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Dielectric dispersion and impedance spectroscopy of B^{3+}-doped $Ba(Ti_{0.9}Sn_{0.1})O_3$ ceramics

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Abstract

In this study, the B_2O_3 doped $Ba(Ti_{0.9}Sn_{0.1})O_3$ ceramics were prepared by using a solid state reaction method. Wide ranges of frequency (0.1 Hz to 1 MHz) and temperature (20–280 °C) dependence of the impedance relaxation were investigated. The impedance study indicates the presence of both dielectric relaxation in bulk and grain boundary effects in the material. The relaxation times for grain and grain boundary estimated from Cole–Cole plots varied with temperature according to the Arrhenius relation. The activation energy for grain and grain boundary were estimated to be 0.73 and 0.85 eV, respectively.

Keywords: A. Sintering; C. Ferroelectric properties; Impedance spectroscopy

1. Introduction

It has been more than a decade since studies focused on relaxor ferroelectric materials owing to their various modern technological applications [1,2]. Barium stannate titanate ($BaTi_{1-x}Sn_xO_3$) (BTS) is one of the most interesting and extensively studied relaxor materials, which has already shown its immense potential in many microelectronic devices. It is noticed that increasing of Sn content in BTS ceramic decreased the temperature of ferroelectric–paraelectric phase transition and the maximum of dielectric peaks became more diffuse [3]. Particularly, the relaxor-like behavior can be observed near room temperatures when the Sn concentration is between 10% and 20% [4]. It has been widely accepted that the electrical properties of modified $BaTiO_3$ can be tailored by doping some rare earth elements, for instance, adding small amount of B_2O_3 can improve the remanent polarization of $Ba_{0.7}Sr_{0.3}TiO_3$ ceramic [5]. However, there were a few attempts to transfer the dopants to BTS ceramics. The purpose of the present study was to investigate the dielectric response of BTS ceramics at different B_2O_3 contents. Impedance spectroscopy formalism has been used as a tool to investigate the dielectric relaxation and dynamics of the ionic movement inside the doped BTS ceramics.

2. Experimental procedure

Polycrystalline $Ba(Ti_{0.9}Sn_{0.1})O_3$:BTS10 ceramic was prepared by the conventional method. Starting materials were $BaCO_3$, SnO_2, and TiO_2. These powders in stoichiometric proportions were thoroughly mixed and ball-milled in isopropanol for 24 h using zirconia grinding media. After mixing, the slurry was dried, sieved and calcined at 1300 °C for 2 h in air. The calcined powder was reground with B_2O_3 powder, equivalent to 2.0 and 3.0 wt%. The mixed powders, with the addition of polyvinyl alcohol as an organic binder, were then ball-milled in isopropanol for 24 h. These slurries were dried at 150 °C and sieved to form fine powders which were then pressed into pellets of 15 mm diameter under 100 MPa force. The pellets were at last sintered at 1350 °C for 4 h and a heating/cooling rate of 5 °C/min after binder burnout at 500 °C for 1 h. Crystalline structures of the sintered samples were checked using a Bruker D8Advance X-ray diffractometer

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with a Cu-Kα source. The surface morphologies of the samples were examined using scanning electron microscopy (SEM). The impedance measurements were carried out from 40 to 280 °C using a Solartron 1260 Impedance/Gain-phase Analyser.

3. Results and discussion

3.1. Microstructural properties

The microstructures of fresh surface of BTS10 doped with different B_2O_3 contents are shown in Fig. 1. There are some small grains on the grain boundary for undoped sample, which is similar to that in the work of Cai et al. [6]. They suggested that these small grains occurred due to the segregation of Sn^{4+} ion on grain boundary and hindered grain growth. It is also observed that most of all sintered BTS ceramics are dense and adding boron oxide can promote liquid phase sintering; however, overdoped B_2O_3 may enhance volatilization and then lead to formation of large pores in the ceramic. Moreover, the size of ionic radius of B^{3+} ion (0.23 Å) differs very much from that of Ti^{4+} (0.61 Å) and Sn^{4+} (0.69 Å) cations in BTS10 ceramics, thus the solubility of B_2O_3 in BTS10 ceramics may be limited.

3.2. Relaxation behavior

Complex impedance spectroscopy analysis is the most commonly used technique to analyze dielectric behavior and dynamics of the ionic movement in electrical materials [7]. Different complex formalisms are used to characterize different solids. The complex impedance (Z^*) plane plots and Debye peak in spectroscopic plots of the imaginary components (Z'') versus log f are the useful technique for determination of more resistive regions such as grain boundaries and sample surface layers whereas the electric modulus (M'') data was found to be a better technique to characterize the contribution of a small capacitance region such as grain interiors [8].

