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Study on relationship between sintering atmosphere and dielectric properties for Bi_2O_3–ZnO–Ta_2O_5 system

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Abstract

The effect of sintering atmosphere on the structure and dielectric properties of Bi_2O_3–ZnO–Ta_2O_5 (BZT) system material has been investigated. The study shows that the sintering atmosphere has little effect on the phase structure for Bi_2O_3–ZnO–Ta_2O_5 system; the dielectric constants of the samples sintered in N_2 are larger than those sintering in air; the dielectric loss at low frequency increases and the microwave quality factor (Qf) decreases when sintered in N_2. Furthermore, the temperature dependence of dielectric constant decreases subtly when sintered in N_2.

Keywords: C. Dielectric properties; Bi_2O_3–ZnO–Ta_2O_5 system; Microwave properties

1. Introduction

Bismuth pyrochlore are recognized as promising microwave material due to its high dielectric constant low loss and low sintering temperature [1–4]. The pyrochlore structure is one of the oxygen octahedron based families. The general formula of the oxide pyrochlore can be written as $A_2B_2O_7$ where the A cations are eight-coordinated and the B cations are six-coordinated. In spite of the immense flexibility of chemical composition in the pyrochlore system, a cubic structure with eight molecules per unit cell ($Z = 8$) and space group $Fd3m$ is the predominant phase [5,6].

Recently, Bi_2O_3–ZnO–Ta_2O_5 system has attracted much attention as a new and promising microwave material due to its excellent dielectric and microwave properties. Bi_2O_3–ZnO–Ta_2O_5 pyrochlore has the same formula $A_2B_2O_7$ with Bi_2O_3–ZnO–Nb_2O_5, therefore, there are many similar properties between them [7].

In order to cofire with the cheap metal electrode material such as Cu and Ni, it is necessary to use N_2 as protective atmosphere because they are easy to be oxidized at high temperatures. However, the structure and properties of BZT can be changed when sintered in N_2 at high temperatures due to the deficiency of oxygen.

The purpose of this work is to study the effect of sintering atmosphere (N_2 and air) on the structure and properties of Bi_2O_3–ZnO–Ta_2O_5 system.

2. Experimental procedure

Conventional method was used in synthesizing $Bi_2(Zn_{1/3}Ta_{2/3})O_7$ (β-BZT) and $(Bi_{3/2}Zn_{1/2})(Zn_{1/2}Ta_{3/2})O_7$ (α-BZT), the starting materials were Bi_2O_3 (about 99.375%) Nb_2O_5 (about 99.5%) ZnO (about 99.5%) and TiO_2 (about 98%). The samples were ball milled for 24 h in a planetary ball miller and then dried and calcined at 800 °C for 4 h. The powder was granulated by adding organic binder before pressing into 12 mm disk. Microwave samples were prepared with diameter of 18 mm and height of 9 mm. Samples were sintered in air and N_2 at various temperatures for 1–4 h.

The density of sintered samples was measured by Archimedes method. The samples were crushed and powder X-ray diffraction (XRD) was performed to examine the phase structure. The microstructure of the surface of the sintered samples was observed by JEOL-scanning

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electronic microscope (SEM) after sputtering gold. A LCR meter (Hewlett–Packard 4284) in conjunction with a computer-interfaced temperature chamber was used in dielectric measurement at temperature range from −60 to +160 °C. The measurement were made with a heating rate of 2 °C/min. The measurement frequencies were varied from 1 kHz to 1 MHz. Temperature dependence of dielectric constant (ppm/°C)was calculated from the slope of the dielectric constant in the temperature range of +20 to +85 °C.

3. Results and discussion

3.1. Crystal structure

Fig. 1 shows that for BZT system the samples sintering in N_2 have the same phase structures with those sintering in air. As expected, sintering atmospheres have little effect on the phase structures of the BZT system.

