MALAYSIAN JOURNAL OF MICROSCOPY

Vol.7 ISSN 1823-7010 December 2011

Malaysian Journal of Microscopy 7 : 132 - 136 (2011) ISSN: 1823-7010

Effect of Heat Treatment on the Grain Orientation of $Bi_{3.25}Nd_{0.75}Ti_3O_{12}$ Ceramic

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Neodymium substituted-bismuth titanate, $Bi_{3.25}Nd_{0.75}Ti_3O_{12}$ (BNT075) ceramic was prepared using soft combustion technique. The dependence of heat treatment on the grain orientation of ceramic was observed. With increasing temperature, the BNT075 ceramic turned from off c-axis-preferential-oriented to c-axis-oriented. The result also corresponded to the change from equiaxed structure to plate-like structure, indicating that the grain orientation had a significance influence on grain growth.

Keywords: c-axis, heat treatment, grain orientation

INTRODUCTION

Over the last decade, much attention has been paid to lanthanide substituted-bismuth titanate for their potential applications in nonvolatile ferroelectric random access memories [1,2]. Neodymium-substituted bismuth titanate is one of the most popular materials investigated for this purpose [3]. The outstanding ferroelectricity such as high remanent polarization ($2P_r$), low coercive field ($2E_c$), good fatigue endurance and low leakage current are essential in this application [4]. As reported, the $2P_r$ is highly dependent on their grain orientation [5]. The $2P_r$ value of the c-axis-oriented BNT films is ~100 $\mu C/cm^2$ whereas the off c-axis oriented thin films has the $2P_r$ of 51 $\mu C/cm^2$ [6, 7]. Based on this result, it would be expected that the $2P_r$ value of c-axis-oriented BNT thin films is much higher than that of off c-axis-oriented films. In the case to enhance the c-axis-oriented, several works have been reported over the last 10 years. Bae and co-workers have reported a fabrication of c-axis-oriented lanthanum-doped bismuth titanate resulting from the increase in annealing temperature [8]. The other way is to use template-grain growth (TGG) method to orient the textured Nb-doped bismuth titanate in c-axis [9]. Tanaka and and co-workers have fabricated c-axis-oriented ZnO with a rotating high magnetic field [10]. In this work, we have prepared the grain orientation in c-axis-oriented and off-c-axis-oriented BNT075 ceramic with various heat-treatments, whereby the results were presented in X-ray structural, Lotgering degree of c-oriented and grain morphologies.

EXPERIMENTAL PROCEDURE

Materials and Reagents

The following materials and reagents were used: bismuth nitrate penthahydrate (Bi $(NO_3)_3.5H_2O$, 98%, Sigma Aldrich), neodymium nitrate hexahydrate (Nd $(NO_3)_3.6H_2O$, 99.9%, Sigma Aldrich), titanium (IV) isopropoxide (Ti

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[OCH $(CH_3)_2]_4$, 97%, Merck), acetylacetone ($C_5H_8O_2$, Merck) and 2-Methaoxyethanol ($CH_3OCH_2CH_2OH$, Merck).

Preparation of BNT075

The required amounts of Bi $(NO_3)_3.5H_2O$ and Nd $(NO_3)_3.6H_2O$ were simultaneously dissolved in $CH_3OCH_2CH_2OH$ by stirring at 40°C and 25°C, respectively, for 30 min. Separately, Ti [OCH $(CH_3)_2]_4$ was also dissolved in the mixture of $CH_3OCH_2CH_2OH$ and $C_5H_8O_2$ with constant stirring at 25°C for 30 min. Then, Nd solution was slowly added into Bi solution while being constantly stirred. It was then followed by Ti solution was added drop-by-drop into Bi-Nd solution and continuously stirred at 40°C for another 2 h. A flow chart is illustrated in *Fig. 1*.

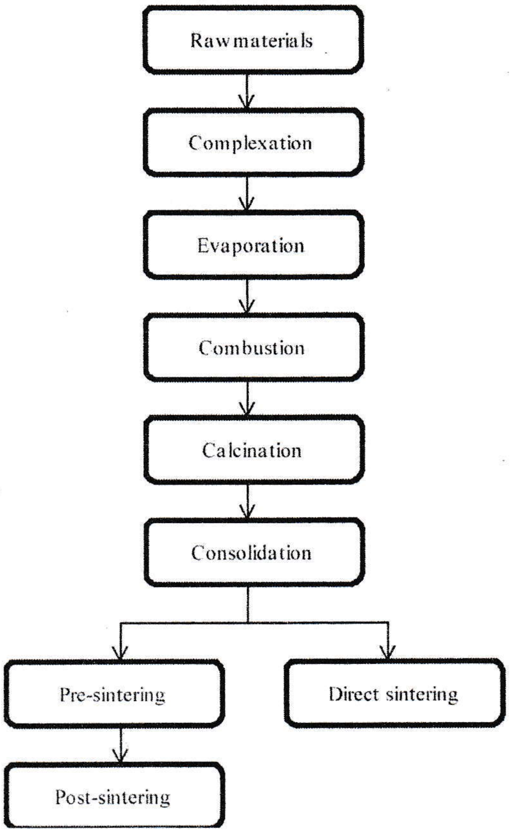

Fig. 1: Simple flow chart of the preparation of BNT075 with various heat-treatments

Stages of heat-treatment

Various heat-treatments were used to investigate their effect on grain orientation and grain morphologies of BNT075. The corresponding samples HT1, HT2 and HT3 were obtained after calcination, pre-sintering and post-sintering, respectively. HT4 was obtained by almost same samples as HT3, except that pre-sintering was skipped in the processing route. It can be simplified as listed in Table 1.

