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FUNDAMENTAL STUDY ON MICROSTRUCTURE OF CeO_2-DOPED $(Na_{0.5}Bi_{0.5})TiO_3$ CERAMICS

Rozidawati Awang[1,*], Nurain Ab. Halim[1], Zalita Zainuddin[1], Mohammad Hafizuddin Haji Jumali[1], Muhammad Yahaya[1] and Muhammad Mat Salleh[2]

[1]*School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia (UKM), 43600 UKM Bangi, Selangor, MALAYSIA*

[2]*Institute of Microengineering and Nanoelectronic (IMEN), Universiti Kebangsaan Malaysia (UKM), 43600 UKM Bangi, Selangor, MALAYSIA*

**Corresponding author: rozida@ukm.my*

ABSTRACT

The effect of CeO_2 additions and methods of preparation on the microstructure of $(Na_{0.5}Bi_{0.5})TiO_3$, (NBT) have been investigated. NBT ceramics was prepared using sol-gel technique and then were doped with the CeO_2 powders (0 – 0.4 wt%) using the solid state reaction method. The morphology and microstructure of the doped ceramics were investigated using SEM and XRD techniques, respectively. Based on the SEM images, the microstructure of ceramics remains unchanged with the additions of CeO_2. However, the microstructure of the ceramics reduced in size significantly by using the sol-gel technique as compared to the solely conventional solid-state processes. While XRD patterns indicate that CeO_2 with 0.1 – 0.3 wt% has diffused into the lattice of NBT ceramics.

Keywords: CeO_2-doped NBT; microstructure; sol-gel

INTRODUCTION

Investigation of lead-free piezoelectric ceramics has attracted much interest in order to replace the widely used of lead-based piezoelectric ceramics. The preparation of lead-based ceramics cause serious environmental pollution [1, 2]. $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) is considered to be the potential candidate because it has good piezoelectric properties [3, 4]. Previous reports demonstrate that the enhancement in piezoelectric properties of NBT can be achieved by altering the composition via addition of dopant such as CeO_2 into NBT-based ceramics [2] and modification of preparation method [5].

Conventional solid state reaction method is being used frequently for the synthesis of NBT ceramics. However, this technique usually results in large particle size [6] and difficult to prevent the formation of secondary $Bi_2Ti_2O_7$ phase [7]. As for to date, many authors have developed alternative methods to conventional solid state method such as sol-gel using either citrate and steric acid as solvent [8, 9, 10]. In this fundamental

study, NBT powders were prepared using sol-gel method and then was doped with the CeO_2 powders (0 – 0.4 wt%) by using solid state method, as an attemp to obtain a smaller particle size. The effects of CeO_2 dopant and method of preparation on the microstructure of NBT ceramics were investigated.

EXPERIMENTAL METHOD

The sol gel technique employed in the present investigation was based on previous work [8]. The starting raw materials for the synthesis are high purity of $NaCH_3COO$, (Sigma-Aldrich, 99.995%), $C_6H_9BiO_6$, (Aldrich, 99.99%) and $Ti[O(CH_2)_3CH_3]_4$, (Aldrich, 97%). The solvents used in this work are 2-methoxyethanol and glacial acetic acid. Firstly, 0.7 g of $NaCH_3COO$ was diluted in 2-methoxyethanol while 3.8 g of $C_6H_9BiO_6$ were diluted in glacial acetic acid and deionized water. Secondly, both solutions were mixed together and stirred for 15 minutes. Then, $Ti[O(CH_2)_3CH_3]_4$ was slowly added into this mixture and stirred at 50^{o}C for another 15 minutes. Next, the sol was cooled down to room temperature to produce homogeneous and clear yellowish sol. Consequently, sol was dried in an oven for 24 hours at 100^{o}C followed by calcined at 700°C for 2 hours. Dried sol was ground in a mortar for 3 hours to get fine NBT powders.

The sol gel technique was then followed by solid state method to get CeO_2-doped NBT samples at five different compositions. The NBT powders from sol gel technique were then mixed with CeO_2 at 0.0, 0.1, 0.2, 0.3 and 0.4 wt% for every 3.5 g NBT powders. The mixture was grounded in mortar for 2 hours followed by sintering process at 850 °C for 2 hours. Next, the CeO_2-doped NBT was further grounded for 1 hour before pressed into disk of 14 mm diameter at pressure of 5 1.0x10^7 Pa for about 10 minutes holding time to ensure good strength. Finally, the compacted disks were sintered at 1110^{o}C for 6 hours in air.