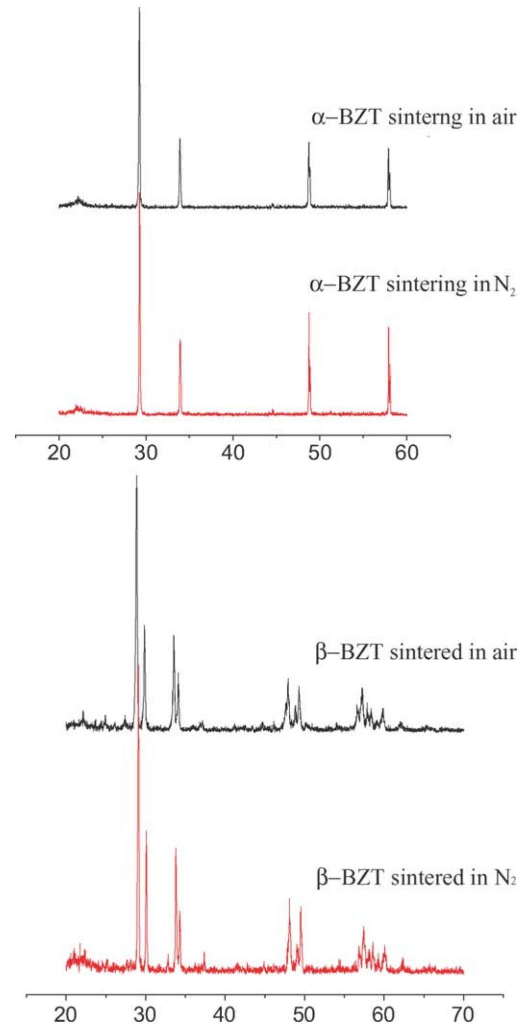

Fig. 1. XRD patterns for various sintering atmosphere.

3.2. SEM analysis

Fig. 2 shows the typical microstructures of $(Bi_{3/2}Zn_{1/2})(Zn_{1/2}Ta_{3/2})O_7$ and $Bi_2(Zn_{1/3}Ta_{2/3})O_7$ sintered in air and N_2. The crystal sizes sintered in air and N_2 are nearly equal. But the microstructures of the samples sintered in air are much denser than those sintered in N_2.

3.3. Dielectric properties under low frequency and microwave frequency

Table 1 shows that the densities of the samples sintered in N_2 are smaller than those sintered in air; the dielectric constants of the samples sintered in N_2 are larger than those sintered in air and the dielectric loss increases when sintered in N_2; furthermore, the microwave quality factor Qf decreases when sintering in N_2. According to Figs. 1 and 2, the samples have the same phase structures, however, the microstructures of the samples sintered in air are much denser than those sintered in N_2. Therefore, the densities of the samples sintered in N_2 are smaller than those sintered in air. The difference of the dielectric properties of the samples can mainly result from the difference of the microstructure caused by the different sintering atmosphere. The defect equation can be written as

$$O_o \rightleftarrows V^{\bullet\bullet}{}_o + \frac{1}{2}O_2 + 2e$$

When the samples were sintered in N_2, the concentration of O_2 decreased dramatically and, according to defect equation, the thermodynamic balance will move toward the right. Therefore, the concentration of oxygen vacancy will increase when sintering in N_2. This maybe results in that the

Table 1
Dielectric properties vs. various sintering atmosphere

Samples	Sintering atmosphere	Density	Dielectric properties under 1 MHz		Microwave dielectric properties		
			ε (r)	$\tan\delta$ ($\times 10^{-4}$)	Frequency (GHz)	ε (r)	Qf (GHz)
α-BZT	Air	8.775	72.6	0.85	5.13	70.2	177
	N_2	8.397	75.0	7.7	5.02	72.8	151
β-BZT	Air	8.863	63.5	2.86	5.2	61	6136
	N_2	8.348	64.5	17.2	5.2	62.3	4976