TABLE 1
List of parameter of heat-treatment with heating rate of 5°C/min

Sample	Heat treatment	Temperature	Soaking
HT1	Calcination	800°C	3 h
HT2	Pre-sintering	700°C	2 h
HT3	Post-sintering	1100°C	3 h
HT4	Direct sintering	1100°C	3 h

Characterization

X-ray diffraction (XRD, Bruker D8 Advanced) analysis was carried out to determine the grain orientation as a result of different heat-treatment. The grain morphologies were displayed by field-emission scanning electron microscopy (FE-SEM, Zeiss Supra 55VP PGT/HKL). The Lotgering degree of grain orientation was calculated according to the following equation [11]:

$$\alpha(\text{c-axis}) = \frac{I_{(00l)}}{I_{(00l)} + I_{(117)}} \quad (1)$$

$$\alpha(\text{off c-axis}) = \frac{I_{(117)}}{I_{(00l)} + I_{(117)}} \quad (2)$$

RESULTS AND DISCUSSIONS

XRD Analysis

Fig. 2 shows XRD patterns of the BNT075 with various heat-treatments. The XRD analysis confirmed that various heat treatments can be used to form single phase of bismuth-layered structure. For the sample produced from HT1 and HT2, the most intense peak was dominated by (117), suggesting the formation of highly off-c-axis orientation. On the other hand, the indexed peak was found to decrease in the sample produced from HT3 and HT4. The increase in intensity of (00*l*) plane is clearly seen in XRD pattern, implying that significance shifted to c-axis-orientation. It is reasonable to suggest that different axis in grain orientation is produced with various type of heat treatment. In addition to that, the degree orientation (α) of c-axis and off-c-axis was calculated for respective sample. As calculated, $\alpha_{c\text{-axis}}$ for HT1, HT2, HT3 and HT4 was about 11.6%, 30.1%, 71.4% and 84.7%, respectively, indicating the increase in c-axis-orientation and decreasing in off-c-axis-orientation. The calculated value is shown in Table 2.

TABLE 2
Degree of orientation for c-axis and off c-axis

Sample	α(c-axis)	α(off c-axis)
HT1	11.60%	88.40%
HT2	30.10%	69.90%
HT3	71.40%	28.60%
HT4	84.70%	15.30%

SEM Analysis

Fig. 3 shows the grain morphologies of the BNT075 ceramic with various heat-treatments. In *Fig. 3(a)*, the HT1 grains mostly consist of equiaxed-like structure with average grain size of 100 nm to 600 nm. As the powder is pre-heated, the HT2 grain size is almost uniform due to grain growth of equiaxed-like grain (*Fig.*