In order to study the effect of preparation method on the microstructure of the sample two other samples were prepared by solid state method. The samples were undoped and CeO_2 doped at 0.4 wt%. The details of this process are similar to other work [11].
The crystal structure of the NBT ceramics was determined by X-ray diffraction (XRD) using a Cu K_α radiation (Bruker D8 Advance). The surface microstructure of the NBT ceramics were observed by scanning electron microscopic (SEM) (Leo 1438VP).

RESULTS AND DISCUSSIONS

Figure 1 shows the pellets of the NBT ceramics CeO_2 doped at 0, 0.1, 0.2, 0.3 and 0.4 wt%. The color of sintered pallets became darker as CeO_2 addition increased. The change of color with CeO_2 addition indicates the incorporation of Ce into the lattice. It was suggested by Chen et al. [12].

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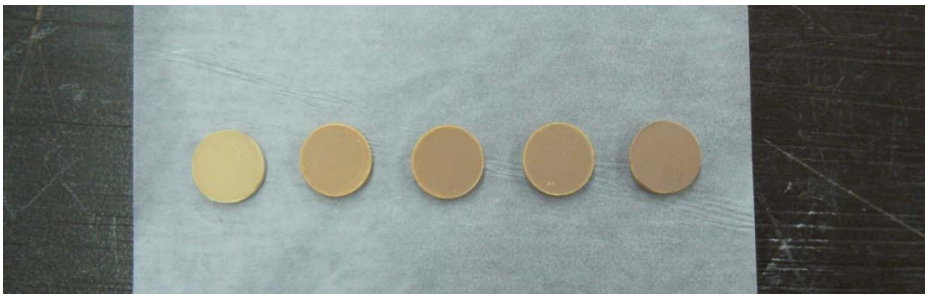

Figure 1: Pellets of the NBT ceramics CeO_2 doped at 0, 0.1, 0.2, 0.3 and 0.4 wt% (left to right)

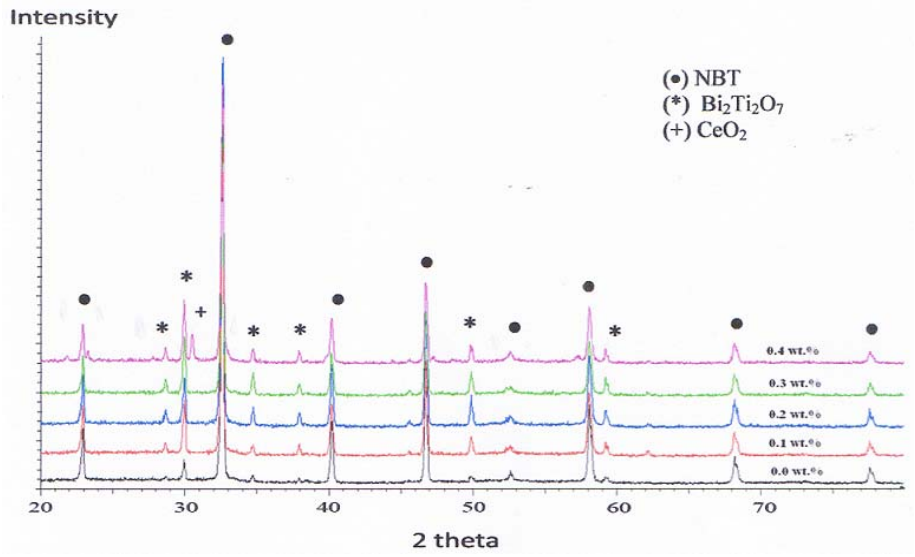

Figure 2: XRD patterns of samples doped at 0, 0.1, 0.2, 0.3 and 0.4 wt%

XRD diffractograms of CeO_2 doped NBT ceramics with different wt% are shown in Figure 2. The XRD analysis revealed that NBT with rhombohedral crystal structure is the main phase in every sample. $Bi_2Ti_2O_7$ as secondary phase in all samples. However, at the highest CeO_2 content, the presence of one unknown peak was noticed at $2\theta = 31^o$ which may represent the existence of CeO_2 as the third crystalline phase in the sample. This observation suggests that additions of CeO_2 up to 0.3 wt% may be successfully incorporated into the crystal structure of NBT ceramics. Above this value, the CeO_2 may not be able to be incorporated into NBT crystal network and left out as ternary phase. Therefore, 0.3 wt% is the limit of CeO_2 to enter the crystalline lattice structure of NBT ceramics.