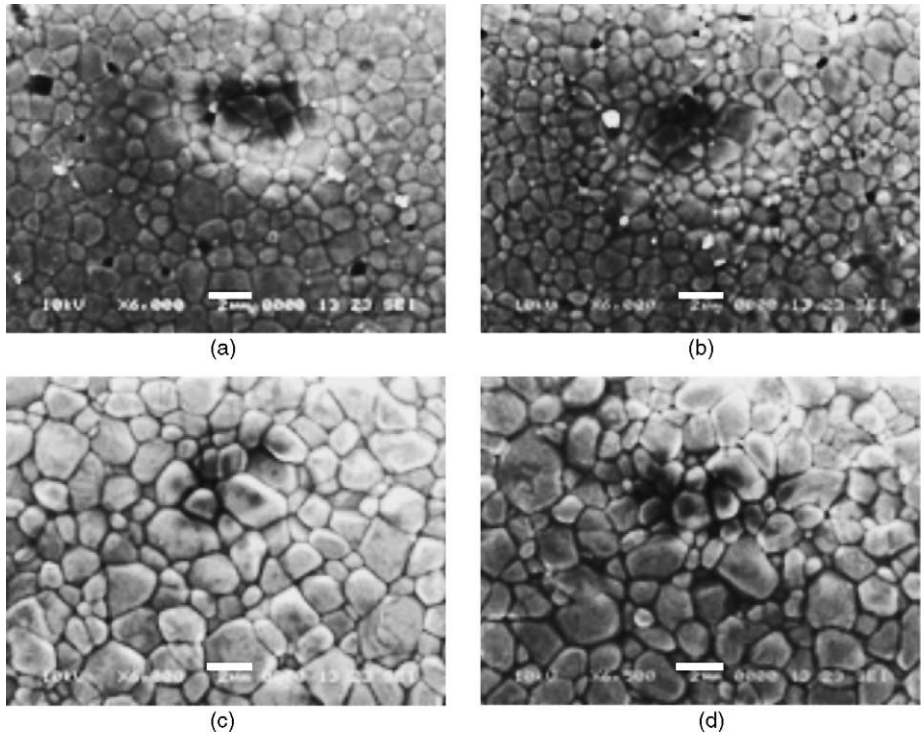

Fig. 2. SEM micrographs of samples sintered at different atmosphere:(a) α-BZT sintering in air, (b) α-BZT sintering in N_2, (c) β-BZT sintering air and (d) β-BZT sintering in N_2.

microstructures of the samples sintered in N_2 are looser than those sintered in air; the dielectric constants of the samples sintered in N_2 are larger than those sintered in air and microwave quality factor Qf sintered in N_2 is lower than that sintered in air.

3.4. Temperature dependence of dielectric constant

Fig. 3 and Table 2 show that the temperature dependence of dielectric constant has not too much distinction when sintered in N_2 and air. According to Fig. 1, the samples have

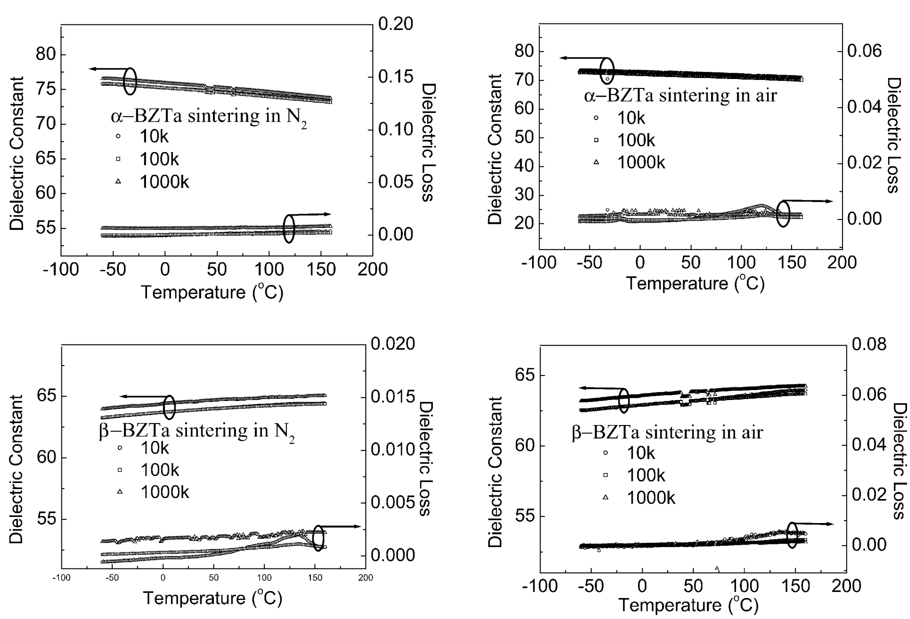

Fig. 3. Temperature dependence of dielectric constant vs. sintering atmosphere for Bi_2O_3–ZnO–Ta_2O_5.

Table 2
Temperature dependence of dielectric constant vs. sintering atmosphere

	Samples			
	α-BZT	α-BZT	β-BZT	β-BZT
Sintering atmosphere	N_2	Air	N_2	Air
Temperature dependence (ppm)	−173.3	−117.5	64.7	75.7

the same phase structures when they sintered in air and N_2. Therefore, it indicates that sintering atmosphere has little effect on the temperature dependence of dielectric constant.

4. Conclusion

1. Sintering atmosphere has little effect on the phase structure for BZT system. The samples sintered in N_2 have the same phase structures with those sintered in air.
2. The samples sintered in N_2 have lower density larger dielectric constant higher dielectric loss at low frequency and lower microwave quality factor Qf than those sintered in air due to more oxygen vacancy.
3. Sintering atmosphere has subtle effect on the temperature coefficient of dielectric constant and the temperature coefficient decreases subtly when sintered in N_2.

Acknowledgements

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