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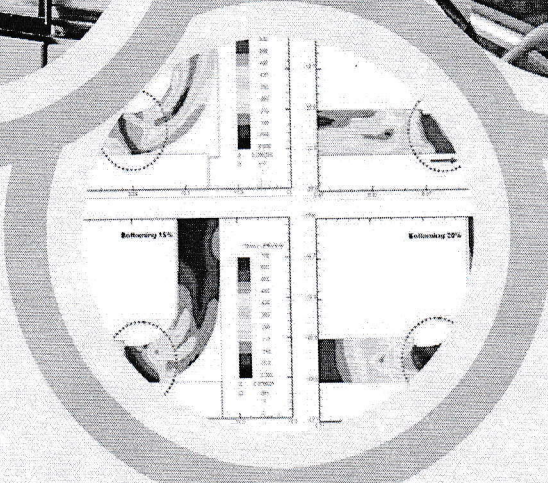
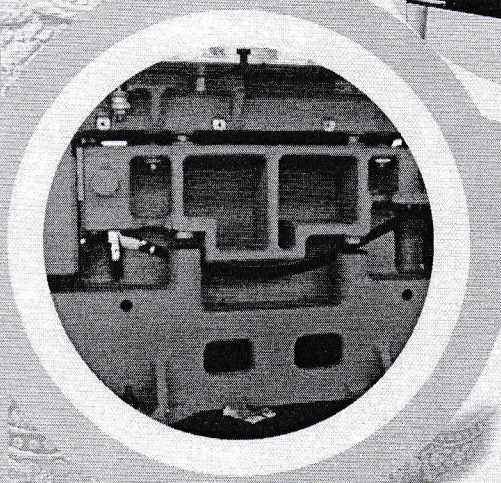
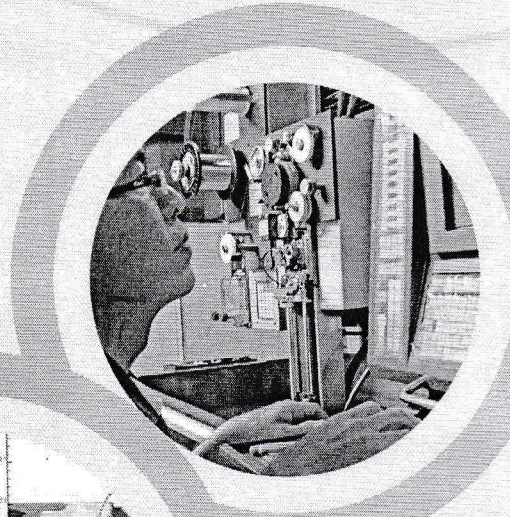
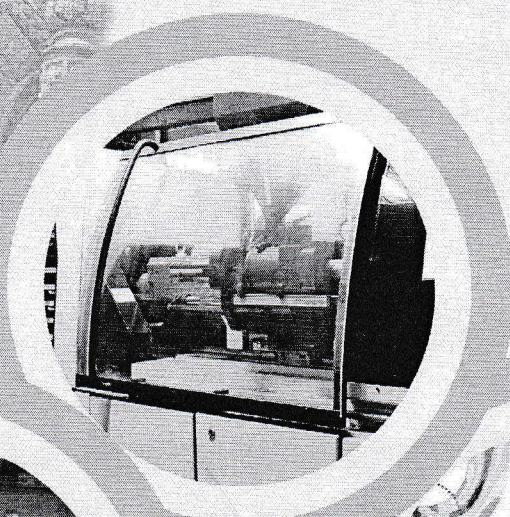
# The International Conference on Materials Processing Technology

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## Preparation of Neodymium Substituted Bismuth Titanate by a Fuel-free Combustion Process

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Fine powders of neodymium substituted-bismuth titanate,  $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$  (BNT) with  $x$  ranging from 0 to 1.0 were prepared by the fuel-free combustion process at low combustion temperature of about  $200^\circ\text{C}$ . The influence of Nd addition on the bismuth titanate system (BIT) was studied and characterized by the methods of XRD, Rietveld method and SEM. It was found that the intermediate phase of  $\text{Bi}_{12}\text{Ti}_{20}\text{O}_{20}$  had reduced with addition of Nd. Crystallinity and orthorhombicity of the system was found to be decreased as the Nd content increases. The size of platey grains is strongly influenced by the Nd added to the system.