The origin of a Debye peak is described by the following equations:

$$Z'' = R[\omega RC/(1+\omega RC^2)] \quad (1)$$

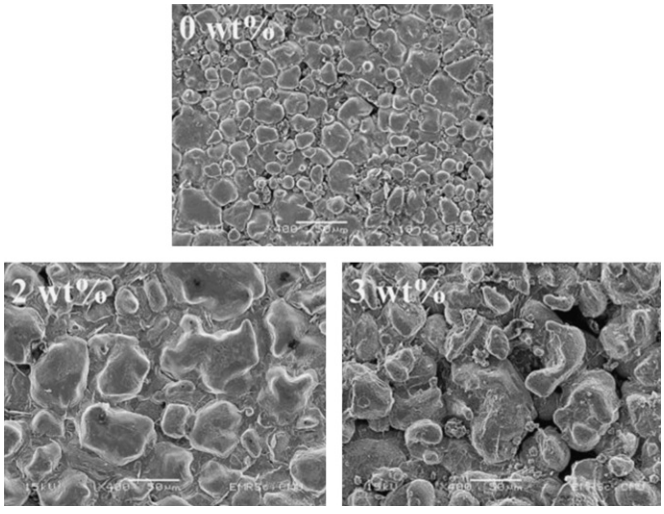

Fig. 1. Surface morphology of barium stannate titanate ceramics with different B_2O_3 additions.

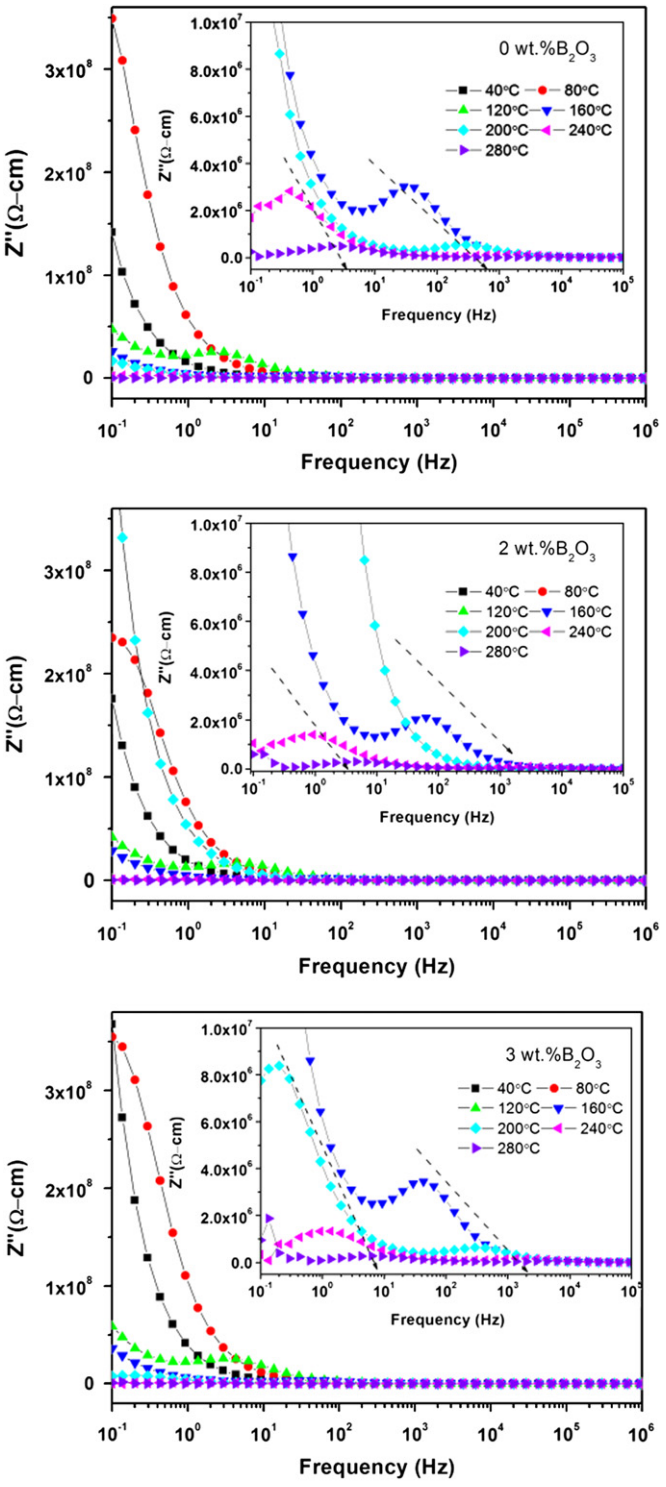

Fig. 2. Frequency dependence of imaginary part of complex impedance Z'' for 0, 2 and 3 wt% B_2O_3-doped BTS10 ceramic at different temperatures.

