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Dielectric properties and phase transition of samarium-doped $BaSn_{0.1}Ti_{0.9}O_3$ ceramics

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Abstract

The dielectric properties and phase transition of Sm^{3+}-doped $BaSn_{0.1}Ti_{0.9}O_3$ (BTS10) ceramics were investigated. The amount of Sm_2O_3 greatly affected the dielectric properties of BTS10. A dielectric constant of 5500 with 0.6 mol% Sm_2O_3 and a dissipation factor of only 0.005 with 0.1 mol% Sm_2O_3 were assessed. The variation in the dielectric constant indicated that Sm^{3+} ion is mainly substituted for the A-site ions when $x \leq 0.6$ mol%, whereas it is mainly substituted for B-site ions when x exceeded 0.6 mol%. Meanwhile, the variation in the dissipation factor showed that a very small amount of Sm^{3+} occupied the B site when $x \leq 0.1$ mol%. The materials showed relaxor-like behaviour with a diffuse-type ferroelectric phase transition. The diffusivity increased when the amount of Sm_2O_3 is increased, which also implied that there should be a very small amount of Sm^{3+} occupying the B site when $x \leq 0.1$ mol%.

Keywords: C. Dielectric properties; D. $BaTiO_3$ and titanates; D. Perovskites; Phase transition

1. Introduction

Since 1970s, ferroelectrics with diffused phase transition (DPT) have attracted much interest due to their physical mechanisms of diffuse-type phase transition [1–4]. Relaxor ferroelectrics (RFEs) have many potential applications, such as high-capacitance, hysteresis-free actuators, and high-performance sensors [5]. Setter and Cross [6] studied the phase transition of $Pb(Sc_{1/2}Ta_{1/2})O_3$ ceramics. They believed that DPT is connected with the disorder state of the ions in the B site, and that the disorder state corresponds to clear DPT. However, DPT disappears when the arrangement of Sc^{3+} and Ta^{5+} ions become ordered after the ceramic is annealed. In perovskites, relaxor behaviour is exhibited in lead-based compositions ($(Pb(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Sb_{0.5}Nb_{0.5})O_3$, $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$, etc.) with more than one type of ions occupying the equivalent six-coordinated crystallographic sites [7]. Lead-free compositions could be of great interest for environmentally friendly applications [8].

There are many opinions about the origination of DPT. Smolensky [9] proposed that the broadened phase transition originated from the compositional fluctuation of the microscopic heterogeneity. Isupov [10] explained some problems of ferroelectrics with DPT in view of the polar region. Although much work [11–14] has been done on ferroelectrics with DPT and RFEs; their relationship has not been clear, e.g., all RFEs have DPT, but not all ferroelectrics with DPT are believed to be RFEs.

$Ba(Ti,Sn)O_3$ (BTS) ceramics with DPT are found to be important materials for studying ferroelectric physics [15,16]. The relaxor behaviour of BTS was caused by the inhomogeneous distribution of Sn and Ti ions at the B site, according to the compositional fluctuation model proposed by Smolensky [9]. When aliovalent cations, such as Sm^{3+}, are incorporated into BTS ceramics, the inhomogeneous distribution of Sn and Ti ions will be changed. Therefore, the relaxor behaviour can occur in BTS ceramics. This relaxor

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behaviour is helpful in improving dielectric properties. Furthermore, the doping of samarium to modify the dielectric properties of BTS ceramics has rarely been reported in the literature. In the present study, BTS+xSm$_2$O$_3$ (x=0.0–0.8 mol%) were prepared using the conventional ceramic processing. The influence of samarium content on the dielectric properties and phase transition of BTS ceramics was investigated. Based on experimental results, the substitution mechanism of Sm^{3+} ion in BaSn$_{0.1}$Ti$_{0.9}$O$_3$ (BTS10) was investigated and discussed.

