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EFFECT OF SINTERING TEMPERATURE AND TIME ON STRUCTURAL AND DIELECTRIC PROPERTIES OF TB-DOPED BATIO₃ CERAMICS

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ARTICLE DETAILS

ABSTRACT

Article History:

Received 26 June 2018 Accepted 2 July 2018 Available online 1 August 2018 Ba_{1-x/2}Ti_{1-x/2}Tb_xO₃ (x = 0.05) ceramics (BTTb5) were prepared at T_s = 1400 °C for t = 6–24 h and at T_s = 1300–1480 °C for t = 24 h using the cold-pressing ceramic processing technique. All of BTTb5 ceramics satisfy EIA X5R dielectric specification and exhibit a tetragonal perovskite structure. The sintering temperature and the sintering time have little influence on the crystal structure and dielectric properties of BTTb5. The optimum preparation condition of BTTb5 is determined as T_s = 1400 °C for t = 12 h because of higher relative density (ρ_r = 94 %) and lower dielectric loss (tan δ = 0.0108). As the sintering time increases, the XRD and EPR results reveal that more B-site Tb⁴⁺ ions are reduced to A-site Tb³⁺. The higher sintering temperature is apt to ceramic densification and the incorporation of more Tb⁴⁺ ions into B-sites.

KEYWORDS

Tb-doped BaTiO3 ceramics, X-ray diffraction, mixed-valent state, dielectric properties, electron paramagnetic resonance.

1. INTRODUCTION

In the dielectric field, researchers had explored Tb-doped BaTiO₃ (ABO₃) ceramics for thirty years [1–7]. Terbium (Tb) is a valence-variable rareearth element. In compounds, Tb is considered to exist as Tb³⁺ or as metastable Tb⁴⁺ with a half-filled 4f shell. Hence, there is controversy over the valence state of Tb in BaTiO₃. In 2001, Tsur *et al* anticipated a tendency of B-site occupancy by Tb⁴⁺ and indicated that in Ba-rich case Tb is incorporated into B-site as Tb⁴⁺ during sintering and on cooling to room temperature Tb⁴⁺ traps a single electron and becomes a large Tb³⁺ [1]. Most research groups thought that Tb ions are incorporated into A-sites as Tb³⁺ in BaTiO₃ before 2012 [2–5]. The abovementioned investigations reveal that the view of point that Tb exists at A-site or B-site as Tb³⁺ prevails in Tb-doped BaTiO₃. Until 2015, the electron paramagnetic resonance (EPR) monitoring of Tb-doped BaTiO₃ provided direct evidence for presence of B-site Tb⁴⁺ [6]. Under different Ba/Ti ratios, Tb ions in BaTiO₃ tend to form self-adjustable site occupations between A-site Tb³⁺ and B-site Tb⁴⁺ [6].

The subsequent studies indicated that the self-compensation mode of $Tb_{Ba}-Tb_{Ti}$ in $(Ba_{1-x}Tb_x)(Ti_{1-x}Tb_x)O_3$ ceramics sintered at a sintering temperature of $T_s = 1400$ °C cannot be formed and it is inevitable that some Tb ions enter B-sites as Tb4+ [7]. Defect notation proposed by Kröger and Vink was adopted [8]. It was also found that Tb cannot exist only as B-site for $(Ba_{1-x}La_x)(Ti_{1-x}Tb_x)O_3$ or only as A-site Tb3+ $(Ba_{1-x}Tb_x)(Ti_{1-x}Dy_x)O_3$ [9,10]. As a whole, Tb3+/Tb4+ is characteristic of Tb ions in singly- or double-doped BaTiO3. However, little is known about structural and dielectric properties of Tbdoped BaTiO₃ ceramics prepared under different conditions.

In this work, the effect of the sintering temperature (T_s) and the sintering time (t) on structural and dielectric properties of Tb-doped BaTiO₃ ceramics was reported. The dielectric stability independent of T_s and t is discovered. The optimum preparation condition is proposed.