$$M'' = \varepsilon_0 / C[\omega RC/(1+\omega RC^2)] \quad (2)$$

where ω is the angular frequency ($2\pi f$) and C is the vacuum capacitance of the measuring cell and electrodes with an air gap in the place of the sample. The contribution of various microscopic elements such as grain, grain boundary, and electrodes to total dielectric response in polycrystalline materials can be identified by the reference to an equivalent circuit, which contains a series array of parallel resistor–capacitor (RC) elements.

Each individual RC element is differentiated by its unique relaxation time ($\tau = RC$). Therefore, response of these components lies in different time domains. In the present case we have used complex impedance along with the electric modulus formalism to analyze B_2O_3 doped BTS10 ceramics data. Fig. 2 depicts the variation of the imaginary part of impedance Z'' as a function of frequency at different temperatures in the 0, 2 and 3 wt% B_2O_3-doped BTS10 system. From the imaginary part of the impedance Z'' plots, it can be seen that impedance relaxation peak started appearing at temperatures above 120 °C for the undoped sample and above 80 °C for the doped samples; this behavior is due to the presence of space charges in the material [9]. Moreover, the curves at different temperatures exhibited broad peak maxima (as shown in the inset of Fig. 2) because of the distribution of relaxation times in the samples. As the temperature increased, the peaks were also observed to shift toward higher frequencies and the magnitude of the Z'' decreased with temperature, indicating multiple relaxations and increasing in loss of the material. Further the merged curve at higher frequencies is the evidence of disappearance of space charge polarization [10]. Fig. 3 shows the spectroscopic plots of electric modulus (M'') at different temperatures for 3 wt% B_2O_3-doped BTS10 ceramic. Each spectrum showed only a single peak in the low frequency region ($f = 104$ Hz) which contributes to the single relaxation process in the grain interior. The peak maxima become narrow and appeared to shift toward higher frequency region with increasing temperature owing to the distribution of relaxation times in the sample.

Fig. 4 shows the complex impedance plane for different boron contents at 280 °C. Results showed that the shapes of Cole–Cole plots depend on boron content.

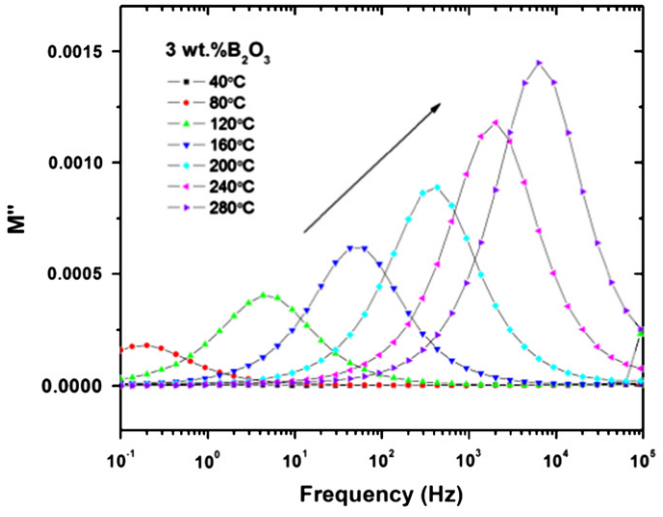

Fig. 3. Frequency dependence of imaginary part of electrical modulus M'' for 3 wt% B_2O_3-doped BTS10 ceramic at different temperatures.

