Nanocrystallization of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ piezoelectric material

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Abstract

With growing concern on health and safety worldwide, a requirement for environmentally benign piezoelectrics are continually increasing. The Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (BNT) ceramic is a promising piezoelectric material without the lethal element, Lead.

Conventional mixed oxide method generally yields BNT with grains in the micron range. Nanocrystalline materials could be obtained by chemical route but at high expense.

Reaction of Bi$_2$Ti$_4$O$_{11}$ with excessive Na$_2$CO$_3$, has been found to produce nanocrystalline BNT at low temperature. SEM showed recrystallization of BNT. Crystallize size calculation from X-ray diffraction confirmed that the size of the crystals were in nanometer range.

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1. Introduction

Commercial piezoelectric materials at the present are of lead zirconium titanate family, they exhibit a range of useful properties with low cost. However, with growing concern on health and safety worldwide, a requirement for environmentally benign piezoelectrics is continually increasing. Bi$_{0.5}$Na$_{0.5}$TiO$_3$ ceramic is a promising piezoelectric material without the lethal element, Lead. This material and its variations are now being investigated intensively. Improvement in piezoelectric characteristics is the main aim, employing various techniques [1–7].

One of the main controlling factors of engineering properties is microstructural features. Grain size is an important microstructural characteristic that affects piezoelectric properties. Although the piezoelectric properties are expected to degrade with smaller grain size, the relative permittivity increases. [8] Moreover, finer grain piezoelectrics offer two main advantages; higher mechanical strength and improved dielectric strength, if the piezoelectric properties could be preserved. TRS Ceramics, Inc. has developed a process by which the grain size effects are compensated to produce fine grain piezoceramics [9].

Conventional mixed-oxide route provide material production at low cost but the grain size is generally in the micron range. Although very fine powder could be employed for smaller grain size, much higher cost is incurred and the risk of contamination from high-power grinding becomes high. Chemical method can also generate fine powders but at an expensive price. This study has shown a new method of reducing the grain size in the submicron range by recrystallization or nanocrystallization.

2. Experimental procedures

2.1. Study of reaction of Bi$_2$Ti$_4$O$_{11}$ and excessive Na$_2$CO$_3$

Bi$_2$O$_3$ (Fluka, puriss) and TiO$_2$ (Fluka, puriss) were used as starting materials. They were mixed in the proportion to yield Bi$_2$Ti$_4$O$_{11}$ using ball milling in plastic bottle with zirconia balls. The mixture was fired at high temperature to form Bi$_2$Ti$_4$O$_{11}$ and ground into fine powder with pestle and mortar. The powder was mixed with excessive Na$_2$CO$_3$ (> 50% by weight) and fired at various temperature. After firing, the mixtures were washed several times with hot water to remove unreacted Na$_2$CO$_3$. Washed mixtures were subjected to analysis with X-ray diffraction (JEOL JDX-3530) for phase identification.
2.2. Preparation of single crystals of Bi$_2$Ti$_4$O$_{11}$ and conversion with Na$_2$CO$_3$

Bi$_2$Ti$_4$O$_{11}$ crystals were produced by molten salt synthesis. The mixture of NaCl–KCl with the molar ratio of 1:1 was selected for the system. Again, Bi$_2$O$_3$ and TiO$_2$ were used as starting materials; the salt mixture was added at equal weight. The synthesis temperature was 1100 °C with cooling rate of 180 °C/min. Salt was washed out with hot water several times. The size and shape of produced crystals were investigated with SEM (JEOL, JSM-6301F). The crystals were mixed with excessive Na$_2$CO$_3$ (> 50% by weight) and fired at selected temperature. After firing, the crystals were washed several times with hot water to remove unreacted Na$_2$CO$_3$. Surface structures of washed crystals were studied with SEM. X-ray diffraction analysis was performed for phase identification, strain and crystallite size calculation. Strain and crystallite size calculation from powder X-ray diffraction pattern are explained elsewhere [10]. Standard LaB$_6$ (NIST) was used as a reference for removing instrumental broadening. Crystallite size and strain plots were produced using Jade 6 software (MDI).

3. Results and discussion

3.1. Reaction of Bi$_2$Ti$_4$O$_{11}$ with excessive Na$_2$CO$_3$

Bi$_2$Ti$_4$O$_{11}$ was formed after firing the mixture of Bi$_2$O$_3$ and TiO$_2$ powders at 900 and 1000 °C (Fig. 1). However, at 850 °C, other oxide compositions with bismuth and titanium existed as meta-phase. The temperature of 1000 °C was thus chosen to ensure the full formation of Bi$_2$Ti$_4$O$_{11}$ phase.

Phase identification of powder of Bi$_2$Ti$_4$O$_{11}$ mixed with excessive Na$_2$CO$_3$ and fired at various temperatures is shown in Fig. 2. At 700 °C and beyond, there existed some remaining Bi$_2$Ti$_4$O$_{11}$ and possibly Bi$_{12}$TiO$_{20}$. Temperatures higher than 800 °C were also tried, but the mixture was melted. Only small trace of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ was found at 700 °C. However, at the lower temperatures of 600 and 650 °C, fully formed Bi$_{0.5}$Na$_{0.5}$TiO$_3$ was obtained.