2. EXPERIMENTAL

BTTb5 ceramics were prepared using a previously published cold

pressing ceramic processing technique according to the nominal formula $Ba_{1-x/2}Ti_{1-x/2}Tb_xO_3$ (x=0.05) [6]. The initial re-agent powders $BaCO_3$, TiO_2 , and Tb_4O_7 were weighed ancarefully mixed. The mixture was calcinated in air at 1100 °C for 5 h for decarbonation. The mixture with a PVA binder was then uniaxially pressed at 200 MPa for 2 min into pellets with 12-mm diameter. These pellets were sintered in air at $T_s=1400$ °C for t=6, 12, and 24 h, respectively (denoted by BTTb5TS); and for t=24 h at $T_s=1300$, 1350, 1400, 1450, and 1480 °C, respectively (BTTb5t). The pellets were densified into crack-free ceramics.

Powder X-ray diffraction (XRD) measurements were performed using a Rint 2200 X-ray diffractometer (Rigaku). All XRD data were collected between $20^{\circ} \leq 20 \leq 120^{\circ}$ in steps of 0.02° at room temperature. Crystal structures were determined by MS Modeling (Accelry). The polished disks with 0.8-mm thickness were electroded with sputtered Au atoms and silver paste and then heat-treated at 500 °C for 30 min for electrical measurements. The dielectric/Impedance spectrometer (Concept 41, Novocontrol) with an applied voltage of 1 V. EPR measurements were performed using an A300-10/12 X-band spectrometer (Bruker) operated at 9.84 GHz.

3. RESULTS AND DISCUSSION

3.1 Crystal Structure and Relative Density

The powder XRD patterns of BTTb5 ceramics sintered at $T_{\rm s}$ = 1400 °C for different sintering time (BTTb5t) are shown in Figure 1. A (002)/(200) peak splitting is characteristic of the tetragonal perovskite structure (Figure 1 insets). The crystal structure of BTTb5t is tetragonal from t = 6 to 24 h and independent of the sintering time. The powder XRD patterns of BTTb5 ceramics sintered for 24 h at different sintering temperatures (BTTb5TS) are shown in Figure 2. Similar to BTTb5t, the crystal structure of BTTb5TS is still tetragonal from $T_{\rm s}$ = 1300 to 1480 °C and independent of the sintering temperature.

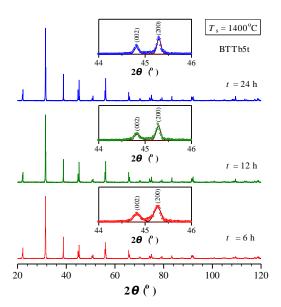


Figure 1: Powder XRD patterns of BTTb5 ceramics sintered at T_s = 1400 °C (BTTb5t) for 6, 12 and 24 h. Three insets show Gaussian fitting of the XRD peaks in the vicinity of 45°.

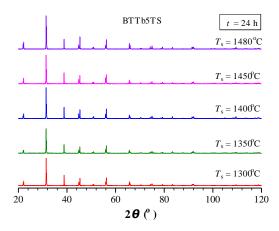


Figure 2: Powder XRD patterns of BTTb5 ceramics sintered at Ts = 1300, 1350, 1400, 1450, 1480 °C for 24 h (BTTb5TS).

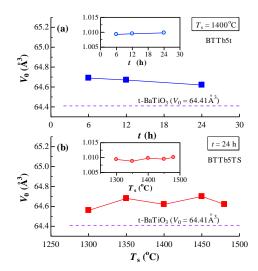


Figure 3: Variations in V_0 as a function of (a) t for BTTb5t and (b) T_s for BTTb5TS. Two insets show c/a vs t for BTTb5t and c/a vs T_s . for BTTb5TS.

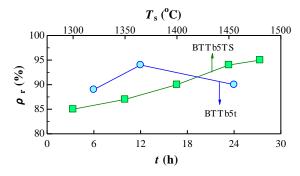


Figure 4: Variations in ρ_r as a function of t for BTTb5t and T_s for BTTb5TS.