*Key words:* fuel-free combustion; neodymium; bismuth titanate; crystallinity

### Introduction

Bismuth titanate or generally called BIT, also often abbreviated as  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  to clearly define its composition, is a ferroelectric material which has a perovskite structure ( $\text{ABO}_3$  structure) that possesses high dielectric constant  $\sim 200$  and low dissipation factor  $\sim 0.017$  [1]. Recently, BIT is believed to be the most promising candidate for dielectric material for wireless application [2]. Previously, this system has been used for ferroelectric random access memory (FRAM), optical display, high temperature piezoelectric application, pyroelectric sensors and electro optic devices [3-5]. The performance of this system is comparable with other perovskite structure systems such as barium titanate ( $\text{BaTiO}_3$ ), lead titanate ( $\text{PbTiO}_3$ ), strontium titanate ( $\text{SrTiO}_3$ ) and calcium titanate ( $\text{CaTiO}_3$ ). Therefore, it is reasonable to say that BIT is an alternative material in ceramic industry and it can be used to replace  $\text{PbTiO}_3$  due to its toxicity and very harmful to the human body [6].

From a material view point, BIT is composed of mixed oxides of  $\text{Bi}_2\text{O}_3$  and  $\text{TiO}_2$  and lanthanide atoms are frequently introduced to the A site in perovskite BIT matrix to replace bismuth (Bi) atoms, thus it is also known as lanthanide doped-BIT. The substitution of lanthanides element in this system has been used

in many studies in order to enhance the ferroelectric properties. For instance, Kan et al [7] showed that the dissipation factor of lanthanum doped-BIT was successfully reduced by about 8-10 times lower than of pure BIT. Besides that, the polarization properties of BIT material were greatly improved with the addition of Nd [8]. In this work, however, the trivalent cation of neodymium ( $\text{Nd}^{3+}$ ) is used as a substitution element in BIT system.

BIT can be prepared by a variety of methods such as mixed oxide route which based on solid state reaction, sol-gel route, and hydrothermal [9-11]. Each of these routes has their merits and drawbacks. However, in present study, a newly process which is known as fuel-free combustion synthesis has been used for the preparation of BIT. It has been developed from self-propagating high-temperature synthesis (SHS) combined with wet chemical techniques for the synthesizing of metal oxide based ceramic powders [12]. Having this in mind, there are three factors to generate ignition and combustion activities and these factors are oxidizer, temperature, and fuel [13]. A fuel-free combustion process, which does not employ any fuel agents such as citric acid, urea, or glycine, makes use of low-cost precursors resulting in a compositionally homogeneous mixture. It is



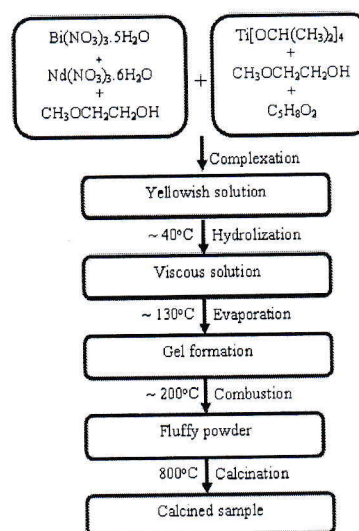
based on the fact that a wet chemical technique (one type of fuel-free combustion process) can form a stable solution with better ion distribution [14]. This process is capable of producing fine powder after combustion, and the experimental setup is very simple [15, 16]. Hence, in this work, pure and neodymium substituted-BIT are synthesized by a fuel-free combustion process using aqueous solutions of nitrate salts and titanium (IV) isopropoxide.