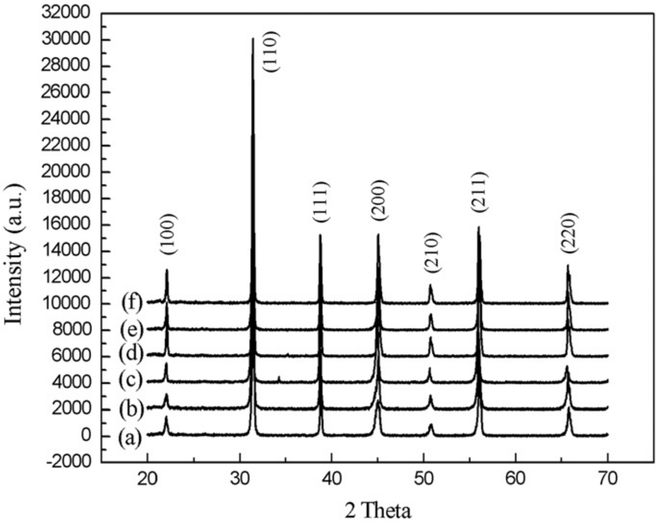

Fig. 1. XRD patterns of the Sm$_2$O$_3$ doped BTS10 ceramics: (a) 0.0 mol%, (b) 0.05 mol%, (c) 0.1 mol%, (d) 0.2 mol%, (e) 0.6 mol% and (f) 0.8 mol%.

2. Experimental procedure

The composition was BTS10+xSm$_2$O$_3$, with x=0.0–0.8 mol%. The samples were prepared by the two-stage method. Reagent-grade oxide powders TiO$_2$ (AR, China), SnO$_2$ (AR, China), BaCO$_3$ (AR, China), Sm$_2$O$_3$ (99.99%, China), MgO (99.99%, China), and MnO$_2$ (CP, China) were used as received. Generally, Mg^{2+} can prevent the reduction of Ti^{4+} to Ti^{3+} [17], while MnO$_2$ can increase the breakdown of the field strength [18]. Firstly, BTS10 powder was synthesised from TiO$_2$, SnO$_2$, and BaCO$_3$ at 1080 °C for 2 h. Secondly, the powder was mixed with x Sm$_2$O$_3$, 0.2 at% MgO, and 0.2 at% MnO$_2$, with polyethylene jar and agate balls milling media. The mixture was then dried at 120 °C, granulated (with polyvinyl alcohol as binder), pressed into pellets ($\Phi \times d$=10.30 × 2.00 mm^2) at 350 MPa, and then sintered at 1280 °C, 1300 °C and 1320 °C for 2 h in the air, respectively. The sintered samples were cleaned using an ultrasonic bath and then dried. Both sides of the specimens for dielectric property measurements were screened with Ag electrode paste, and then fired at 530 °C for 10 min.

The crystal structure of the samples was analysed by X-ray diffraction (XRD, GIRAKU D/MAX 2500V/PC, Japan) from 20° to 70°. The micrographs of the samples

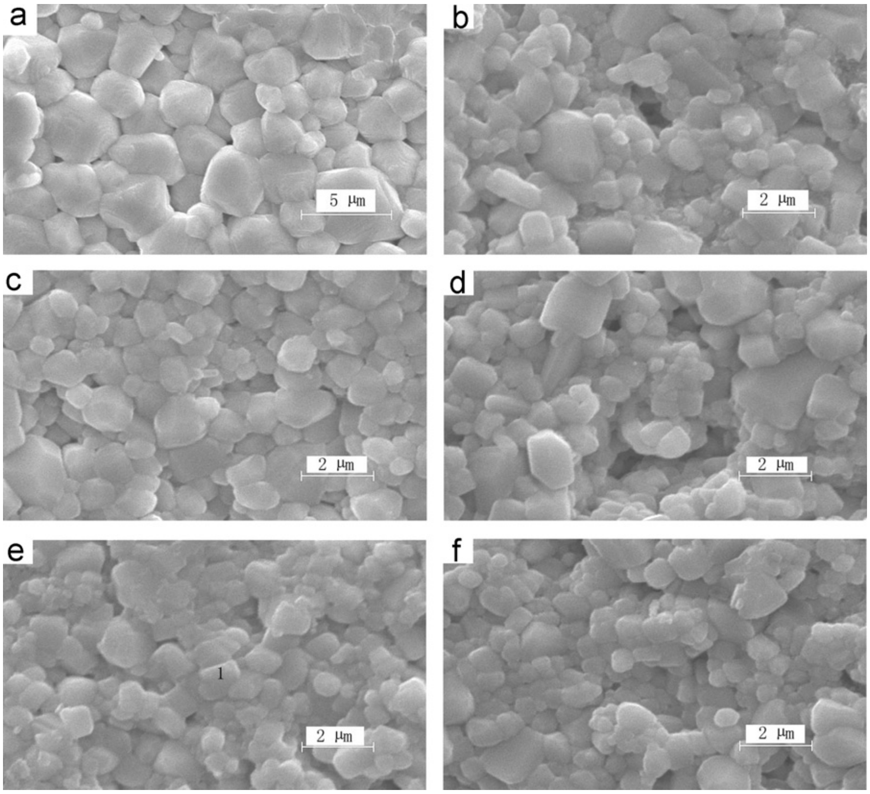

Fig. 2. Surface SEM images of the Sm$_2$O$_3$ doped BTS10 specimens: (a) 0.0 mol%, (b) 0.05 mol%, (c) 0.1 mol%, (d) 0.2 mol%, (e) 0.6 mol% and (f) 0.8 mol%.

