

THERMAL, MICROSTRUCTURE AND DIELECTRIC BEHAVIOR OF La-MODIFIED BISMUTH TITANATE CERAMIC

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Abstract

Environmentally safe and lead free La-modified bismuth titanate (BLT) was synthesized by conventional solid state reaction method. The thermal, dielectric, Microstructural behaviors of BLT ceramic have been investigated. Based on the thermal stability of BLT, samples were calcined at 750^o C, percentage weight loss and thermal behavior was studied by TGA/DSC. The influence of La on crystal structure of BLT showed orthorhombic crystal structure. Increase of La concentration does not show a secondary phase. Among all the La-doped BLT ceramic samples, x = 0.60 exemplified good results. Dielectric permittivity of BLT is higher at x = 0.60 comparing to other, microstructure study of sintered ceramic sample showed plate-like shape with enhanced density. The results show that the La³⁺ doped BLT ceramics may be used as a probe for the phase transition of the ferroelectric materials.

Keywords: La-substituted bismuth titanates, Thermal, Microstructure, Dielectric.

1. INTRODUCTION

During the past 10-12 years, a flurry of interest has grown towards the study of lanthanum (La)-doped bismuth titanate (Bi_{4-x}La_xTi₃O₁₂, BLT) in ferroelectric materials, due to their prominent applications in the fabrication of non-volatile random access memories, based on the existence of two opposite polarization states which can store binary information in a non-volatile electric field [1-2]. It is now well recognized that the BLT has the positive effect of reducing its ferroelectric fatigue properties, improving its remanent polarization and lowering its Curie temperature. Remanent polarization of bismuth titanate (BT) is enhanced considerably by the magnitude of structural distortion within the perovskite block by partially replacing Bi ions with differently sized rare earth ions [3].

La is well-known to substitute at Bi sites but the distribution of these substitutions appears to depend on the method of preparation and processing [4-5]. The behavior of BLT illustrated higher remnant polarization and an exceptional fatigue resistance. The purpose to improve properties of BLT ceramics is by doping BT with rare earth elements, so as to replace Bi in the perovskite unit of BT [6-7]. The structure of BT has a layered perovskite structure, also known as Aurivillius structure which can be represented by the general formula (Bi₂O₃) [A_{m-1} (B)_m O_{3m+1}], consists of (Bi₂O₂)²⁺ sheet alternating with (Bi₂Ti₃O₁₀)²⁻ perovskite-like layers. It is known that oxygen-vacancy migration in BT produces significant degradation problems associated with the ferroelectric properties. It has been reported that the oxygen-vacancy resettlement with A-site rare earth ion substitution for the volatile Bi ion and also significantly affects its properties [8-10].

Till-date, ferroelectric and dielectric properties of rare earth doped BT or related Bi-layered oxide films have been

widely studied at room temperature (RT) whereas their temperature dependence is rarely found in the literature [11]. In this paper, La-modified bismuth titanate powders were prepared by conventional solid state reaction method and were characterized by thermal, dielectric, and microstructural studies. La doping with x = 0.60 exhibited good results as compared to other La-doped BLT ceramics.

2. MATERIALS AND METHOD

High-purity powders Bi₂O₃ (99.99%), La₂O₃ (99.99%) and TiO₂ (99.99%) were used as starting materials to synthesize La doped bismuth titanate, Bi_{4-x}La_xTi₃O₁₂ (BLT, x = 0.60, 0.75, 0.90, 1.00) ceramics by a conventional solid-state reaction technique. These ceramic compounds were prepared by taking powders in the stoichiometric ratio, mixed in alcohol by agate balls for 4 h, and then dried and calcined in a tubular temperature controlled programmable Si-based furnace at 750^o C for 2 h. After remilled, powder was mixed thoroughly with a PVA binder solution and pressed into pellets using hard metal die with diameter of 10mm at room temperature and compaction pressure of 130 to 150MPa, Pellets were sintered at 1100^o C for 4 h in air. For carrying out the electrical measurement, sintered pellet were coated by silver paste on both sides. Thermal behavior of starting precursor sample was examined by simultaneous thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) up to 1100^o C using Thermal Analyzer STA PT 1600 (Linseis make, Germany) in air atmosphere with heating rate of 5^o C/min. The surface morphology was recorded by scanning electron microscopy (SEM). Temperature dependent dielectric measurements were carried out using standard two probe setup.