### Methodology

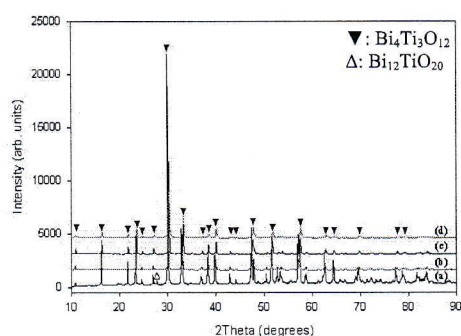
$\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$  (BNT) systems where  $x = 0, 0.2, 0.6$  and  $1$  were synthesized via fuel-free combustion process. Bismuth nitrate pentahydrate,  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and neodymium nitrate hexahydrate,  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  were initially dissolved in 2-Methoxyethanol,  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$  at  $40^\circ\text{C}$  on hot plate and stirred for about 30 min. Separately, titanium (IV) isopropoxide,  $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$  was dissolved in a homogeneous solution of 2-ME and acetylacetone,  $\text{C}_5\text{H}_8\text{O}_2$  at room temperature and stirred for 30 min. The Ti solution was then poured into the Bi solution with continuous stirring at  $40^\circ\text{C}$  for another 2 h. After that, the temperature of hot plate was then set to reach at  $\sim 130^\circ\text{C}$  to form a sticky gel. Within a few seconds, the temperature was then increased rapidly, and when it reached to  $\sim 200^\circ\text{C}$ , large amount of gases ( $\text{NH}_3$ ,  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) were liberated and a dark fluffy powder was produced after the combustion process. The process was consistently repeated for other powder ratios. Their phase formation was determined by XRD (Bruker D8 Advanced) with  $\text{Cu } \alpha$  ( $\lambda_{\text{K}\alpha 1} = 1.5405 \text{ \AA}$  and  $\lambda_{\text{K}\alpha 2} = 1.5443 \text{ \AA}$ ,  $2\theta$  range between  $10^\circ$  and  $90^\circ$ , step size of  $0.034^\circ$  ( $2\theta$ ), fixed divergence slit =  $0.2^\circ$ , receiving slit =  $0.2\text{mm}$ ). In addition, the crystallite size was calculated by Rietveld method. A Zeiss Supra 55VP PGT/HKL Field Emission Scanning Electron Microscope (FE-SEM) was used to observe the microstructure and morphology in the bulk ceramics. The process flow for the preparation of those powders is shown in Figure 1.

### Result and discussion

Figure 2 shows the XRD pattern of  $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$  after calcination at  $800^\circ\text{C}$  for 3 h. It was found that a small amount of  $\text{Bi}_{12}\text{TiO}_{20}$  intermediate phase was formed in the pure BIT sample, while no such an intermediate phase was observed in the samples with Nd addition. This result indicates that the peak corresponding to intermediate phase had reduced as the Nd content increases. It was similarly reported in other work that the incorporation of Nd into BIT lattice had reduced the formation of the intermediate phase [8]. Other factor such as heat-treated at a higher temperature could reduce the intermediate phase while increase the crystallinity of BIT phase. Kan et al. [17] reported that the presence of  $\text{Bi}_{12}\text{TiO}_{20}$  intermediate phase at  $825^\circ\text{C}$  was greatly reduced after being heated to  $1000^\circ\text{C}$ . Through this analysis, the intermediate phase in BIT compound can be reduced at a temperature as low as  $800^\circ\text{C}$  in a condition of introducing the lanthanide element.



**Figure 1** Process flow for the preparation of  $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$  via fuel-free combustion process.



**Figure 2** XRD patterns of  $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$  powders calcined at  $800^\circ\text{C}$  for 3 h: (a) pure BIT, (b) 0.2BNT, (c) 0.6BNT and (d) 1.0BNT.

It was also found that the (117) peak had shifted to high angle of  $2\theta$  (Figure 3). In other words, the peak position at (117) had changed its characteristic as a result of Nd addition. There were two things that could be observed from this characteristic. Firstly, the peak intensity of pure BIT is relatively high as compared to other BNT samples. This indicates that the crystallinity of pure BIT is the highest among all. However, it was found to be decreased when Bi atoms were then substituted with Nd atoms in bismuth titanate system. Secondly, the peak position of all powders varies from the Nd (or Bi) concentration in accordance to Vegard's Law, which means that the crystal lattice parameter and the concentration of the constituent elements have a linear relation that exists at constant temperature [18].

To estimate qualitatively the lattice parameter as well as other structure, the Rietveld method was used from the *TOPAZ software with version 3.0* provided by Bruker Advanced X-Ray Solutions. The Nd content dependence of the lattice parameter 'a', 'b', 'c' and the unit cell volume, 'V' of the powders is shown in Table 1. According to Table 1, BIT and 0.2BNT had an orthorhombic structure by considering the lattice constant of 'a' is larger than that of 'b'. However, this structure has higher tendency to form in tetragonal-type with additional of Nd content. It was confirmed by the lattice of 'a' and 'b'

become closer. Besides that, the shift of structural system is due to the change in ionic radius and atomic mass of Nd ions.

Having this in mind, the ionic radius of  $\text{Nd}^{3+}$  is about 0.111 nm which is smaller than that of  $\text{Bi}^{3+}$  (0.117 nm) [19]. Thus, the replacement of Bi atoms with Nd atoms would lead to the structural distortion from orthorhombic to tetragonal which also resulted in reducing of cell unit volume, V.