were observed by environmental scanning electron microscopy (ESEM, Philip XL 30 ESME).

Capacitance (*C*) and loss factor (*D*) were measured using a capacitance apparatus (Model YY 281 automatic LCR Metre 4225, China) at 1 kHz. The dielectric constant (ε_r) and dissipation factor (tanδ) were calculated as follows:

$$\varepsilon_r = \frac{14.4Ch}{\varphi^2} \tag{1}$$

$$\tan\delta = \frac{fD}{1000} \tag{2}$$

where *C* and *D* are the measured capacitances and loss factors of the samples, respectively; *h*, *Φ*, and *f* are the thickness, diameter of the samples, and testing frequency, respectively. The temperature dependence of the dielectric constant and the dissipation factor were obtained from – 30 °C to 125 °C. The phase transition temperature (T_m) was determined from the temperature dependences of the dielectric constant.

3. Results

The XRD patterns of the samples with different amounts of Sm_2O_3 contents sintered at 1300 °C for 2 h are shown in Fig. 1. The patterns indicate that all samples are at the cubic perovskite phase. Fig. 2 shows the SEM images of Sm^{3+}-doped BTS10 ceramics. The diameter of pure BTS10 granule was approximately 1.0 µm. After being doped with Sm_2O_3 over 0.05 mol%, the grain diameter was reduced to approximately 0.5 µm, as shown in Fig. 2(c–f). This implies that there is a very small amount of Sm^{3+} segregated at grain boundaries to inhibit grain growth [19]. The energy dispersive spectroscopy (EDS) of the selected grain is shown in Fig. 3. Sm, together with Sn, Ti, Ba and O, was detected in the grain, which confirms the existence of Sm^{3+} in perovskite lattice. The homogeneous distribution of the Sm element is shown at the surface of 0.6 mol% Sm_2O_3-doped samples, as shown in Fig. 4(b).

Fig. 5 presents the dielectric constants of the samples sintered at 1280 °C, 1300 °C and 1320 °C for 2 h. The dielectric constants were enhanced with the increase in Sm_2O_3 of upto 0.6 mol%, beyond which the dielectric constants exhibited a slight drop. The sample with 0.6 mol% Sm_2O_3 has the highest dielectric constant of 5500.

Fig. 6 shows the dissipation factors of the samples as a function of the Sm_2O_3 content. The sample with 0.1 mol%

