



Dielectric spectroscopy and ferroelectric properties of magnesium modified bismuth titanate ceramics



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ARTICLE INFO

Article history:

Received 1 June 2016

Received in revised form

12 July 2016

Accepted 17 July 2016

Available online 18 July 2016

Keywords:

Ceramics

Dielectric properties

Ferroelectricity

Electrical properties

ABSTRACT

Mg doped bismuth titanate ceramics $\text{Bi}_4\text{Ti}_{3-x}\text{Mg}_x\text{O}_{12}$ ($x = 0.2, 0.4, 0.6$) (BMgT) synthesized using a solution combustion technique are studied in this paper. This work examines the effect of Mg doping at B site of bismuth titanate on its crystalline structure, ferroelectric properties and electrical conduction characteristics over a broad temperature range. Addition of Mg^{2+} does affect the lattice symmetry of bismuth titanate by causing shrinkage in the unit cell. An increase in the dielectric constant and decrease in loss tangent is observed due to increase in magnesium content. The Nyquist plots are interpreted using a RC model which explains the contribution of the grain-bulk and the grain boundary resistivities to the total resistivity of the materials. The P-E loops are observed to become lossier with an increase in magnesium content due to increase in leakage current as a result of lattice distortion introduced in the unit cell.

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1. Introduction

Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) belongs to the Aurivillius family and has attracted considerable interest due to its potential application in a variety of electronic devices such as capacitors, memory devices and sensors [1–3]. The structure of these ferroelectrics consists of $[\text{Bi}_2\text{O}_2]^{2+}$ layers interleaved with perovskite-like $[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]^{2-}$ units stacked along the *c*-axes [4]. The ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ based ceramics have a number of advantages for device applications such as being a lead-free ceramic, having a high Curie temperature, high breakdown strength and exhibiting electro-optic switching behavior [3].

The microstructure and electrical properties of bismuth titanate can be modified by the addition of a variety of dopants such as La^{3+} , Ce^{3+} , Mn^{4+} , Nb^{5+} , Nd^{3+} , Cr^{3+} , Zr^{4+} , Sr^{2+} and Si^{4+} that occupy the Bi^{3+} positions on A-sites or Ti^{4+} on B-sites to form a solid solution [5]. In addition, the modification of B-site of bismuth titanate ceramics with high valent ions (Nb^{5+} , V^{5+} , W^{6+}) may aid in the removal of defects such as oxygen vacancies [6,7]. The increase in

remanent polarization (P_r) for B-site substituted ceramics can be attributed to the fact that the ionic radius of the substituted ion is larger than the Ti^{4+} it replaces and this increases the structural distortion of oxygen octahedral. Nevertheless, there remains ambiguity in terms of understanding the B-site substitution in these intriguing materials.

It has been reported [8] that the substitution of Ti^{4+} with lower valent Mg^{2+} ions in barium titanate reduces its electrical conductivity. Moreover, Mg^{2+} has ionic radius of 0.57 Å, which is very close to that of Ti^{4+} (0.61 Å). Therefore, it would readily replace Ti^{4+} ions in bismuth titanate lattice as it is in accordance with Hume Rothery rules which state that the atomic radius of the solute and solvent atoms must differ by no more than 15%. In addition, the replacement of Ti^{4+} with Mg^{2+} does not give rise to significant changes in the lattice constants. In terms of microstructural changes, Yoon et al. [9] found that the addition of Mg^{2+} can decrease the grain size of barium titanate. Miao et al. [10] prepared Mg-doped barium titanate by the hydrothermal method and found that the dielectric peaks shifted to a lower temperature with increasing Mg^{2+} concentration. While work to date has examined Mg-doped barium titanate, studies have not discussed the electrical behavior of Mg modified bismuth titanate ceramics. As a result, this paper examines the detail of the microstructure, dielectric and electrical

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properties of Mg doped bismuth titanate ceramics synthesized by the solution combustion technique.

2. Experimental

2.1. Synthesis

Polycrystalline samples of Mg (B site) doped bismuth titanate $\text{Bi}_4\text{Ti}_3\text{-xMg}_x\text{O}_{12}$ $x = 0.2, 0.4, 0.6$ with different doping concentrations of magnesium were synthesized using a solution combustion technique. Bismuth (III) nitrate pentahydrate (Merck), magnesium (II) nitrate (Sigma Aldrich) and titanium (IV) isopropoxide (Sigma Aldrich) were used as starting materials with the molar ratio of 4:3. All the raw materials used were analytical grade having 99.9% purity. Bismuth nitrate pentahydrate and magnesium nitrate were dissolved in 2-methoxyethanol at room temperature, and dextrose was added as a fuel to aid in the combustion process. Titanium isopropoxide solution along with acetyl acetone (a chelating agent), was added to the bismuth solution drop wise with continuous stirring. The final mixture was then stirred for 1 h at room temperature, and was heated on a hot plate at 200 °C leading to evaporation followed by combustion process which is an exothermic chemical reaction that resulted in the production of a flame. The combustion reaction lasted for approximately 5 min and resulted in the production of dry 'foam-like' flakes. These flakes were then crushed in an agate mortar pestel and then calcined at 800 °C for 3 h. After calcination, the powders were mixed with 3 wt % of organic binder (polyvinyl alcohol) and pressed uniaxially at a pressure of 8 tons/cm² into discs of 10 mm diameter in a hydraulic press using a rigid steel die. Following binder burnout at 500 °C the samples were finally sintered at 1000 °C in covered alumina crucible for 5 h.