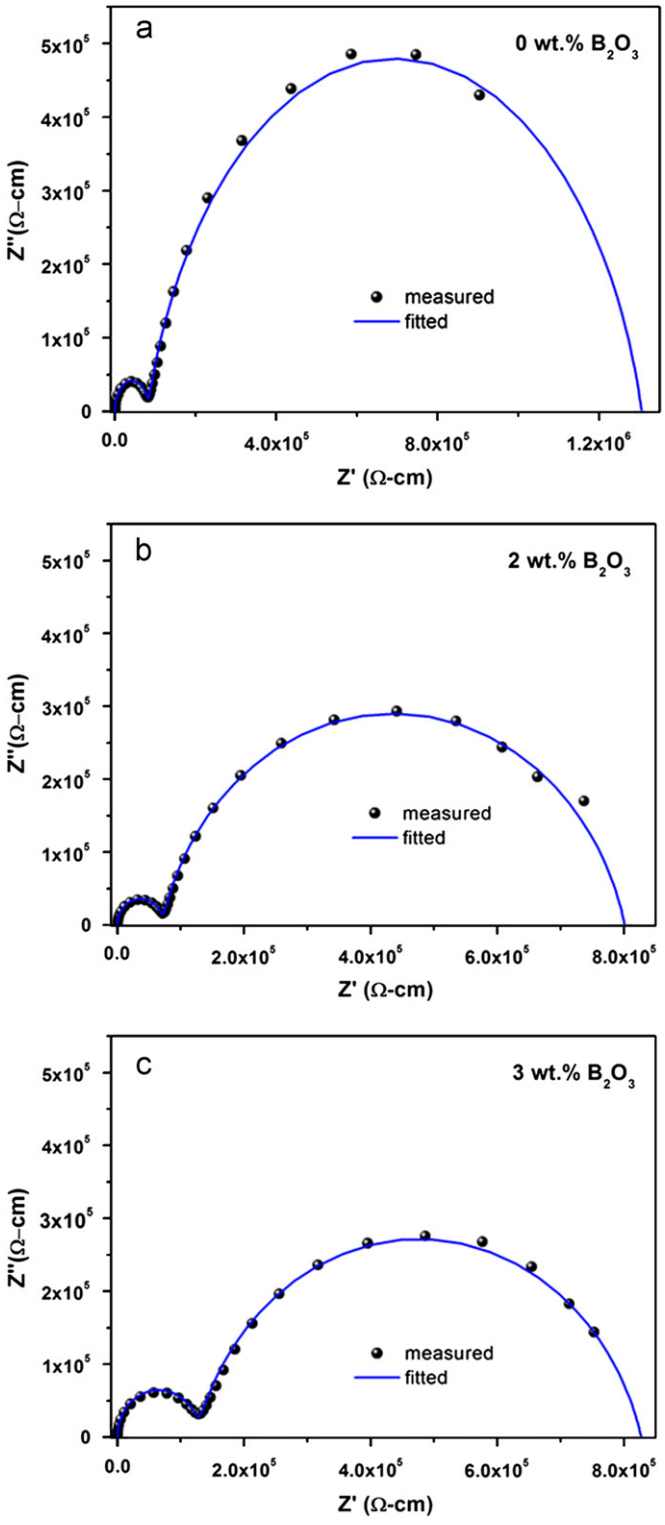

Fig. 4. Complex impedance plots for different compositions of B_2O_3 doped BTS10 ceramics at 280 °C.

Table 1
Calculated parameters from the Cole–Cole plots at 280 °C.

B_2O_3 (wt%)	R_g (Ω)	C_g (F) × 10^{-10}	R_{gb} (Ω)	C_{gb} (F) × 10^{-8}
0	81,005	3.13	1.224×10^6	7.78
2	92,751	1.26	1.105×10^6	4.34
3	124,780	2.13	0.707×10^6	6.34

Table 2
Relaxation time and activation energies of ceramics.

B_2O_3 (wt%)	τ_g (s)	τ_{gb} (s)	$E_{a(g)}$ (eV)	$E_{a(gb)}$ (eV)
0	0.99×10^{-5}	9.51×10^{-2}	0.82	0.92
2	1.17×10^{-5}	4.79×10^{-2}	1.02	0.99
3	2.66×10^{-5}	4.49×10^{-2}	0.73	0.85

According to the literature, the first arc at high frequency region is ascribed to grain-interior relaxation phenomena, while the second one at low frequency is the contribution from partial or complete blockings of charge carriers at the grain boundary [11]. It can be seen that the measured data and fitted line are well-matched. Then, the resistance and capacitance at grain and grain boundary for all samples were estimated and are reported in Table 1. The grain boundary contribution decreased for higher boron content; meanwhile, the grain interior contribution slightly increased. The associated relaxation time for grain (τ_g) and grain boundary (τ_{gb}) can also be calculated from the Cole–Cole plots. Normally, the relaxation time is a geometry independent parameter; it does not depend on microstructure but depends only on the intrinsic conductivity of material [12].