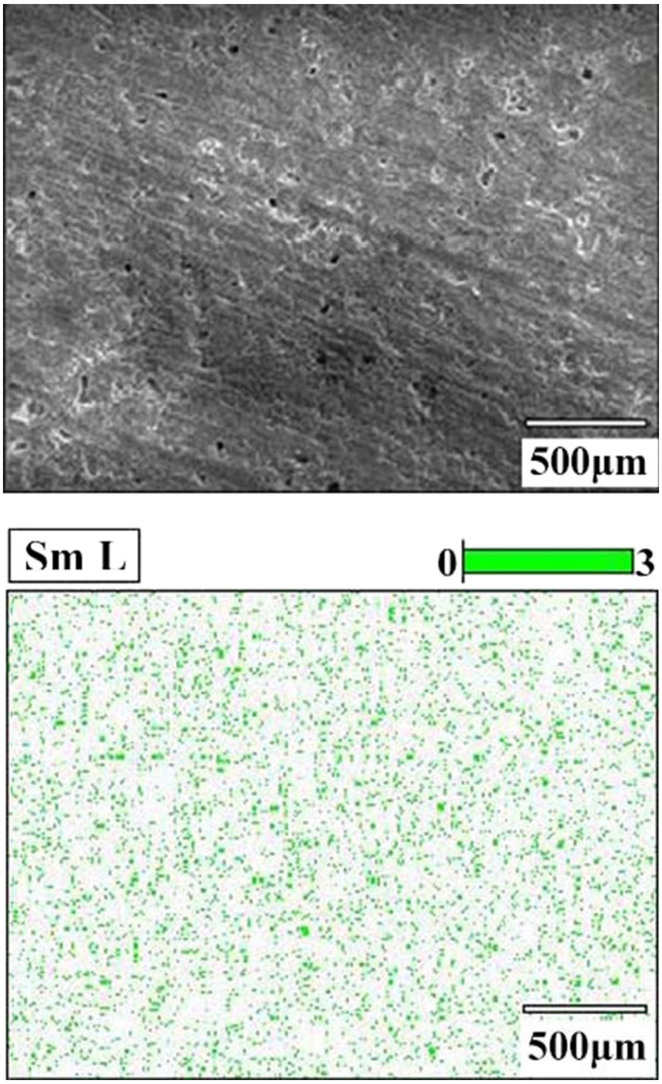

Fig. 4. Surface distribution of Sm for 0.6 mol% Sm_2O_3 doped BTS10 ceramics.

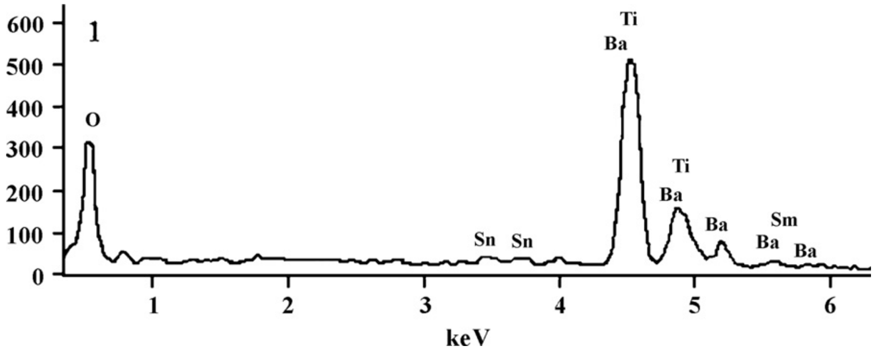

Fig. 3. EDS spectra of the 0.6 mol% Sm_2O_3 doped BTS10 ceramics.

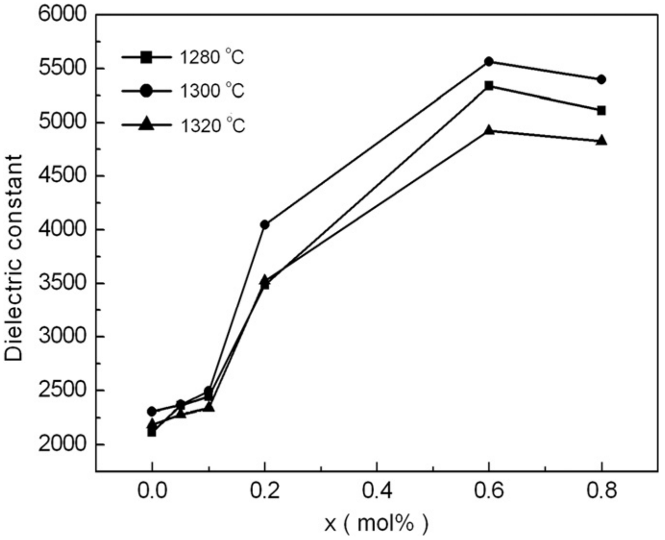

Fig. 5. Dielectric constant of the BTS10 ceramics as a function of Sm_2O_3 content.

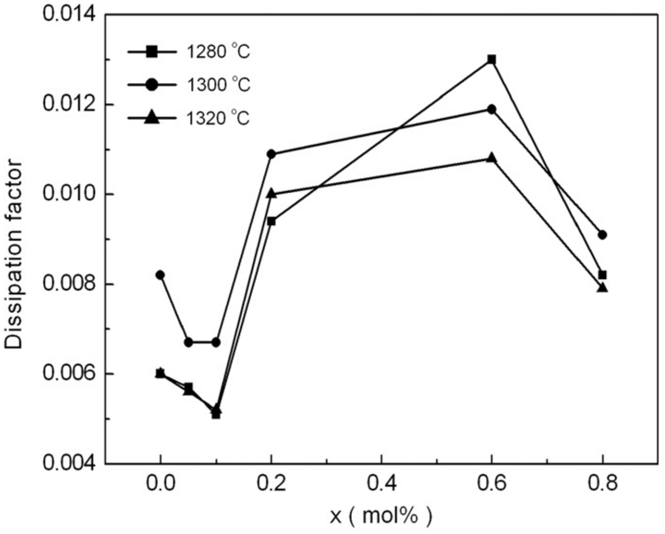

Fig. 6. Dissipation factor of the Sm_2O_3 doped BTS10 ceramics.