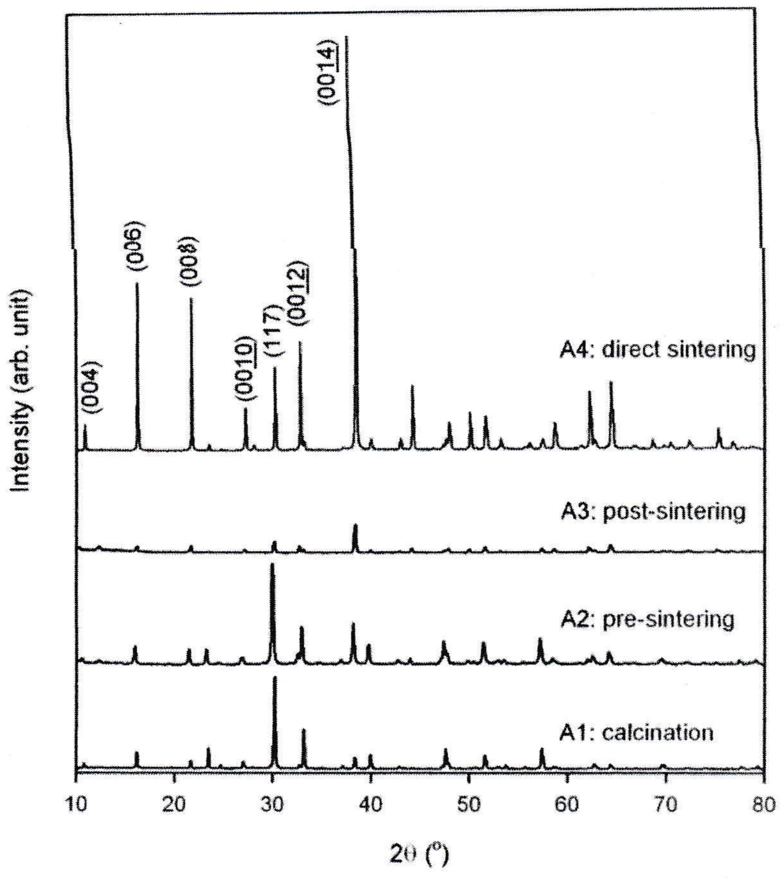

Fig. 2: X-ray diffraction patterns of BNT075 at different heat treatment

3(b)). This particular grain growth occurs very extensive during post-sintering resulted in HT3 plate-like structure (*Fig. 3(c)*). The platey grain is more uniform with average grain size of 2 µm to 8 µm. The largest HT4 plate-like structure is clearly seen resulting from direct sintering as shown in *Fig. 3(d)*. The morphology results are consistent with the results of XRD and degree of orientation as reported earlier.

CONCLUSION

In summary, the grain orientation of BNT075 ceramic is highly dependent on heat treatment. Similar observation was found in the sample produced from HT1 and HT2, whereby the off-c-axis became a dominant orientation. However, it did not occur in the sample produced from HT3 and HT4. The increase in c-axis-orientation was also confirmed by degree orientation. The change in grain orientation was clearly seen in grain morphology, whereby highly-c-axis-orientation corresponds to plate-like structure.

ACKNOWLEDGMENT

The authors appreciate the technical support from School of Materials and Mineral Resources

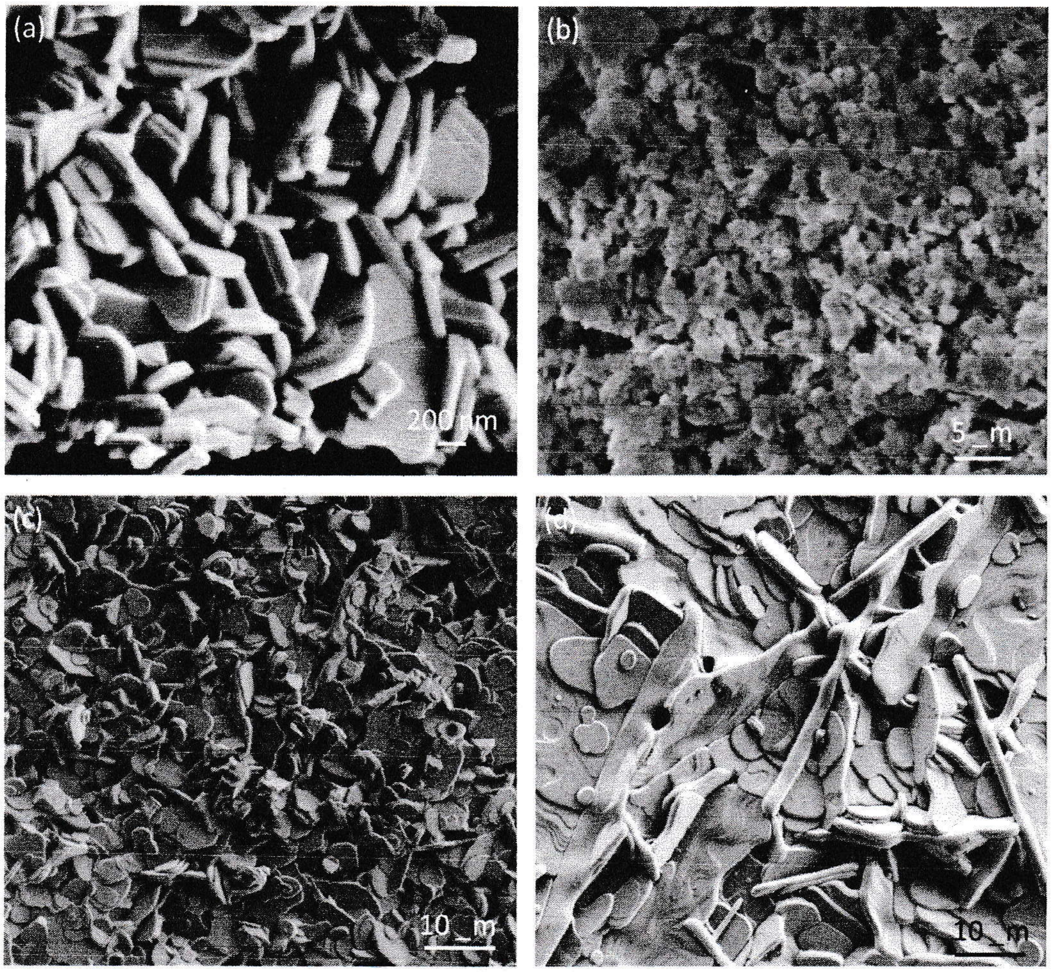

Fig. 3: Grain morphologies of BNT075 with various heat-treatments: (a) HT1, (b) HT2, (c) HT3 and (d) HT4

Engineering, Universiti Sains Malaysia. This research was supported by the E-science Fund 305/Pbahan/6013357, USM-RU grant 1001/Pbahan/8042018 and 811069.

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