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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:

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

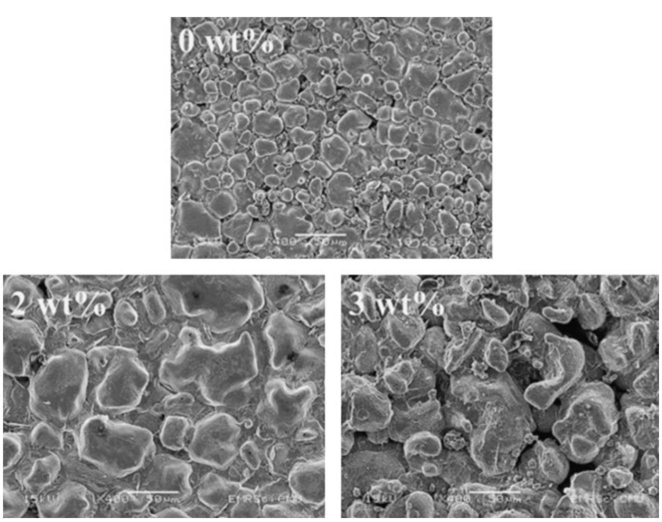

Fig. 1. Surface morphology of barium stannate titanate ceramics with different B_2O_3 additions.

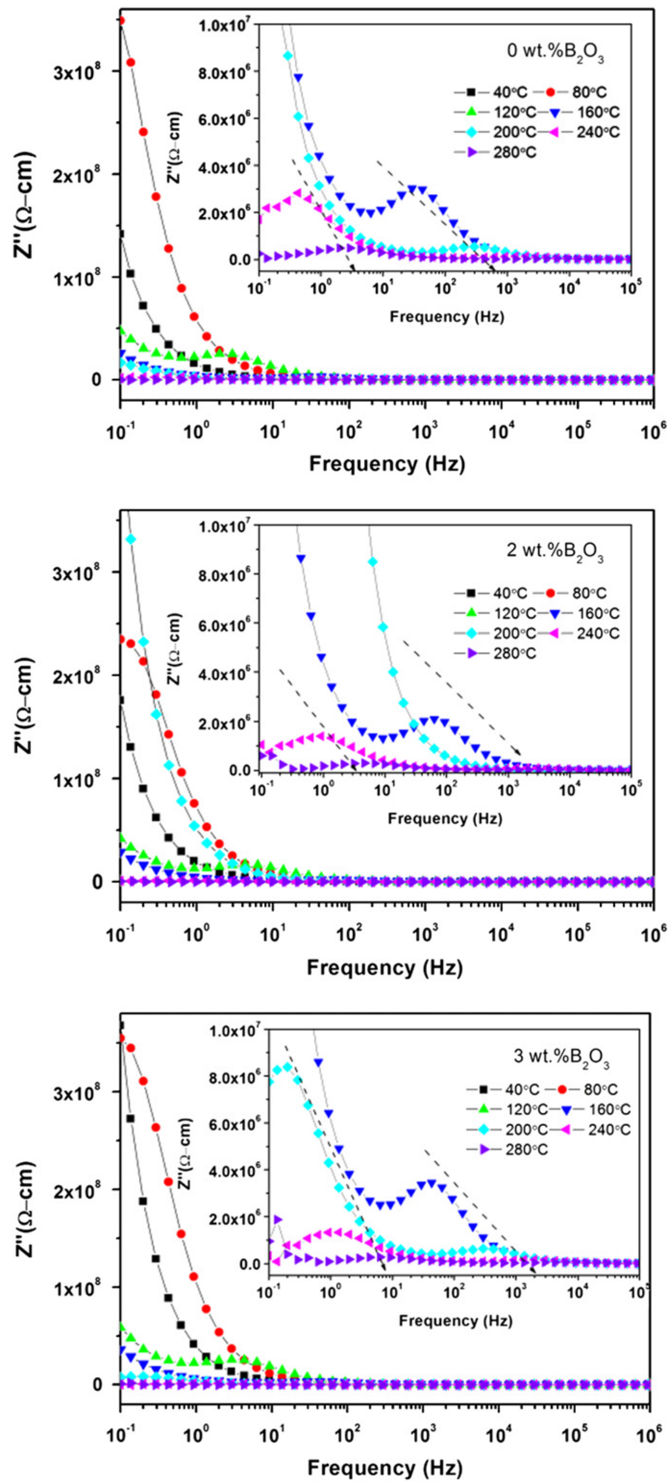

Fig. 2. Frequency dependence of imaginary part of complex impedance Z'' for 0, 2 and 3 wt% B_2O_3-doped BTS10 ceramic at different temperatures.