Sm_2O_3 has the lowest dissipation of 0.005, whereas the ceramics with 0.6 mol% Sm_2O_3 have the highest dissipation factor of 0.013. Therefore, the trace amount of Sm^{3+} could remarkably influence the dielectric properties of BTS10.

Fig. 7 shows the temperature dependences of the dielectric constants of the samples sintered at 1300 °C. The maximum value of the dielectric constant showed no clear change when Sm_2O_3 is less than 0.1 mol%, and it reached the highest value when x equals 0.6 mol%. Additionally, T_m did not exhibit any shift when Sm_2O_3 is less than 0.1 mol%, but it rose from –27 °C to –3 °C when the amount of Sm_2O_3 was increased from 0.1 mol% to 0.6 mol%. A slight drop in T_m was observed when the Sm_2O_3 content was increased to 0.8 mol%.

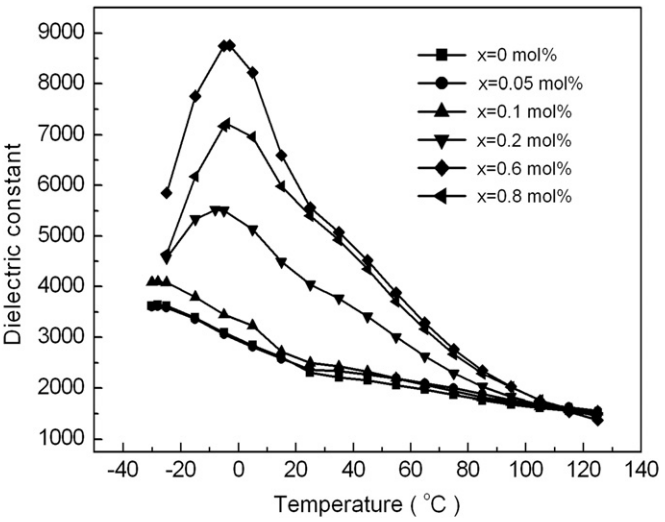

Fig. 7. Temperature dependence of dielectric constant of selected samples.

Table 1
Tolerance factor t for Sm^{3+} ions doping in BTS ceramics.

Substitution site	t
A (in $BaTiO_3$ crystal)	0.93
A (in $BaSnO_3$ crystal)	0.88
B (Ti^{4+} or Sn^{4+})	0.90

Interestingly, when the addition of Sm_2O_3 content was no more than 0.1 mol%, T_m did not show any shift. The dissipation factor was the lowest with 0.1 mol% Sm_2O_3 doping, whereas, samples with 0.6 mol% Sm_2O_3 doping have the highest dielectric constant, dissipation factor, T_m, and the maximum value of dielectric constant; we do not believe that this is coincidental.

4. Discussion

The ionic radii of Ba^{2+} in 12 coordinates and the Sn^{4+} or Ti^{4+} in 6 coordinates are 0.161 nm, 0.071 nm, and 0.061 nm, respectively. The ionic radii of Sm^{3+} in 12 and 6 coordinates are 0.124 nm and 0.096 nm [20], respectively. Therefore, in terms of size, Sm^{3+} can occupy either the A site or B site in BTS. Moreover, according to the crystal chemistry theory, the structural stability of doping ions in perovskite lattice can be measured by the tolerance factor (t), given by the following equation:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \tag{3}$$

where r_A, r_B, and r_O are the ionic radii of the A- and B-site ions and the O^{2-} ion, respectively. The tolerance factor increases and reaches to unity when the system becomes an ideal perovskite. As shown in Table 1, t is 0.93 and 0.88 when Sm^{3+} ions occupy the A site in $BaTiO_3$ and $BaSnO_3$, respectively. It is 0.90 when Sm^{3+} ions replace Ti^{4+} or

Sn^{4+}. The tolerance factors are very close when Sm^{3+} ions occupy either the A site or the B site. Therefore, Sm^{3+} ions could occupy either the A site as a donor or the B site as an acceptor.

