SYNTHESIS AND DIELECTRIC PROPERTIES OF $Bi_{4-x}Nd_xTi_3O_{12}$ OBTAINED BY SOLUTION COMBUSTION SYNTHESIS

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ABSTRACT

Bismuth neodymium titanate, BNdT ($Bi_{4-x}Nd_xTi_3O_{12}$ where x=0.2, 0.4, 0.6, 0.8, 1.0) powders were synthesized via solution combustion synthesis for ferroelectric memory devices. The as-synthesized powders were calcined at 800°C for 3 hour and subsequently, sintered at 1100°C for 6 hours. The formation of pure phase and c-axis-oriented BNdT were characterized by X-ray diffraction (XRD). It was found that the orientation degree of c-axis increases with the increase of Nd content in BNdT, and at the same time the grain morphology grows from rod-like to plate-like structure. Additionally, the dielectric properties of BNdT are greatly influenced by the grain orientation.

1.0 INTRODUCTION

Aurivillius material of bismuth-based has been widely studied due to its outstanding in ferroelectric properties [1]. Bismuth titanate, $Bi_4Ti_3O_{12}$ is a good candidate for ferroelectric memory devices application [2]. The substitution of rare-earth such as La^{3+}, Pr^{3+}, Sm^{3+} and Nd^{3+} in $Bi_4Ti_3O_{12}$ has been extensively performed to improve the ferroelectricity in such devices [3]. However, those rare-earths added in $Bi_4Ti_3O_{12}$ exhibits different axis-oriented i.e. a-axis and c-axis [4]. In a-axis-oriented, the diffraction peak is indexed (1 1 7). On the other hand, the diffraction peak of c-axis-oriented corresponds to (0 0 6). According to Fouskova and Cross [5] the conductivity in the a-direction is approximately 30 times higher than in the c-direction in the single crystal of $Bi_4Ti_3O_{12}$. Therefore, highly a-axis crystal orientation is preferable in order to obtain high conductivity hence it can improve the dielectric properties.

In this study, a solution combustion synthesis was selected as an alternative approach to prepare BNdT. This method was developed from the concepts of self-propagating high-temperature synthesis (SHS) combined with wet chemical techniques in order to synthesize metal-oxide-based ceramic powder. Generally, three factors influence the generation of fire, which can be described as self-generated combustion. These factors are the oxidizer, temperature, and fuel, which produce heat, light, and ash [6]. The fuel-free combustion method does not employ fuel agents such as citric acid, urea, or glycine. The process is relatively low-cost, requires a simple setup, and has high reproducibility. In this work, Nd^{3+} will be used to substitute Bi^{3+} ions in $Bi_4Ti_3O_{12}$ and the peak characteristic and grain morphology will be studied as well as dielectric properties.

2.0 EXPERIMENTAL PROCEDURE

$Bi_{4-x}Nd_xTi_3O_{12}$ (BNdT) where x = 0.2, 0.4, 0.6, 0.8 and 1 were synthesized via solution combustion. Bismuth nitrate penthahydrate, $Bi(NO_3)_3.5H_2O$ and neodymium nitrate hexahydrate, $Nd(NO_3)_3.6H_2O$ were initially dissolved in 2-Methaoxyethanol, $CH_3OCH_2CH_2OH$ at 40°C on hot plate and stirred for about 30 min. Separately, titanium (IV) isopropoxide, $Ti[OCH(CH_3)_2]_4$ was dissolved in a homogeneous solution of 2-ME and acetylacetone, $C_5H_8O_2$ at room temperature and stirred for 30 min. The Ti solution was then poured into the Bi solution with continuous stirring at 40^{o}C for another 2 h. After that, the temperature of hot plate was then set to reach at ~130^{o}C to form a sticky gel. Within a few seconds, the temperature was then increased rapidly, and when it reached to ~200^{o}C, large amount of gases (NH_3, H_2, CO_2 and H_2O) were liberated and a dark fluffy powder was produced after the combustion process. The process was consistently repeated for other Nd content. Those powders were calcined at 800^{o}C for 3 hours and pressed to form pellets with diameter of 13mm. The pellets were then sintered at 1100^{o}C for 6 hours. Their phase formation was determined by XRD (Bruker D8 Advanced). A Zeiss Supra 55VP PGT/HKL Field Emission Scanning Electron Microscope (FE-SEM) was used to observe the microstructure and morphology of BNdT sintered pellets. The dielectric properties were measured by Hewlett Packard, 4291B impedance analyser.