The conversion of Bi$_2$Ti$_4$O$_{11}$ to Bi$_{0.5}$Na$_{0.5}$TiO$_3$ is limited to low temperature around 600–650 °C, which at higher temperature other phases exist. This clearly indicates that, at low temperature, the conversion is controlled by low energy diffusion of Na ion into Bi$_2$Ti$_4$O$_{11}$ to form Bi$_{0.5}$Na$_{0.5}$TiO$_3$. Therefore, the excessive amount of Na$_2$CO$_3$ did not participate in the reaction. When all Bi$_2$Ti$_4$O$_{11}$ was converted to Bi$_{0.5}$Na$_{0.5}$TiO$_3$, no more influx of Na ion was allowed. At higher temperature, diffusion of other species became more active and excessive amount of Na$_2$CO$_3$ was included in the energy minimization process of the whole system, resulting in new and more stable phases.

3.2. Confirmation of nanocrystallization of Bi$_{0.5}$Na$_{0.5}$TiO$_3$

Fig. 3 shows the rectangular platelet shape of Bi$_2$Ti$_4$O$_{11}$ obtained from molten salt synthesis with NaCl–KCl salt. The platelets are 5–10 microns in length. They were identified as Bi$_2$Ti$_4$O$_{11}$ by X-ray diffraction (Fig. 4, labeled as ‘before’). The relative intensity pattern of packed Bi$_2$Ti$_4$O$_{11}$ crystals is different from that of powder due to some orientation in packed Bi$_2$Ti$_4$O$_{11}$ crystals.

X-ray diffraction pattern of Bi$_2$Ti$_4$O$_{11}$ crystals after conversion with excessive Na$_2$CO$_3$ at 600 °C is shown in Fig. 4 (labeled as ‘After’). It is clear that Bi$_2$Ti$_4$O$_{11}$ crystals were mostly converted to Bi$_{0.5}$Na$_{0.5}$TiO$_3$ after 12 hours of conversion. As the process of conversion is controlled by diffusion mechanism, large crystals require long time for the conversion to complete.

Fig. 5 shows the surface structure of the converted crystals. The surface became rough after conversion.
This might be the appearance of recrystallization of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ into many small grains on the original crystal. Strain and crystallite size plot from X-ray diffraction analysis of the crystals after conversion are shown in Fig. 6. The calculated crystallite size of converted Bi$_{0.5}$Na$_{0.5}$TiO$_3$ is just 80 ± 10 nanometers, 100 times less than the original size of Bi$_2$Ti$_4$O$_{11}$ crystals. The reduction in crystallite size has confirmed the recrystallization of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ into many small grains on the original crystal. This kind of recrystallization of a new phase while retaining the crystal shape characteristics is termed ‘pseudoform’ [11]. As the crystallite size of recrystallized Bi$_{0.5}$Na$_{0.5}$TiO$_3$ is in submicron or nanometer range, the term ‘nanocrystallization’ is an obvious term to be used.

The average strain was calculated to be 0.08% (+0.02). These strains are termed microstrains as they are the result

Fig. 2. X-ray diffraction patterns of the mixture of Bi$_2$Ti$_4$O$_{11}$ and excessive Na$_2$CO$_3$ fired at various temperatures.

Fig. 3. Bi$_2$Ti$_4$O$_{11}$ crystals obtained from molten salt synthesis with NaCl–KCl (1:1 mole).

Fig. 4. X-ray diffraction patterns of the Bi$_2$Ti$_4$O$_{11}$ crystals before and after reaction with excessive Na$_2$CO$_3$.

Fig. 5. Surface structure of reacted Bi$_2$Ti$_4$O$_{11}$ crystals with excessive Na$_2$CO$_3$. 
of distribution of both tensile and compressive, local stress [10]. The existence of microstrains indicates that stresses are induced by the structural change in the unit cell after conversion. Recrystallization into nanograins is likely to provide a mechanism to relieve stresses induced in the conversion process.

4. Conclusion

The optimal conversion of Bi$_2$Ti$_4$O$_{11}$ to Bi$_{0.5}$Na$_{0.5}$TiO$_3$ is limited to low temperature around 600–650 °C, which at higher temperature other phases exist. This clearly indicates that the conversion was controlled by low energy diffusion of Na ion into Bi$_2$Ti$_4$O$_{11}$ crystals to form Bi$_{0.5}$Na$_{0.5}$TiO$_3$.

After the conversion of the Bi$_2$Ti$_4$O$_{11}$ crystal into Bi$_{0.5}$Na$_{0.5}$TiO$_3$, the crystal surface became rough as a result of the recrystallization of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ into many small grains on the original crystal. Nanocrystallization of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ is confirmed by crystallite size reduction in nanometer range, calculated from X-ray diffraction analysis. Recrystallization into nanograins is likely to provide a mechanism to relieve stresses induced in the conversion process.

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Fig. 6. Crystallite size and strain plot from X-ray diffraction from X-ray diffraction analysis of converted Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (XS=crystallite size).