3 RESULTS AND DISCUSSIONS

3.1. Thermal Analysis

Fig. 1 depicts thermal behavior of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ($x=0.60$, BLT) sample. The percentage of weight loss of as-synthesized sample is studied by thermo-gravimetric (TG) curve. It illustrates three weight loss steps in between 300°C and 800°C . First, is because of evaporation of solvent added at the time of grinding, further weight loss is because of dehydration in ceramic sample. It confirms that BLT is a stable compound having weight loss about 5%. Such steps were also characterized by two endothermic and one exothermic peak on the differential scanning calorimetry (DSC) curve. After 800°C , no weight loss was observed on the TG curve and also no thermal change is found on the DSC curve.

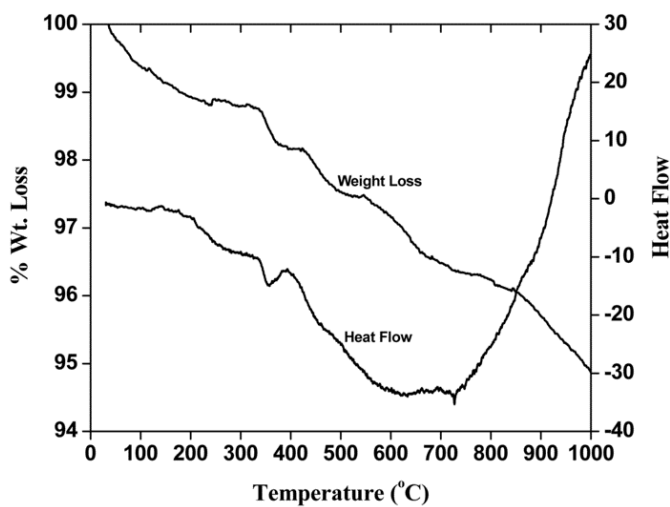


Fig. 1 TG/DSC curve of BLT ceramics

3.2. Microstructural Analysis

Fig. 2 shows SEM image of the polished $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ($x=0.60$) ceramics sintered at 1100°C . It is observed that particles were agglomerated with an irregular shape; the formation of large grains with irregular shape could be the result of the variations on the kinetics of movements from boundary to boundary. An average grain size is found to be $\approx 10\mu\text{m}$. It is known that rare-earth ions of large radius suppress the grain growth in the ceramic sample [12]. The morphology was plate-like in shape and better arrangement of the particles during sintering process resulted into enhancement of densification of the ceramic samples.

To determine the chemical composition of BLT powders, the EDAX is performed on the powder sintered at 1100°C (Fig. 3). It is seen that all the peaks of the pure BLT powder are detected without any other secondary phases. Also, the atomic percentages obtained were 66.15, 11.55, 4.21 and 18.09 corresponding to O, Ti, La and Bi ions, respectively, which confirms the chemical composition of BLT.

