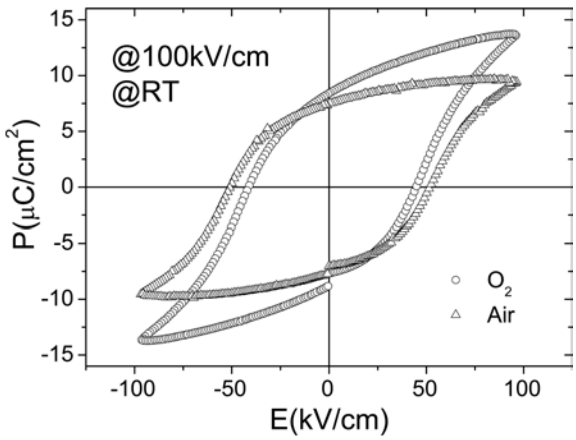

Fig. 6. P-E hysteresis loop of the SBT ferroelectric ceramics at different annealed atmosphere.

according to the Arrhenius formula. As shown in Fig. 5, the conductivity of the sample sintered in the oxygen atmosphere is Ea = 0.94 eV, the diffusion activation energy Ea = 1.0 eV is close to that of oxygen vacancy. And the conductivity of the sintered sample in the air atmosphere is Ea = 0.66 eV [20], which is close to the activation potential of oxygen vacancy secondary ionization [21-22]. The oxygen vacancy is due to the charge imbalance caused by the volatilization of Bi elements and the Ti element valence during the sintering process of ceramic samples. The more defects there are in the sample, the smaller the conduction activation energy is [23]. Therefore, there are less oxygen vacancy concentration and defects in samples sintered in oxygen atmosphere than those sintered in air atmosphere.

Fig. 6 shows the hysteresis loop of SBT samples sintered in air atmosphere and oxygen atmosphere, respectively, and the measured electric field strength is 100 kV/cm. The residual polarization intensity of the ceramic sample sintered in air atmosphere is 2Pr = 15.3 $\mu C/cm^2$, the corresponding coercive field is about Ec = 51 kV/cm, the residual polarization strength of the ceramic sample sintered in oxygen atmosphere is 2Pr = 16.6 $\mu C/cm^2$, the corresponding coercive field is about Ec = 45 kV / cm. The reason for the difference is as follows: the samples have larger lattice distortion, lower oxygen vacancy concentration and more a-axis oriented grains after sintering in oxygen atmosphere, which are favorable for the increase of the remnant polarization and the reduction of the coercive field.

Conclusions

The effect of sintering atmosphere on the properties of SBT ferroelectric ceramics was studied. It was found that the samples sintered in oxygen atmosphere had more a-axis oriented grains and were more perpendicular to the plane of the grain than those sintered in the air atmosphere. The Curie temperature of oxygen atmosphere sintered sample is 273 ºC, and that of air atmosphere sintered sample is 265 ºC. The reason for the difference is the interaction between oxygen vacancy and crystal structure. The conductivity of the samples sintered in the oxygen atmosphere is Ea = 0.94 eV, which is close to the diffusion activation energy of the oxygen vacancy. And the activation energy of the sample in the air atmosphere is Ea = 0.66 eV, which is close to the activation energy of the oxygen vacancy secondary ionization. The residual polarization intensity of the sample sintered in the air atmosphere is 2Pr = 15.3 $\mu C/cm^2$, and that sintered in the oxygen atmosphere is 2Pr = 16.6 $\mu C/cm^2$. That is because the samples sintered in the oxygen atmosphere has larger lattice distortion, lower oxygen vacancy concentration and larger a-axis oriented grains, which are favorable for the increase of the remnant polarization and reduction of the coercive field.

Acknowledgments

This work was supported by funding from A Project of Shandong Province Higher Educational Science and Technology Program (Grant No. J15LA05), Research Fund for the Doctoral Program of Shandong Jianzhu University(Grant No.XNBS1626) and the National Natural Science Foundation of China(Grant No.51272142).

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