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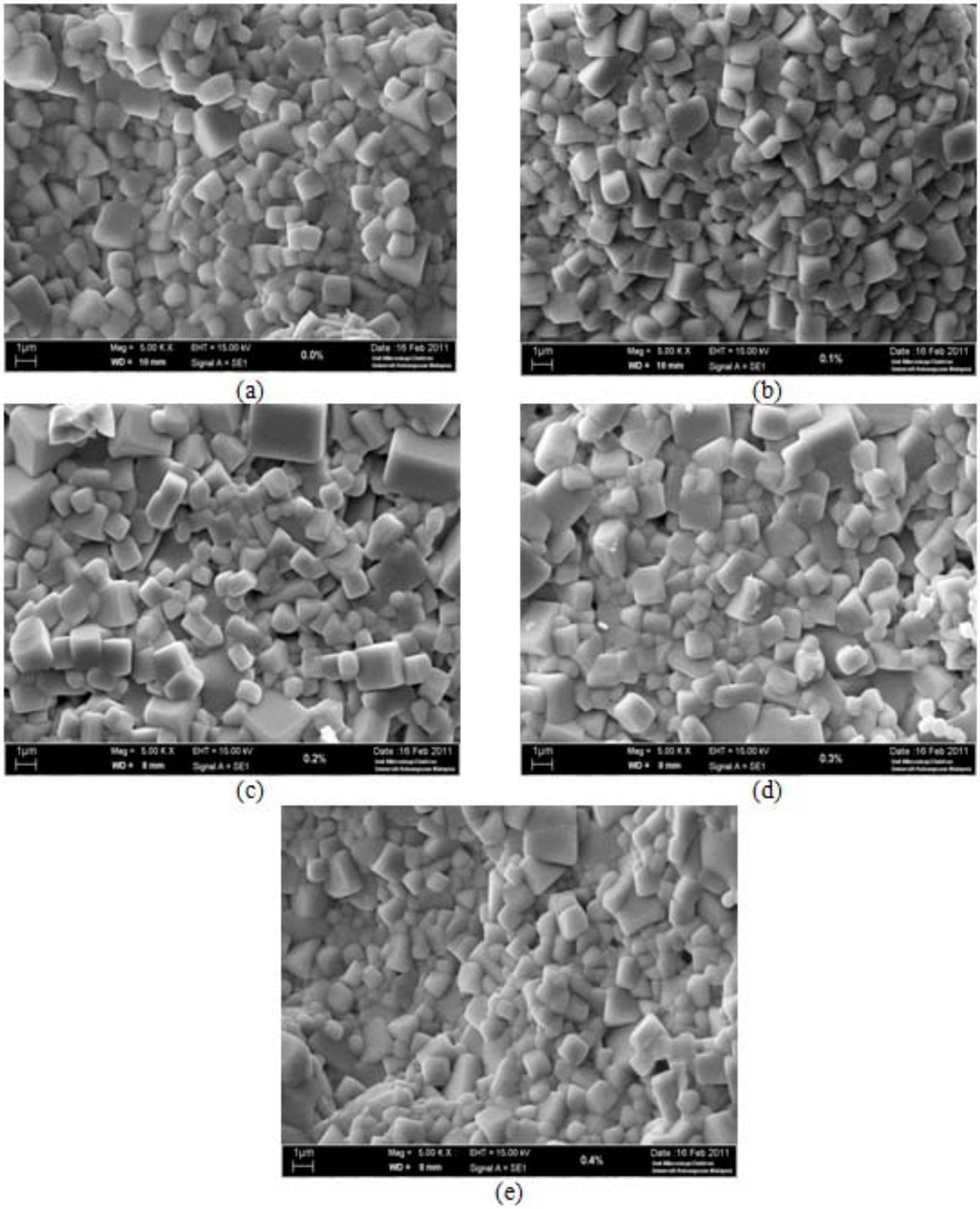

Figure 3: SEM micrographs of samples doped at (a) 0, (b) 0.1, (c) 0.2, (d) 0.3 and (e) 0.4 wt%

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Figure 3 shows the SEM micrographs of NBT pellets doped at 0, 0.1, 0.2, 0.3 and 0.4 wt%. The grain is observed and almost no pores are revealed in all samples. The morphology of the samples shows no apparent changes with the CeO_2 addition. This shows that the addition of CeO_2 did not cause a significant modification in the microstructure of the samples. But the microstructure of the sample remarkably reduced in size by using the sol-gel technique (or combination techniques for doped sample) as compared to the solely conventional solid-state processes as shown in Figure 4 and Figure 5 for undoped and 0.4 wt% doped samples respectively. This result shows the improved microstructure homogeneity and high density NBT ceramics can be obtained by sol gel technique (or combination techniques for doped sample). Form this observation, the different fabrication processes will lead to different morphologies of undoped and CeO_2 doped $(Na_{0.5}Bi_{0.5})TiO_3$ ceramics. This will lead to different dielectric characteristics.