3.0 RESULT AND DISCUSSION

Fig. 1a shows the XRD pattern of BIT and BNdT with various Nd content calcined at 800°C for 3 hours in air. Almost all of the diffraction peaks are indexed according to the standard powder diffraction data of $Bi_4Ti_3O_{12}$ (JCPDS 01-089-7500). When the sintering temperature increases to 1100^{o}C for 6 hours, strong c-axis-orientation reflection peaks dominate X-ray diffraction pattern (Fig. 1b). On the other hand, the reflection peak of (117) which corresponds to off-c-axis-orientation decrease with increasing of Nd addition. It demonstrates that 0.6BNdT, 0.8BNdT and 1.0BNdT show the preferred c-orientation, and the intensity of *00l* reflections (i.e. 004, 006, 008 and 0014) increases with Nd content. Simplified approximation of the Lotgering degree of orientation (f) was evaluated according to the following equation [7]:

$$f = \frac{I_{006}}{I_{006} + I_{117}}$$

where I_{006} and I_{117} are 006 and 117 peak intensities.

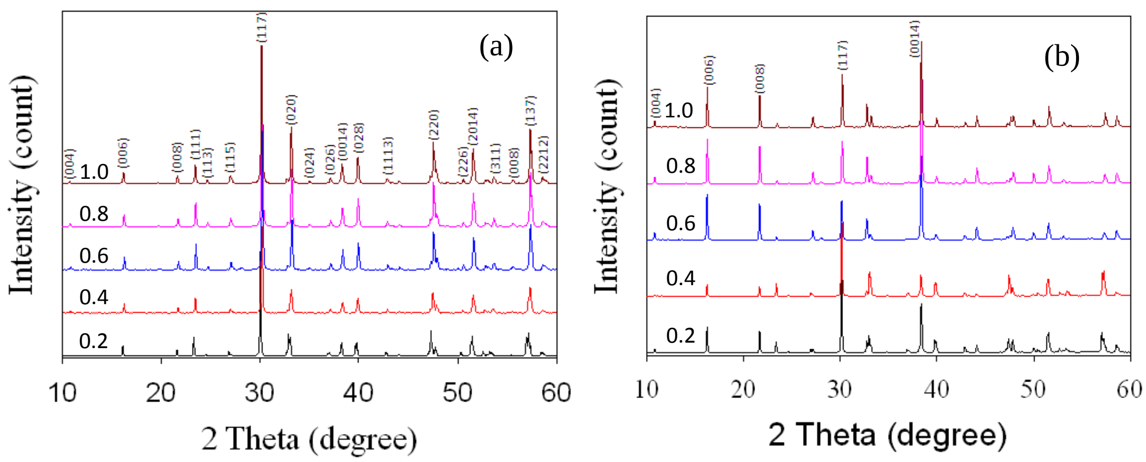

Fig. 1: Compilation of XRD patterns for BNdT (x=0.2, 0.4, 0.6, 0.8, and 1.0) powders calcined and sintered at (a) 800^{o}C and (b) 1100^{o}C, respectively

The orientation degrees (f) of 0.6BNdT, 0.8BNdT and 1.0BNdT are estimated to be 57.3%, 72.5% and 79.4%, respectively, suggesting that the degree of orientation increases with the increase of Nd content which agrees with XRD in Fig. 1b. It is believed that the development of c-orientation closely relates to the anisotropic growth of $Bi_4Ti_3O_{12}$ grain.

Fig. 2 shows the grain morphology of BNdT sintered pellets captured by FE-SEM. The rod-like grains are found in 0.2BNdT and 0.4BNdT whereas the plate-like grains appear in 0.6BNdT, 0.8BNdT and 1.0BNdT. According to Yu et al. rod-like grains and plate-like grains correspond to off-c-axis-oriented and c-axis-oriented, respectively [4]. It can be seen that most of the grains are rod-like while only a few of them are plate-like as shown in Fig. 2a and b. On the other hand, more plate-like grains are observed in Fig. 2c, d, and e. It is evident that the result is consistent with that observed using XRD.