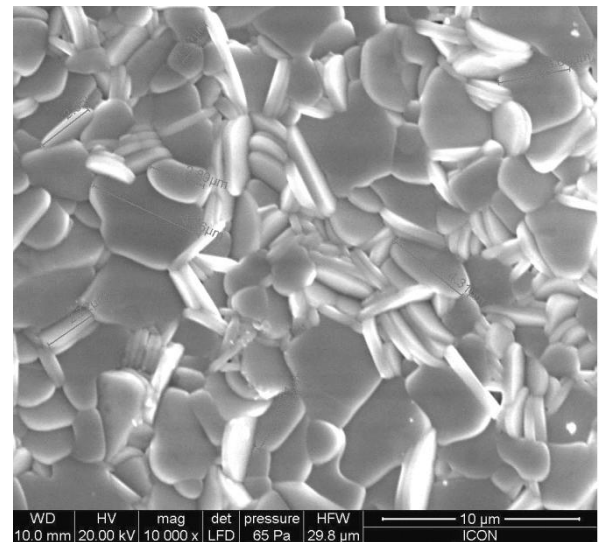


Fig. 2 SEM image of BLT60 ceramics

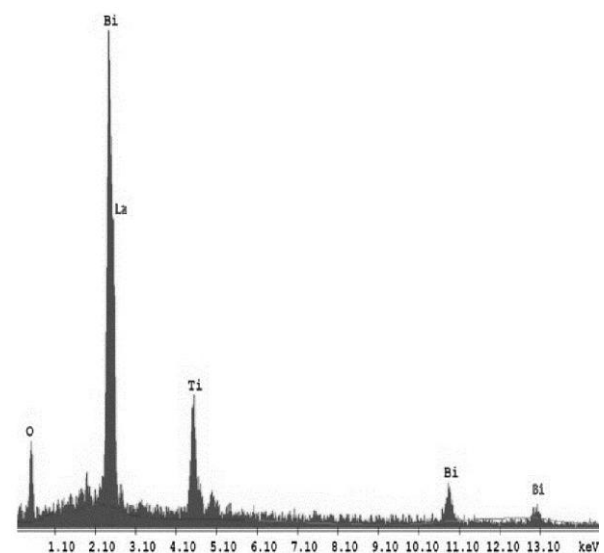


Fig. 3 EDAX of BLT60 ceramics

3.3. Electrical Analysis

The temperature dependent dielectric behavior of synthesized samples were carried out by coating silver paste to use as the electrode and dried at 400°C for 1 hr. The dielectric permittivity (ϵ_r) was calculated from the capacitance using the following formula,

$$\epsilon_r = \frac{Cd}{\epsilon_0 A}$$

Where C is the capacitance (F), ϵ_0 is the free space dielectric constant value (8.854×10^{-12} F/M), A is the capacitor area and d is the thickness of the sample.

The variation of dielectric permittivity of BLT samples with temperature is shown in Fig. 4. Temperature is ranging from room temperature to 600°C . ϵ_r is found to increase with increase in temperature in all the samples. Curie

temperature (T_c) is different for all BLT ceramic samples. Among the all ceramic samples, maximum ϵ_r of 5812 was observed for $x = 0.60$, at T_c of 520°C . It was also observed that BLT samples compared with our previously reported BT ($x = 0$) ceramics [10] possess a higher ϵ_r indicating that La plays an important role in the electrical properties of the BT layers. Doping BT with La has a strong influence on the dielectric behavior of the material even at low and high concentration [13].

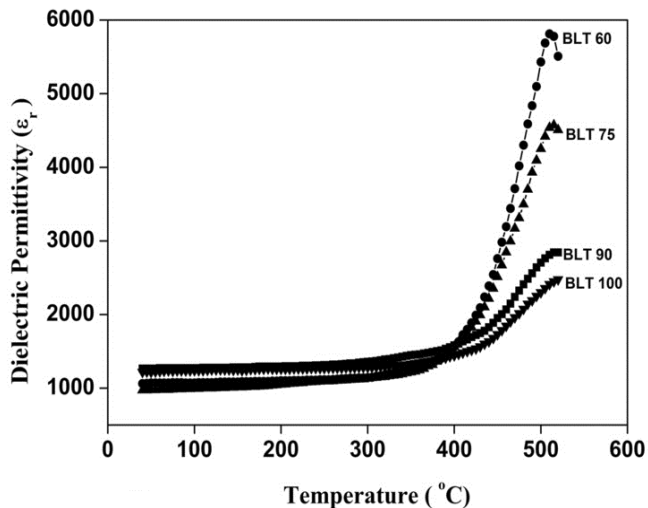


Fig. 4 Temperature dependent dielectric behavior of BLT ceramics

A peak of high dielectric permittivity was also observed by several researchers at 675°C in BT and modified BT ceramics. The low temperature maximum ϵ_r was seen because of the space charge and ion-jump relaxation in the synthesized ceramic samples. It is believed that defects such as oxygen vacancies intrinsically present in these materials. Due to the volatilization of Bi-O species, space charges are created whose polarization respond to the externally applied field. This kind of problem can be overcome by proper covering of crucibles. When dielectric measurements were taken at several applied frequencies, the high phase transformation temperature and high ϵ_r was observed because the space charges take enough time to move longer distance in the ceramic sample at applied frequency. This type of behavior is not seen during measurement of temperature dependent dielectric permittivity [14].