The variations in unit-cell volume (V_0) as a function of t for BTTb5t and T_s for BTTb5TS are shown in Figure 3. The V_0 at T_s = 1400 °C decreases with increasing t (Figure 3a), implying that more B-site Tb⁴⁺ ions are reduced to A-site Tb³⁺. The V_0 at t = 24 h changes in M-type when T_s increases from 1300 to 1480 °C (Figure 3b). The tendency to increase in V_0 implies that the higher T_s is apt to the incorporation of Tb⁴⁺ ions into B-sites. The tetragonality (c/a) is nearly a constant (1.009–1.010), independent of T_s and t (Figure 3 insets). This fact reveals that Tb ions can be completely incorporated into the BaTiO₃ lattice when $T_s \ge 1300$ °C and $t \ge 6$ h.

The relative density (ρ_r) of BTTb5TS increases from 85 to 95 % continuously with increasing T_s from 1300 to 1480 °C. The ρ_r of BTTb5t sintered at T_s = 1400 °C reaches a maximum value of 94 % at t = 12 h, as shown in Figure 4. Thus, to achieve dense Tb-doped BaTiO₃ ceramics, the optimum condition is chosen as T_s = 1400 °C for t = 12 h.

3.2 Dielectric Properties

The temperature dependences of the dielectric permittivity (ϵ') and the dielectric loss (tan δ) for BTTb5t are shown in Figure 5. All the BTTb5t ceramics exhibit dielectric-temperature stability below 85 °C, satisfying EIA (Electronic Industries Association) X5R specification. As t increases, the change in dielectric-peak temperature ($T_{\rm m}$) is less than 5 °C, revealing that the concentrations of A-site Tb³+ and B-site Tb⁴+ alters little, independent of t. The room-temperature permittivity ($\epsilon'_{\rm RT}$) is 1120. BTTb5t exhibits a lower tan δ (0.0108) at roo, temperature when $t \ge 12$ h. The shorter sintering time (e.g. t = 6 h) will result in an increase in tan δ .

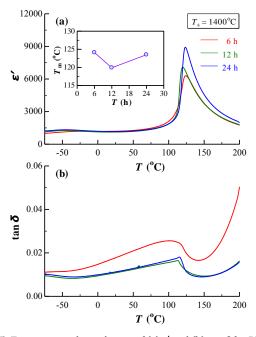


Figure 5: Temperature dependences of (a) ε' and (b) tan δ for BTTb5t, measured at 1 kHz. The inset depicts $T_{\rm m}$ vs t for BTTb5t.

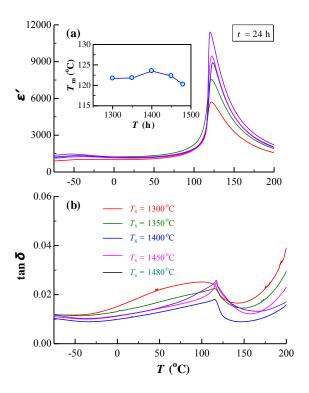


Figure 6: Temperature dependences of (a) ε' and (b) $\tan \delta$ for BTTb5TS, measured at 1 kHz. The inset depicts $T_{\rm m}$ vs t for BTTb5T

The temperature dependences of ε' and $\tan \delta$ for BTTb5TS are shown in Figure 6. BTTb5TS keeps a stable permittivity in the X5R temperature region. A lower sintering temperature of $T_s=1300\,^{\circ}\mathrm{C}$ is not advantageous to the fabrication of Tb-doped BaTiO_3 ceramic owing its lower ε' and higher $\tan \delta$. Raising T_s has little influence on $\varepsilon'_{\mathrm{RT}}$, but the maximum permittivity ($\varepsilon'_{\mathrm{m}}$) is greatly improved. At $T_s=1400\,^{\circ}\mathrm{C}$, when t is increased from 12 to 24 h, $\varepsilon'_{\mathrm{RT}}$ is increased slightly from 1120 to 1170, suggesting that the selection of t=12 h is very reasonable. It can be seen from Figure 6 that BTTb5TS sintered at $T_s=1400\,^{\circ}\mathrm{C}$ relative to other ceramics exhibits the lowest $\tan \delta$. These investigations further clarify that the optimum condition is $T_s=1400\,^{\circ}\mathrm{C}$ for t=12 h for Tb-doped BaTiO_3 ceramics. Thus, we prepared $(\mathrm{Ba}_{1-x}\mathrm{La}_x)(\mathrm{Ti}_{1-x}\mathrm{Tb}_x)\mathrm{O}_3$ [9] and $(\mathrm{Ba}_{1-x}\mathrm{Tb}_x)(\mathrm{Ti}_{1-x}\mathrm{Dy}_x)\mathrm{O}_3$ [10] ceramics according to this condition [9,10].