2.2. Characterization

The calcined powders were subjected to phase analysis using an X-ray diffractometer (XRD, Rigaku – Miniflex II) equipped with $\text{CuK}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation. The surface morphology of the pellets was investigated using a Scanning Electron Microscope (JEOL-JSM6390). Platinum coating was undertaken on both surfaces of the pellets for the formation of ohmic electrical contacts. The dielectric measurements were performed using an Alpha High Resolution

Dielectric impedance analyzer using Nova Controls in the frequency range from 1 Hz to 1 MHz from room temperature to 750 °C. The variation of electrical polarization as a function of electric field (P-E loop) was characterized using a ferroelectric test system (aixACT TF analyzer, Aachen Germany) at room temperature at a frequency of 2 Hz. The samples were immersed in silicone oil during the measurements to prevent the breakdown from the sample edges. The *I*-*V* characteristics of the samples were measured in "switched triangular mode" with maximum applied electric field of 20 kV/cm.

3. Results and discussions

3.1. XRD analysis

In order to confirm whether magnesium entered into the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ lattice as a solid solution or existed as the secondary phase besides $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, XRD measurement of the samples was performed. XRD patterns of Mg-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics with various magnesium concentrations are shown in Fig. 1(a). It is clear that all the peaks are indexed based on the JCPDS file No., 72-1019 that belongs to the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase which indicates that the magnesium dopant did not form other new secondary phases such as MgO , MgCl_2 or MgTiO_3 for all the doping concentrations. In addition, the sharp peaks observed in the XRD pattern suggest that the samples have reached complete crystallinity after sintering at 1000 °C. A magnified examination at the major peak positioned at $2\theta = 30^\circ$ having (*hkl*) values (117) in Fig. 1(b) indicates a shift in the peak position towards higher values of 2θ with increasing magnesium addition; this signifies a shrinkage in the volume of the unit cell of bismuth titanate due to addition of Mg^{2+} . From the XRD data the lattice parameters of the materials with different doping concentrations were calculated using Eq. (1):

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (1)$$

where 'd' is calculated using Bragg's equation $2d\sin\theta = n\lambda$, where d is the inter planar spacing, θ is the scattering angle, n is an integer and λ is the wavelength of the incident wave.

Table 1 summarizes the lattice parameters and it can be seen that both *a* and *c* lattice parameters decrease with an increase in magnesium doping level while *b* increases slightly (although it remains lower than that of pure bismuth titanate) thus lowering

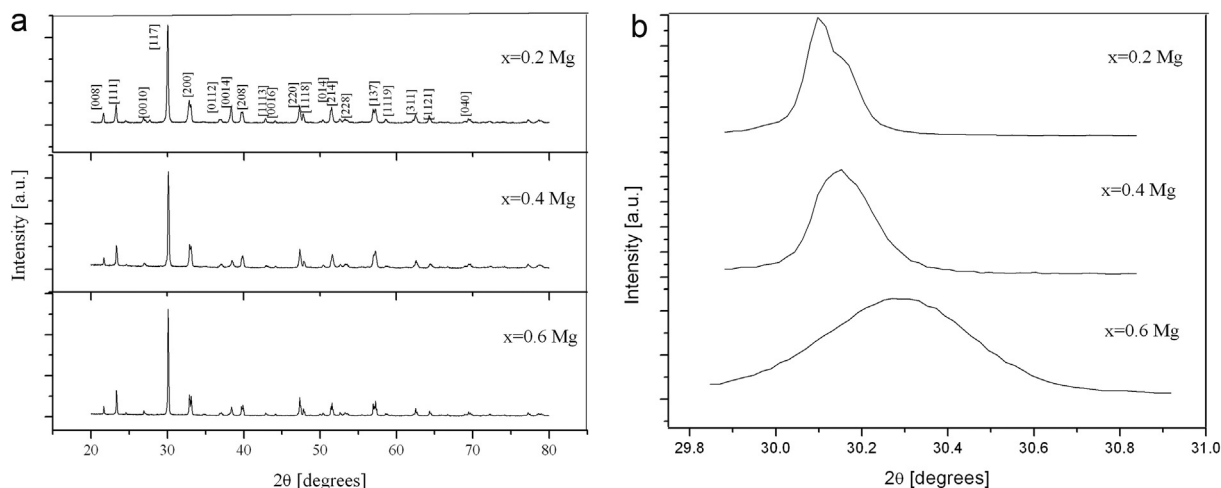


Fig. 1. (a): XRD pattern of Mg-doped bismuth titanate for different doping concentrations. (b): XRD pattern of Mg doped bismuth titanate ceramics expanded in the range $2\theta = 29^\circ\text{--}31^\circ$.

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