Preparation and Pyroelectricity of $\text{Sr}_{0.3}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$ Ceramics

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1. INTRODUCTION

$\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6 (0.25 \leq x \leq 0.75)$, referred to as SBN:X, is a ferroelectric with tungsten bronze structure. Among the tungsten bronze ferroelectrics, SBN can be classified as partially filled bronze because of the site occupancy of 5/6 in the 15- and 12-fold coordinated oxygen octahedra sites. SBN shows large optical non-linearity and also very large pyroelectric coefficient. Therefore, attention has been focused on the growth of transparent crystals with a variety of ferroelectric properties. Compared with the extensive investigations of the SBN single crystals, a limited number of studies have been done for the fabrication of SBN ceramics. Similar to other tungsten bronze ferroelectrics, SBN has essentially strong anisotropy which is derived from the structure. The anisotropy distinguishes the ferroelectrics with tungsten bronze structure from those of the isotropic perovskite family, and potentially leads to the production of a different kind of sophisticated materials.

The purpose of this study is to establish the fabrication method of the SBN ceramics with specified properties for pyroelectric infrared detector applications. The composition selected is SBN:30 ($x=0.3$) because of a higher Curie temperature ($T_c \sim 180^\circ\text{C}$) in the SBN solid solution. The highly densified SBN:30 ceramics are fabricated by various sintering procedures and/or using active powders prepared by solution method. The relationship between the fabrication procedures and the ferroelectric and pyroelectric properties of the products is examined.

2. EXPERIMENTAL

Starting powders for sintering were prepared by different mixing procedures: (1) mechanical mixing of $\text{Nb}_2\text{O}_5$ and carbonates of Sr and Ba, and (2) intimate mixing by coprecipitation during which a required amount
of Nb$^{5+}$, Sr$^{2+}$ and Ba$^{2+}$ was deposited as a precursor in an aqueous solution of ammonium carbonate. The mixed powders were calcined at 800 - 1100°C for 6 - 24h. The pressureless sintering of green compacts (CIPped at 100MPa) was conducted in air under various conditions. (1300 - 1400°C for 2 - 24h) Some selected samples were successively processed by HIPping in Ar or Ar-O$_2$ atmosphere. The density measurement, microstructure observation with SEM, and estimation of temperature dependence of dielectric constant and pyroelectric current were made for the sintered SBN:30.

3. RESULTS AND DISCUSSION

The green compact of the SBN:30 powder prepared by calcining a mechanical mixture at 1100°C(6h) could be densified to a polycrystalline body with 97% of relative density by pressureless sintering at 1400°C for 4h. The microstructure of the ceramic is presented in Fig.1(A). The average grain size of the sample is estimated to be around 2μm. It should be noted that little change in the microstructure of the SBN:30 ceramics occurred after sintering for 24h at 1400°C.

It is preferable to fabricate fully densified ceramics for property measurement, since pore-free bodies could minimize the external contribution to the intrinsic property. Hot isostatic pressing (HIPping) was employed for further densification of the SBN:30 samples. The results obtained are summarized in Table 1. HIPping in Ar at 1300°C produced a melted and dark blue sample, indicating that Nb$^{5+}$ ions might be strongly reduced in the oxygen-free high pressure atmosphere. On the contrary, HIPping under a high oxygen pressure(16MPa) caused full densification of the SBN:30 sample with translucency at 1350°C. (procedures [3] and [5]) The microstructure of the pore-free SBN:30 ceramic can be seen in Fig.1(B). No grain growth occurs during HIPping. The fabrication of a fully-densified sample with different microstructure was attained by starting with a coprecipitated precursor. (procedure [6]) In this procedure, a compact of calcined (800°C) and pre-sintered (1100°C) powder was encapsulated in an evacuated glass tube and HIPped in Ar(150MPa) at 1200°C. As shown in Fig.1(C), this procedure enabled the SBN:30 ceramics to be fully densified with a smaller grain size.

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Table I. Sintering procedures and some properties of the sintered bodies.

<table>
<thead>
<tr>
<th>Procedures</th>
<th>R.D. (%)</th>
<th>Ave.G.S. (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1] Pressureless sintering at 1400°C/4h(PL)</td>
<td>97</td>
<td>~2</td>
</tr>
<tr>
<td>[2] PL + HIPping in Ar(150MPa;1300°C/1h)</td>
<td>melt</td>
<td>~2</td>
</tr>
<tr>
<td>[3] PL + HIPping in Ar-O₂(20%) (80MPa;1350°C/2h)</td>
<td>100</td>
<td>~2</td>
</tr>
<tr>
<td>[4] PL of coppt-powder at 1400°C/4h(PLC)</td>
<td>97</td>
<td>~2</td>
</tr>
<tr>
<td>[5] PLC + HIPping in Ar-O₂(20%) (80MPa;1350°C/2h)</td>
<td>100</td>
<td>~2</td>
</tr>
<tr>
<td>[6] Pre-sintered + HIPping in Ar (150MPa;1200°C/1h)</td>
<td>100</td>
<td>~1</td>
</tr>
</tbody>
</table>

*R.D.* = relative density, *G.S.* = grain size, *coppt* = coprecipitated

Figure 2 shows the temperature dependence of the dielectric constant (*ε*) of the SBN:30 samples fabricated. The symbols, P-1, -3, -4, -5 and -6, indicate the corresponding number of the procedure described in Table I. The temperature at which the sample shows a maximum value of the dielectric constant (*ε*<sub>max</sub>) is 175 - 185°C except for the P-6 sample. It is also evident that HIPping in oxygen-rich atmosphere increases the *ε*<sub>max</sub> without a marked sharpening of the dielectric anomaly peak. This is because firstly that the density of the sample is raised by HIPping. In addition, a high oxygen pressure may provide some contribution to the modification of the bronze structure or the grain boundary structure. A detailed examination is needed for further discussion. A considerable broadening of the anomaly peak with *ε*<sub>max</sub> at 140°C is observed in the P-6 sample. Although X-ray diffraction revealed the production of the single-phase SBN:30 ceramics for the HIPped sample, the processing at lower temperatures(calcining at 1100°C and HIPping at 1200°C) might cause the incomplete formation of the SBN:30 solid solution. The effect of the fabrication procedure on the pyroelectric property of the SBN:30 ceramics was also examined.
Fig. 1 SEM microphotographs of (A) P-1, (B) P-3 and (C) P-6 samples.

Fig. 2 Temperature dependence of the $\varepsilon$ for the SBN:30 ceramics.