It has been reported that aliovalent cations incorporated in perovskite lattice, as either donors or acceptors, could greatly affect the electrical properties of a material [21]. In our previous study [22], on one hand, when Sm^{3+} ion occupies the A site as a donor, V''_{Ba} and Ti^{3+} will be produced, leading to an increase in dielectric constant. On the other hand, if Sm^{3+} ion substitutes for the B- site ions, as an acceptor, V''_{O} will be produced. In such case, the vibration of Sm^{3+} ion in the Ti–O octahedron becomes weak, leading to a drop in dielectric constant. In addition, V''_{O} has a pinning effect [23], resulting in a drop in dielectric constant. Therefore, in our present study, it can be assumed that Sm^{3+} ion mainly substitutes for the A-site ions when x is ≤ 0.6 mol%, leading to a rise in dielectric constant; it starts to substitute for the B-site ions when x exceeds 0.6 mol%, leading to a drop in dielectric constant.

However, the ceramics with 0.1 mol% Sm_2O_3 have the lowest dissipation factor of 0.005. On one hand, electrons are generated when Sm^{3+} ion is introduced into BTS10; hence more Ti^{4+} will be reduced to Ti^{3+}, and the dissipation factor should increase. On the other hand, oxygen vacancies are also produced, which prevents the reduction of Ti^{4+}, and the dissipation factor is reduced accordingly. Therefore, we believe that most Sm^{3+} ions occupied the A site and that only a very small amount of Sm^{3+} occupied the B site when $x \leq 0.1$ mol%.

In the vicinity of transition temperature, the dielectric constant ε and the Curie temperature T_c of ferroelectrics can be described by the Curie–Weiss law:

$$\varepsilon = \frac{C}{T - T_0} \tag{4}$$

where C is the Curie constant and T_0 is the Curie–Weiss temperature. Fig. 8 shows the dielectric constant and inverse dielectric constant versus temperature of four samples sintered at 1300 °C. A clear deviation from the

