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Nanocrystallization of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ 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 $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (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 $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ with excessive Na_2CO_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. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Nanocrystallization; $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$; Pseudoform; Lead-free; Piezoelectrics; Conversion

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. $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ 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 $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ and excessive Na_2CO_3

Bi_2O_3 (Fluka, puriss) and TiO_2 (Fluka, puriss) were used as starting materials. They were mixed in the proportion to yield $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ using ball milling in plastic bottle with zirconia balls. The mixture was fired at high temperature to form $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ and ground into fine powder with pestle and mortar. The powder was mixed with excessive Na_2CO_3 (> 50% by weight) and fired at various temperature. After firing, the mixtures were washed several times with hot water to remove unreacted Na_2CO_3 . Washed mixtures were subjected to analysis with X-ray diffraction (JEOL JDX-3530) for phase identification.

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2.2. Preparation of single crystals of $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ and conversion with Na_2CO_3

$\text{Bi}_2\text{Ti}_4\text{O}_{11}$ 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_2O_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_2CO_3 (> 50% by weight) and fired at selected temperature. After firing, the crystals were washed several times with hot water to remove unreacted Na_2CO_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 $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ with excessive Na_2CO_3

$\text{Bi}_2\text{Ti}_4\text{O}_{11}$ was formed after firing the mixture of Bi_2O_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 $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ phase.

Phase identification of powder of $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ mixed with excessive Na_2CO_3 and fired at various temperatures is shown in Fig. 2. At 700 °C and beyond, there existed some

remaining $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ and possibly $\text{Bi}_{12}\text{Ti}_{20}\text{O}_{20}$. Temperatures higher than 800 °C were also tried, but the mixture was melted. Only small trace of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ was found at 700 °C. However, at the lower temperatures of 600 and 650 °C, fully formed $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ was obtained.

The conversion of $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ to $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ 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 $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ to form $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$. Therefore, the excessive amount of Na_2CO_3 did not participate in the reaction. When all $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ was converted to $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$, no more influx of Na ion was allowed. At higher temperature, diffusion of other species became more active and excessive amount of Na_2CO_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 $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$

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

X-ray diffraction pattern of $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ crystals after conversion with excessive Na_2CO_3 at 600 °C is shown in Fig. 4 (labeled as ‘After’). It is clear that $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ crystals were mostly converted to $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ 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.

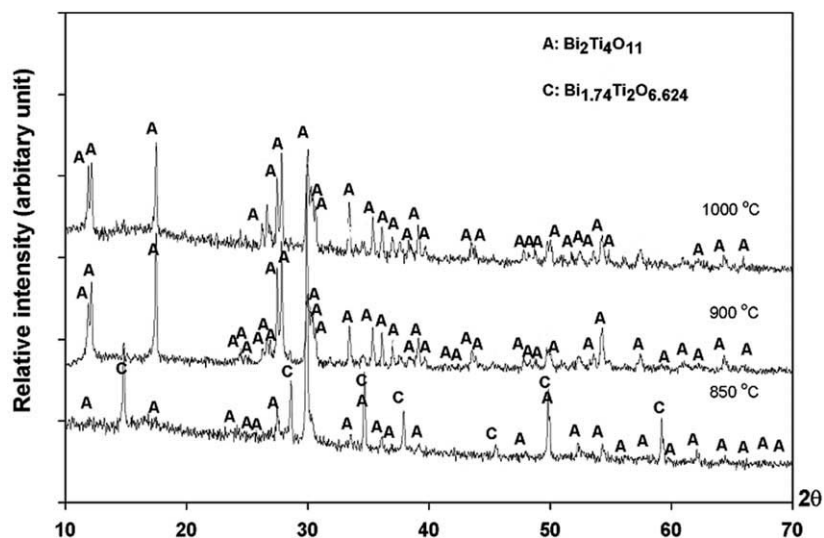


Fig. 1. X-ray diffraction patterns of the mixture for $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ fired at various temperatures.

