Effect of Heat Treatment on the Grain Orientation of Bi$_{3.25}$Nd$_{0.75}$Ti$_3$O$_{12}$ Ceramic

A. Umar Al-Amanli, S. Srimalai, M.N. Ahmad Fauzi, A.R. Khairunisak, S. Tanaka and K. Uematsu

1School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, MALAYSIA
2Department of Materials Science and Engineering, Faculty of Engineering Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, JAPAN

Neodymium substituted-bismuth titanate, Bi$_{3.25}$Nd$_{0.75}$Ti$_3$O$_{12}$ (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 ($P_r$), low coercive field ($E_c$), good fatigue endurance and low leakage current are essential in this application [4]. As reported, the $P_r$ is highly dependent on their grain orientation [5]. The $P_r$ value of the c-axis-oriented BNT films is ~100 µC/cm$^2$ whereas the off-c-axis oriented thin films has the $P_r$ of 51 µC/cm$^2$ [6, 7]. Based on this result, it would be expected that the $P_r$ 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 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 pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O, 98%, Sigma Aldrich), neodymium nitrate hexahydrate (Nd(NO$_3$)$_3$·6H$_2$O, 99.9%, Sigma Aldrich), titanium (IV) isopropoxide (Ti(OiPr)$_4$) and...
Effect of Heat Treatment on the Grain Orientation of Bi$_{1-x}$Nd$_x$Ti$_3$O$_{12}$ Ceramic

[OCH (CH$_3$)$_3$, 97%, Merck], acetylacetone (C$_5$H$_9$O$_2$, Merck) and 2-Methoxyethanol (CH$_3$OCH$_2$CH$_2$OH, Merck).

Preparation of BNT075
The required amounts of Bi(NO$_3$)$_3$.5H$_2$O and Nd(NO$_3$)$_3$.6H$_2$O were simultaneously dissolved in CH$_3$OCH$_2$CH$_2$OH by stirring at 40°C and 25°C, respectively, for 30 min. Separately, Ti [OCH (CH$_3$)$_3$] was also dissolved in the mixture of CH$_3$OCH$_2$CH$_2$OH and C$_5$H$_9$O$_2$ 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.

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>
<thead>
<tr>
<th>Sample</th>
<th>Heat treatment</th>
<th>Temperature</th>
<th>Soaking</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT1</td>
<td>Calcination</td>
<td>800°C</td>
<td>3 h</td>
</tr>
<tr>
<td>HT2</td>
<td>Pre-sintering</td>
<td>700°C</td>
<td>2 h</td>
</tr>
<tr>
<td>HT3</td>
<td>Post-sintering</td>
<td>1100°C</td>
<td>3 h</td>
</tr>
<tr>
<td>HT4</td>
<td>Direct sintering</td>
<td>1100°C</td>
<td>3 h</td>
</tr>
</tbody>
</table>

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]:

$$\alpha(\text{c-axis}) = \frac{I_{(000)}}{I_{(000)} + I_{(117)}}$$  \hspace{1cm} (1)

$$\alpha(\text{off c-axis}) = \frac{I_{(117)}}{I_{(000)} + I_{(117)}}$$  \hspace{1cm} (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
A. Umar Al-Amani, S. Srimala, M.N. Ahmad Fauzi, A.R. Khairunisak, S. Tanaka and K. Uematsu

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 (00l) 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 (\(\alpha\)) of c-axis and off-c-axis was calculated for respective sample. As calculated, \(\alpha_{\text{c-axis}}\) 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>
<thead>
<tr>
<th>Sample</th>
<th>(\alpha_{\text{c-axis}})</th>
<th>(\alpha_{\text{off c-axis}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT1</td>
<td>11.60%</td>
<td>88.40%</td>
</tr>
<tr>
<td>HT2</td>
<td>30.10%</td>
<td>69.90%</td>
</tr>
<tr>
<td>HT3</td>
<td>71.40%</td>
<td>28.60%</td>
</tr>
<tr>
<td>HT4</td>
<td>84.70%</td>
<td>15.30%</td>
</tr>
</tbody>
</table>

**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.
Effect of Heat Treatment on the Grain Orientation of Bi$_{32}$Nd$_{65}$Ti$_3$O$_{12}$ Ceramic

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.

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