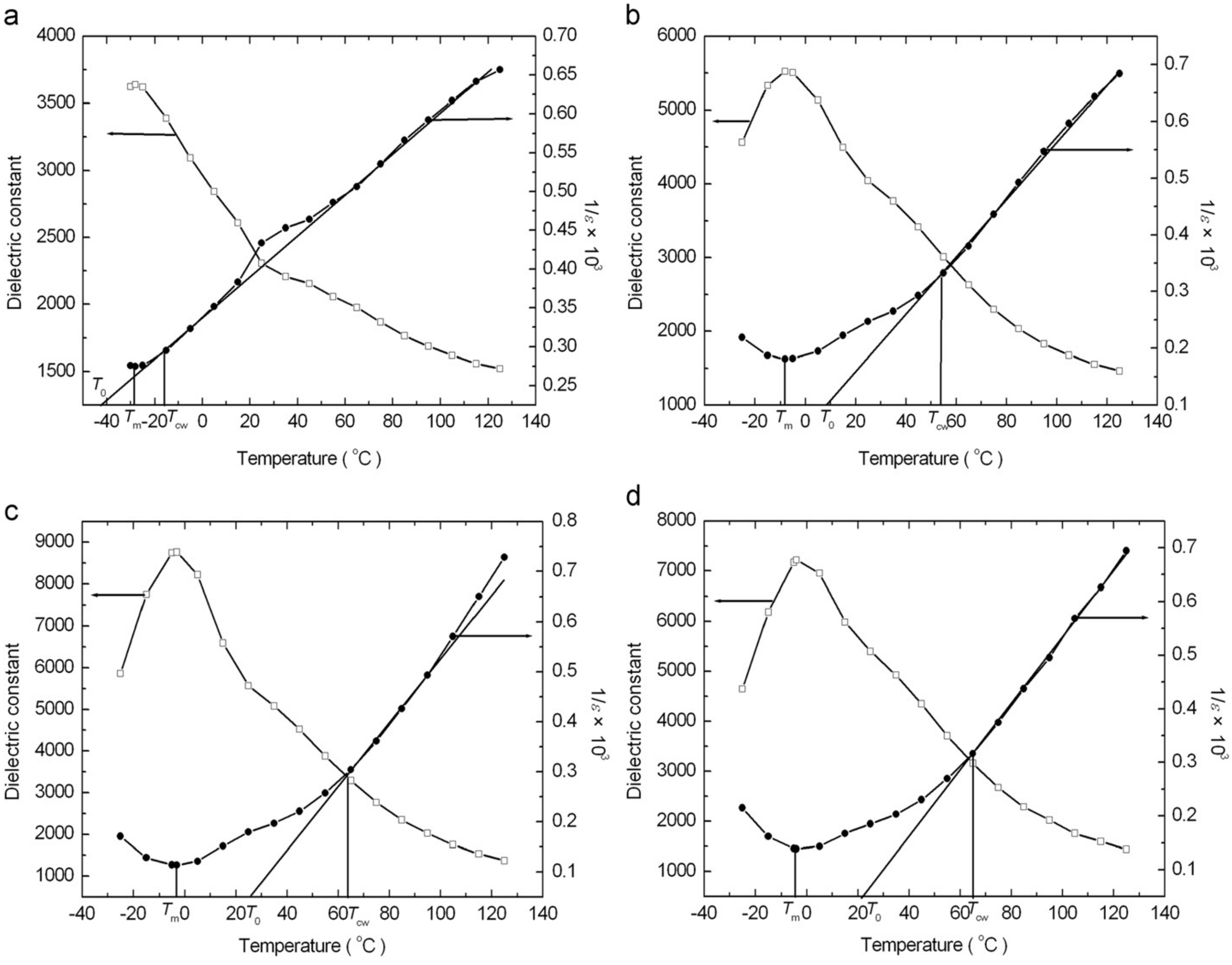

Fig. 8. Temperature dependence of 1/ε of the Sm_2O_3 doped BTS10 ceramics: (a) 0.0 mol%, (b) 0.2 mol%, (c) 0.6 mol% and (d) 0.8 mol%.

Curie–Weiss law can be seen in the samples with Sm_2O_3. The BTS10 sample without Sm_2O_3 abides by the conventional Curie–Weiss law above the phase transition temperature. The parameter ΔT_m, which describes the degree of the deviation from the Curie–Weiss law, is defined as follows:

$$\Delta T_m = T_{cw} - T_m \tag{5}$$

where T_{cw} denotes the temperature from which the dielectric constant starts to deviate from the Curie–Weiss law and T_m represents the temperature of the dielectric maximum. It can be seen that ΔT_m increases with the increase in the amount of Sm_2O_3, as shown in Fig. 8(b–d), which demonstrated that the degree of deviation from the Curie–Weiss law becomes more and more pronounced.

A modified Curie–Weiss law has been proposed to describe the diffuseness of a phase transition:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^\gamma}{C'} \tag{6}$$

where γ and C' are assumed to be constant. For $\gamma = 1$, a normal Curie–Weiss law is obtained; for $\gamma = 2$, a complete diffused phase transition is observed. The plots of $\ln(T - T_{max})$ versus $\ln(1/\varepsilon_r - 1/\varepsilon_{max})$ for the four samples are shown in Fig. 9. Linear relationships were observed. The slopes of the fitting curve were used to determine the parameter γ. The values of γ are listed in Table 2. It can be seen that γ is 1 for pure BTS10, which is in accordance with the result in Fig. 8(a) and that reported in Ref. [3]. The increase in the value of γ with Sm_2O_3 content (Table 2) indicates an increase in diffusivity. According to Smolensky