In Table 2, the crystallite size of those samples prepared in this work was significantly decreased as increase the Nd content in bismuth titanate compound. The crystallite size measured by Scherrer's formula for pure BIT is about 69.1 nm and it is also considered larger than other BNT samples. Upon increasing the Nd content, the vacancy site that already left by Bi atoms is then occupied by Nd atoms which finally results the decrease in degree of crystallinity as well as crystallite size. This is parallel with the diffraction profile obtained by XRD shown in Figure 3.

**Table 1** Structure and parameter refinement using Rietveld Method

Sample	Pure BIT	0.2BNT	0.6BNT	1.0BNT
Space group	B2cb	B2cb	B2cb	B2cb
Lattice parameter				
Crystal system	Orthorhombic	Orthorhombic	Tetragonal	Tetragonal
a, Å	5.4432	5.4320	5.4052	5.4007
b, Å	5.4075	5.4050	5.4175	5.4030
c, Å	32.8127	32.8161	32.8437	32.7928
V, Å <sup>3</sup>	965.80	963.47	961.75	956.90
Density, g/cm <sup>3</sup>	7.8354	7.4040	7.4227	7.4596
Refinement index				
R <sub>wp</sub> %	10.65	12.15	10.00	9.94
R <sub>exp</sub>	4.12	7.46	7.73	6.66

Figure 4 shows the SEM images of pure BIT and 1.0BNT which were calcined at  $800^\circ\text{C}$  for 3 h. It can be clearly seen that pure BIT exhibits a plate-like structure and its size is over  $1\mu\text{m}$  as shown in Figure 4(a). On the other hand, a remarkable decrease in the grain size with less than  $1\mu\text{m}$  was observed in 1.0BNT (Figure 4(b)). From the size comparison between both samples,



it is reasonable to say that the substituted  $\text{Nd}^{3+}$  ions act as a grain-growth inhibitor in BIT-type systems. These results are consistent with the XRD results where a decrease in peak sharpness and intensity was observed with Nd addition.

Table 2: Crystallite size calculated by Scherrer's formula

Sample	Pure BIT	0.2BNT	0.6BNT	1.0BNT
Crystallite size, nm	69.1	67.0	64.3	41.9

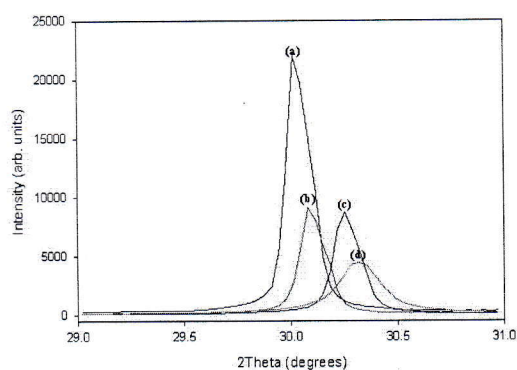


Figure 3 XRD patterns of (a) pure BIT, (b) 0.2BNT, (c) 0.6BNT and (d) 1.0BNT calcined powders at the (1 1 7) peak position.

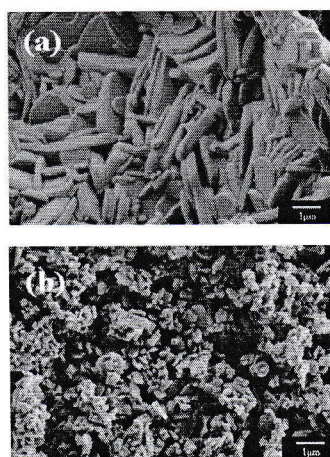


Figure 4 Grains morphology of calcined powder (a) pure BIT and (b) 1.0BNT.

## Conclusion

In present work, pure BIT and BNT were successfully prepared by a fuel-free combustion synthesis. The influence of Nd addition on bismuth titanate-type system was clearly seen through the elimination of intermediate phase of  $\text{Bi}_{12}\text{TiO}_{20}$  in the XRD pattern and the changed of peak characteristic at peak position (117). Upon increasing of Nd content, the structural system of bismuth titanate was also changed from orthorhombic to form in tetragonal. Such influence with this addition was also shown in the grain morphology which the grain size of pure BIT was recorded to be over  $1\mu\text{m}$  but it tends to change to be less than  $1\mu\text{m}$  with Nd addition.

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