3.3 Electron Paramagnetic Resonance and Point Defects

The EPR spectra of BTTb5t are shown in Figure 7. A broad signal at g=5.68-5.81 is assigned to Tb⁴⁺ and its g value decreases slightly with increasing t [6,7,9,10]. It is known that the g value increases with increasing the Ba/Ti ratio. That is to say, an increase in g is in accordance with an increase in the concentration of B-site Tb⁴⁺ ions [6]. This fact suggests that the increase in sintering time results in a decrease in the concentration of B-site Tb⁴⁺ ions, which agree with the XRD result.

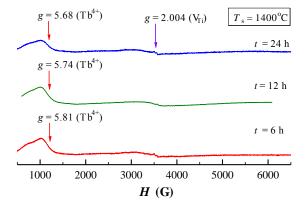


Figure 7: EPR spectra of BTTb5t.

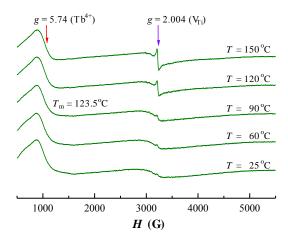


Figure 8: Temperature-dependent EPR spectra of BTTb5 sintered at Ts = 1400 °C for 12 h (i.e. BTTb5t with t = 12 h).

A weak signal appears in the vicinity of 3500 G. To investigate the origin of this weak signal, the temperature-dependent EPR spectra of BTTb5 sintered at T_s = 1400 °C for 12 h (i.e. BTTb5t with t = 12 h) were measured, as shown in Figure 8. This weak signal is markedly activated above 120 °C, near the tetragonal-cubic phase transition point (T_m = 123.5 °C). For this reason, this weak signal is attributed to ionized Ti vacancies [6]. The existence of Ti vacancies in BTTb5t is apt to the Ti-site occupations by the larger Tb⁴⁺ ions (0.76 Å) [11].

The formula $(Ba_{1-x/2}Tb_{x/2})(Ti_{1-x/2}Tb_{x/2})O_3$ with a self-compensation mode cannot be formed due to the existence of B-site Tb^{4+} and Ti vacancies. The concentration of A-site Tb^{3+} ions must be higher than that of B-site Tb^{4+} ions to keep lattice electroneutrality.

4. CONCLUSION

Ba_{1-x/2}Ti_{1-x/2}Tb_xO₃ (x=0.05) ceramics (BTTb5) were prepared at $T_s=1400$ °C for t=6-24 h (BTTb5t) and at $T_s=1300-1480$ °C for t=24 h (BTTb5TS) using the cold-pressing ceramic processing technique. All the BTTb5 ceramics satisfy EIA X5R specification and exhibit a tetragonal perovskite structure. The sintering temperature and the sintering time have little influence on the crystal structure and dielectric properties of BTTb5. The optimum preparation condition of BTTb5 is determined as $T_s=1400$ °C for t=12 h because of higher relative density ($\rho_r=94$ %) and lower dielectric loss ($\tan\delta=0.0108$). When $T_s=1400$ °C, as the sintering time increases, both V_0 and the g value of the EPR signal of Tb⁴⁺ decrease (from 5.81 to 5.68). These two XRD and EPR results reveal that more B-site Tb⁴⁺ ions are reduced to A-site Tb³⁺. The higher T_s is apt to ceramic densification and incorporation of more Tb⁴⁺ ions into B-sites.

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