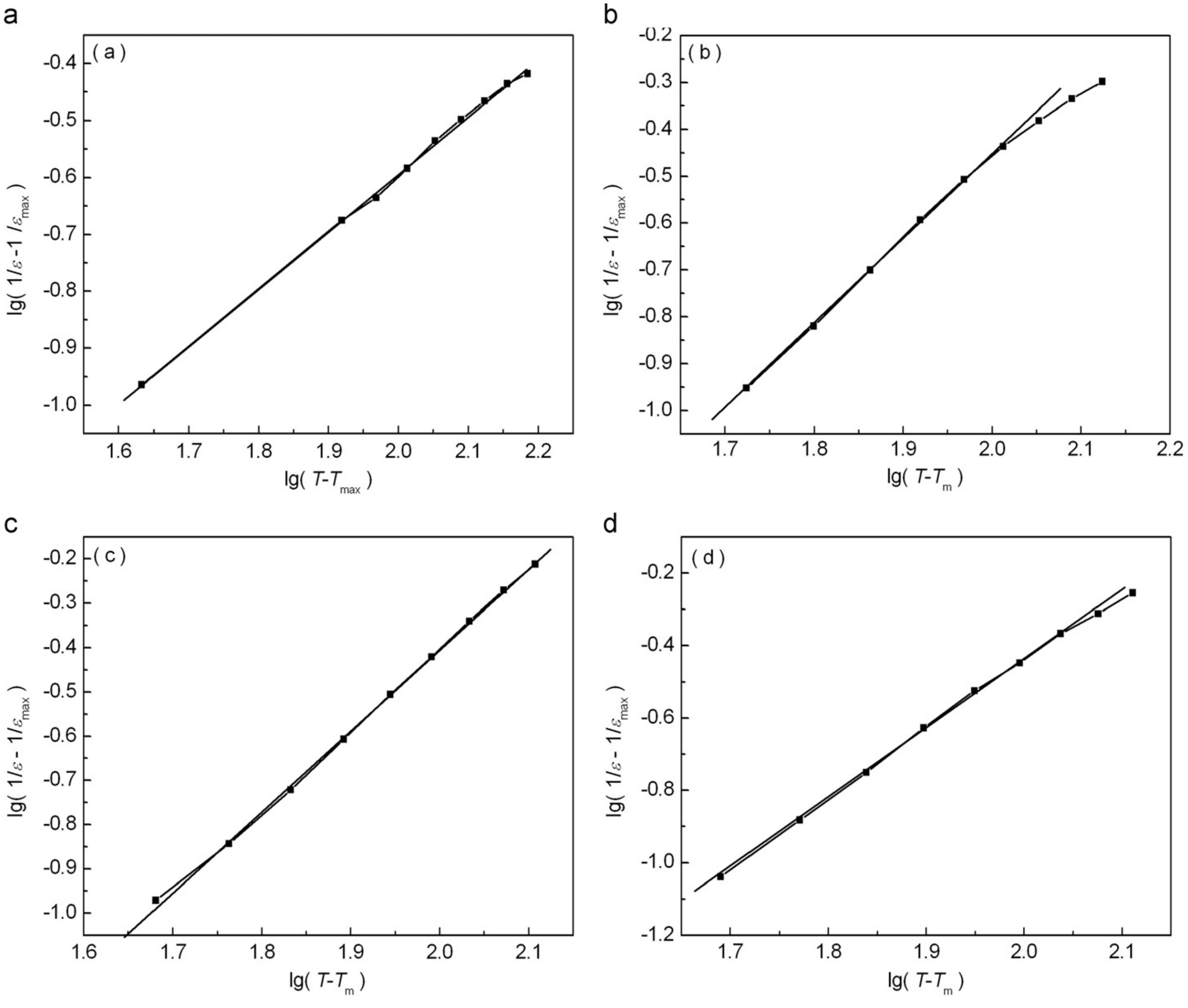

Fig. 9. Plot of $\ln(T - T_{max}) - \ln(1/\varepsilon_r - 1/\varepsilon_{max})$ of the Sm_2O_3 doped BTS10 ceramics: (a) 0.0 mol%, (b) 0.2 mol%, (c) 0.6 mol% and (d) 0.8 mol%.

Table 2
Variation in γ as a function of dopant concentration.

X	γ
0.0	1.01
0.05	1.11
0.1	1.34
0.2	1.78
0.6	1.84
0.8	1.94

[9], diffused phase transition may arise from the inhomogeneous distribution of Sn and Ti ions. Additionally, when Sm^{3+} occupies the B site, it will result in an inhomogeneous distribution of Sn and Ti ions. As a result, the behaviour of diffused phase transition occurs, which in turn proves that there is a very small amount of Sm^{3+} occupying the B site when $x \leq 0.1$ mol%. Furthermore, it also explains why T_m did not exhibit any shift when the additional Sm_2O_3 content is less than 0.1 mol%.

5. Conclusions

The dielectric properties and phase transition of Sm^{3+}-doped BTS10 ceramics were investigated. Due to the modifications in Sm^{3+} doping, the sample with 0.6 mol% Sm_2O_3 had the highest dielectric constant (5500), whereas that with 0.1 mol% Sm_2O_3 had the lowest dissipation factor (0.005). The variation of the dielectric constant showed that Sm^{3+} ion mainly substituted for the A-site ions when $x \leq 0.6$ mol%, whereas it mainly substituted for B-site ions when x exceeded 0.6 mol%. Meanwhile, the variation of the dissipation factor showed that a very small amount of Sm^{3+} occupied the B site when $x \leq 0.1$ mol%. The materials were of relaxor type and diffuse-type ferroelectric phase transition, and the diffusivity increased with the increase in Sm_2O_3 content.

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