4. CONCLUSIONS

In summary, La-modified bismuth titanate powders were successfully prepared by conventional solid state reaction method. An orthorhombic crystal structure of La doped with 0.60 in BT shows single phase after calcination at 750°C for 2hrs. TGA curve depicts the stability of the ceramic sample. Dielectric behavior exhibits a very high value of ϵ_r for La-doped BT at $x = 0.60$ compared to other doped ceramics. This type of high value of dielectric permittivity of La-doped BIT can be accredited to the polarization effects of the space charges ensuing from defects such as oxygen vacancies. La-doping is found to improve the

dielectric properties of BT. The microstructure study of BLT shown the agglomerated particles having irregular shape with an average particle size of $\approx 10\ \mu\text{m}$. Morphology was plate-like in shape and elemental constituents of ceramics were identified by their energy dispersive values.

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REFERENCES

- [1]. A. Garg, X. Hu, Z.H. Barbar: *Ferroelectrics* 328, 93-97(2005).
- [2]. S. Tatsuhiro, K. Hajime, N. Junya, I. Hidenobu, T. Junichi: *Jpn. J. Appl. Phys.* 47 (9), 7617- 7622(2008).
- [3]. S.W. Kang, W.K. Kim, S.W. Rhee: *J. Mater. Sci.* 42, 652-659(2007).
- [4]. F. Pinyang, F. Huiqing, Q. Shaojun, L. Liajun, C. Jin: *J. Sol-Gel Sci. Technol.* 50, 290- 295(2009).
- [5]. S.H. Shah, P.D. Bristowe: *J. Phys: Condens. Mat.* 23, 155902 (1-12)(2011).
- [6]. J. Arreuin-Zavala, M.E. Villafuerte-Castrejon, F. Gonzalez, L. Bucio, O. Novelo-Peralta, R.Y. Sato-Berru, J. Ocotlan-Flores: *Mater. Char.* 60, 219-224(2009).
- [7]. L. Jang-Sik, Q.X. Jin: *Electro. Mater. Lett.* 4(3), 95-98(2008).
- [8]. A. Chang Won, L. Hai Joon, K. Sun Hee, K. Ill Won, C. Mun Seok, L. Jae Shin, K. Hyung Wook, J. Byung Moon: *J. Electroceram.* 21, 847-850 (2008).
- [9]. S. Pasinee, W. Anucha, J. Sukanda: *J. Microscopy. Soc.Thailand* 1, 17-20(2010).
- [10]. Nagbasavanna Sharanappa, Shivanand Madolappa, Raghavendra Sagar, R. L. Raibagkar: *Ferro. Lett.* 39, 81-87(2012).
- [11]. Z. Shan-Tao, C. Zhong, Z. Chong, Y. Guo-Liang: *Appl. Surf. Sci.* 256, 2468-2473(2010).
- [12]. A.Z. Simoes, C.S. Riccardi, F. Moura, A. Ries, N.L.A. Junior, M.A. Zaghete, B. Stojanovic, E. Longo, J.A. Varela: *Mater. Lett.* 58, 2842-2847(2004).
- [13]. K. Babooram, D.K. Chin, Z.-G. Ye: *J. Electroceram.* 21, 43-48(2008).
- [14]. A. Hardy, M.K. Van Bael, H. Van den Rul, D. Vangechten, J. Mullens, J. D'Haen, L. Goux, D.J. Wouters: *J. Sol-Gel Sci. Techn.* 42, 239-245(2007).