The activation energies (E_a) for relaxations are calculated using the relation

$$\tau = \tau_0 \exp\left(-E_a/k_B T\right) \quad (3)$$

where k_B is the Boltzmann constant and T is the absolute temperature. It was found that the plots followed the Arrhenius law and the activation energy obtained in these samples is presented in Table 2. These values are similar to those reported by Marković et al. [13] and Shvartsman [14]. The value of activation energy clearly suggested a possibility that the conduction in the high temperature range was ionic in nature due to oxygen vacancies. In perovskite ferroelectric materials oxygen vacancies are considered to be one of the mobile charge carriers and mostly in titanates, ionization of oxygen vacancies creates conduction electrons. In our case, activation energy for grain boundaries was more than the grain contribution that showed the resistive nature of the grain boundaries.

4. Conclusions

$Ba(Ti_{0.9}Sn_{0.1})O_3$ ceramics doped with B_2O_3 were fabricated by the conventional solid-state route. At high temperature, impedance and electric modulus were found to be temperature dependent and showed distributed relaxation phenomena which provided the evidence of typical relaxor properties. The complex impedance plots revealed the existence of grain and grain boundary contributions. The relaxation time followed the Arrhenius behavior and showed different activation energies for grain and grain boundaries.

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References

[1] K.Z.D. Dragan, S. Nava, Dielectric and electro-mechanical properties of ferroelectric-relaxor $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ thin films, Journal of Applied Physics 90 (2001) 4682–4689.
[2] T. Takenaka, H. Nagata, Y. Hiruma, Y. Yoshii, K. Matumoto, Lead-free piezoelectric ceramics based on perovskite structures, Journal of Electroceramics 19 (2007) 259–265.
[3] V.V. Shvartsman, J. Dec, Z.K. Xu, J. Banys, P. Keburis, W. Kleemann, Crossover from ferroelectric to relaxor behavior in $BaTi_{1-x}Sn_xO_3$ solid solutions, Phase Transitions 81 (2008) 1013–1021.
[4] X. Wei, X. Yao, Preparation, structure and dielectric property of barium stannate titanate ceramics, Materials Science and Engineering B 137 (2007) 184–188.
[5] S.M. Rhim, S. Hong, H. Bak, O.K. Kim, Effects of B_2O_3 addition on the dielectric and ferroelectric properties of $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics, Journal of the American Ceramic Society 83 (2000) 1145–1148.
[6] W. Cai, Y. Fan, J. Gao, C. Fu, X. Deng, Microstructure, dielectric properties and diffuse phase transition of barium stannate titanate ceramics, Journal of Materials Science: Materials in Electronics 22 (2011) 265–272.
[7] D.C. Sinclair, A.R. West, Impedance and modulus spectroscopy of semiconducting $BaTiO_3$ showing positive temperature coefficient of resistance, Journal of Applied Physics 66 (1989) 3850–3856.
[8] F.D. Morrison, D.C. Sinclair, A.R. West, Characterization of lanthanum-doped barium titanate ceramics using impedance spectroscopy, Journal of the American Ceramic Society 84 (2001) 531–538.
[9] A.R. James, K. Srinivas, Low temperature fabrication and impedance spectroscopy of PMN-PT ceramics, Materials Research Bulletin 34 (1999) 1301–1310.
[10] M. Sandeep, Ferroelectric relaxor behaviour and impedance spectroscopy of Bi_2O_3-doped barium zirconium titanate ceramics, Journal of Physics D: Applied Physics 42 (2009) 065413.
[11] J.R. Macdonald, Impedance spectroscopy: emphasizing solid materials and systems, Wiley, New York, 1987.
[12] P. Sooksaen, I. Reaney, D. Sinclair, Crystallization and dielectric properties of borate-based ferroelectric $PbTiO_3$ glass-ceramics, Journal of Electroceramics 19 (2007) 221–228.
[13] S. Marković, Č. Jovalekić, L. Veselinović, S. Mentus, D. Uskoković, Electrical properties of barium titanate stannate functionally graded materials, Journal of the European Ceramic Society 30 (2010) 1427–1435.
[14] V.V. Shvartsman, Diffuse phase transition in $BaTi_{1-x}Sn_xO_3$ ceramics: an intermediate state between ferroelectric and relaxor behavior, Journal of Applied Physics 99 (2006) 124111.