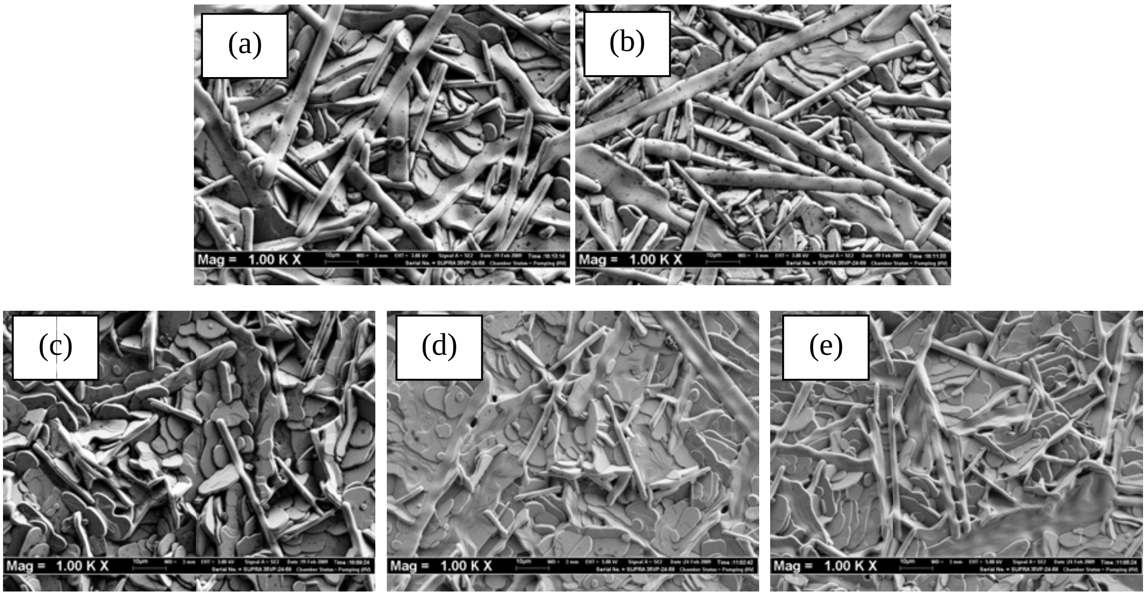

Fig. 2: FESEM images of $Bi_{4-x}Nd_xTi_30_{12}$ pellets microstructure with (a) x=0.2, (b) x=0.4, (c) x=0.6, (d) x=0.8 and (e) x=1.0 sintered at 1100°C.

Fig. 3a and b illustrate the Nd content in BNdT materials dependence of dielectric constant and dielectric loss at frequency of 1MHz and electric field at 500mV, respectively. The dielectric properties also varies with the Nd content in BNdT. Combined with the XRD results, the correlation between the dielectric properties and the grain orientation is very clear that is better dielectric properties are obtained with lesser plate-like grain. Apparently, our results show that better dielectric constant was obtained with 0.2Nd and 0.4Nd and slightly decrease at a subsequent Nd content. In other words, the dielectric constant of BNdT is much better with off-c-axis than c-axis.

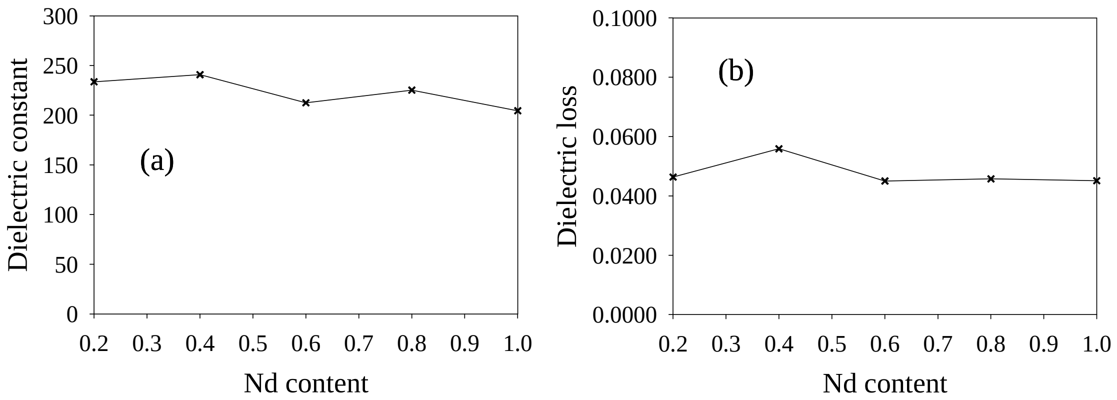

Fig. 3: Dielectric properties of BNdT measured at frequency of 1MHz with electric field of 500mV: (a) Dielectric constant and (b) Dielectric loss

4.0 CONCLUSION

BNdT ($Bi_{4-x}Nd_xTi_3O_{12}$ where x=0.2, 0.4, 0.6, 0.8, 1.0) were successfully synthesized by solution combustion method. X-ray diffraction shows that degree of c-axis-orientation increases with the increase of Nd content, accompanying with the change of grain morphology from rod-like to plate-like. It was also found that such orientation and grain morphology has a great influence on dielectric properties.

5.0 ACKNOWLEDGMENT

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6.0 REFERENCE

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