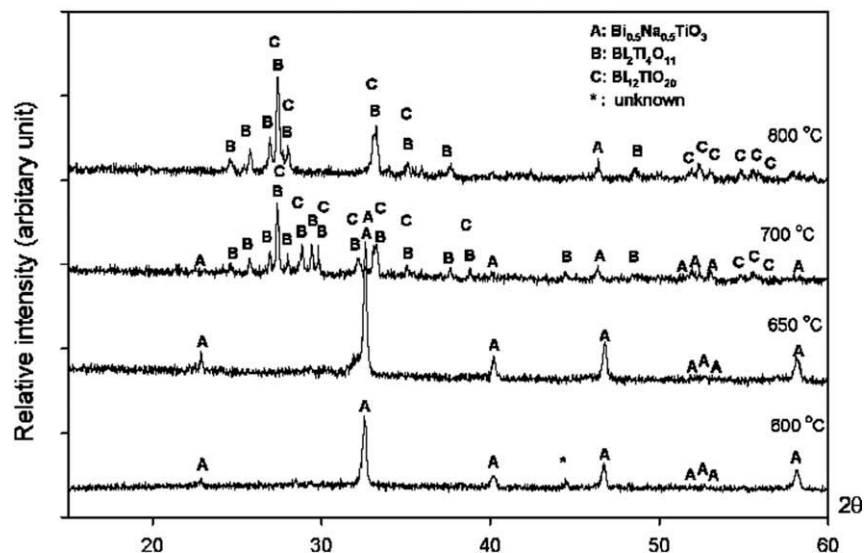


Fig. 2. X-ray diffraction patterns of the mixture of $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ and excessive Na_2CO_3 fired at various temperatures.

This might be the appearance of recrystallization of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ 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 $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ is just 80 ± 10 nanometers, 100 times less than the original size of $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ crystals. The reduction in crystallite size has confirmed the recrystallization of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ 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 $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ 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

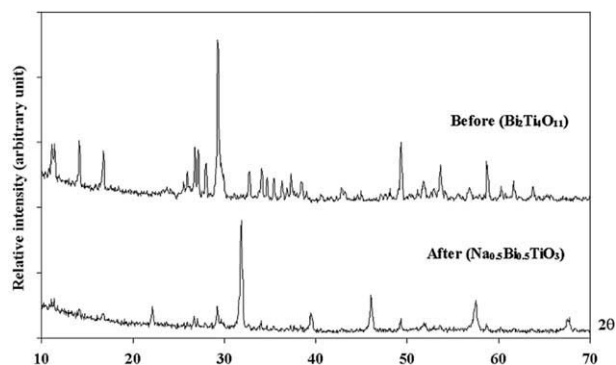


Fig. 4. X-ray diffraction patterns of the $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ crystals before and after reaction with excessive Na_2CO_3 .

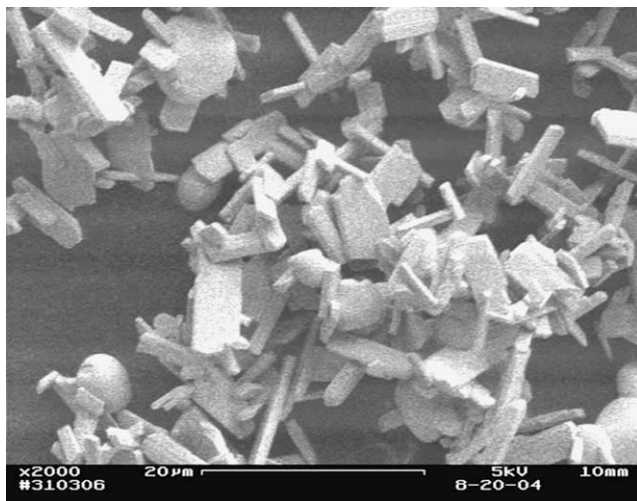


Fig. 3. $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ crystals obtained from molten salt synthesis with NaCl – KCl (1:1 mole).



Fig. 5. Surface structure of reacted $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ crystals with excessive Na_2CO_3 .

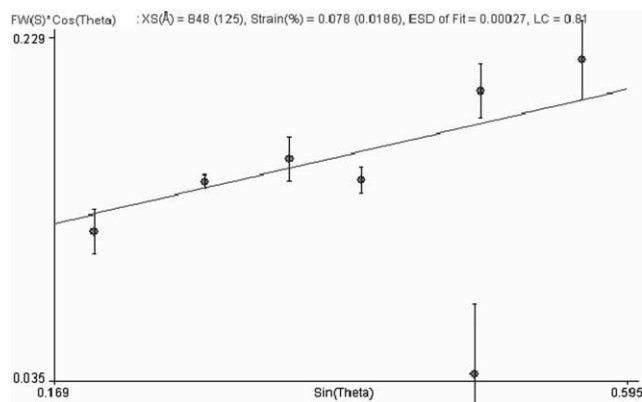


Fig. 6. Crystallite size and strain plot from X-ray diffraction from X-ray diffraction analysis of converted $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (XS=crystallite size).

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 $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ to $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ 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 $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ crystals to form $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$.

After the conversion of the $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ crystal into $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$, the crystal surface became rough as a result of the recrystallization of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ into many small grains on the original crystal. Nanocrystallization of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ 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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