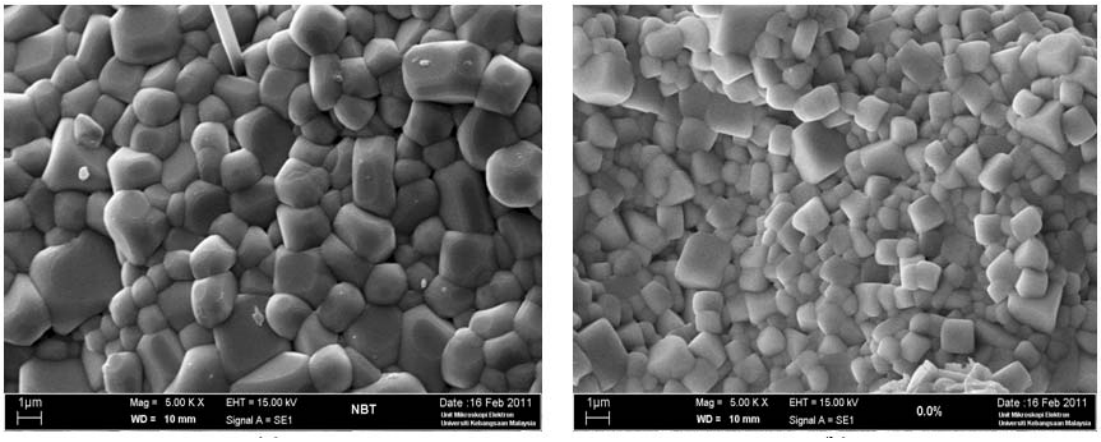
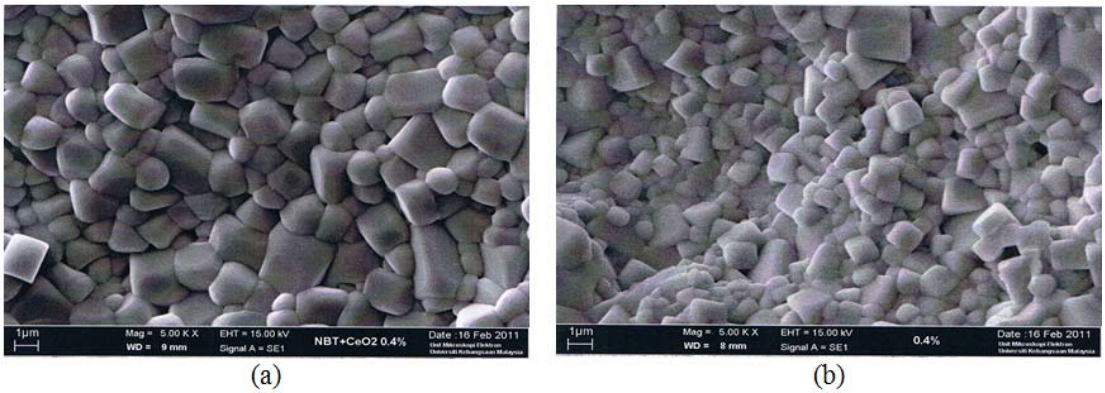


Figure 4: SEM micrographs of samples by (a) solid-state processes (b) sol-gel technique, of undoped samples



(a) (b)

Figure 5: SEM micrographs of samples by (a) solid-state processes (b) sol-gel technique, of samples of CeO_2 doped at 0.4 wt%

CONCLUSIONS

Addition of CeO_2 with 0.1 – 0.3 wt% has diffused into the lattice of NBT ceramics. While microstructure of the ceramics does not change with the addition of a small amount of CeO_2, it has reduced in size significantly by using the sol-gel technique as compared to the solely conventional solid-state processes. It is expected that this study will be able to invite interests for more in-depth researches in this area, particularly on the prevention of the formation of secondary $Bi_2Ti_2O_7$ phase.

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