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Presynthesis of raw materials used for the growth of $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ single crystals by a modified Bridgman method

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Abstract

Single crystals of $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ (PZNT91/9) were grown by a modified flux Bridgman method with an allomeric seed crystal. To reduce the formation of pyrochlore phase during crystal growth, we use B-site precursor synthesis method to presynthesize the raw materials. X-ray powder diffraction results of the pre-and-post-calcined powders and of the obtained PZNT91/9 crystals show that B-site precursor synthesis method can effectively prevent the formation of pyrochlore phase and the as-grown crystals are of pure perovskite structure. We measured the electrical properties of the obtained PZNT91/9 crystals and compared with those grown by other techniques. The results show that the electrical properties are as well as or better than the Vertical Bridgman method PZNT91/9 single crystals and the Conventional Flux method. The above discussions demonstrate that homogeneous raw powder morphology and fine distribution of particle size can greatly improve the quality of the obtained crystals.

Keywords: B-site precursor synthesis method; Particle size distribution; PZNT single crystal; Bridgman technique; Electric property; Dielectric constant; Single crystal; Large piezoelectric constant

1. Introduction

Piezoelectric single crystals of $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ [hereafter abbreviated as $(1-x)$PZN–xPT] have attracted much attention in recent years because single crystals exhibit an extremely large piezoelectric constant and a very high electromechanical coupling factor with the composition near morphotropic phase boundary (MPB) [1–4]. Such excellent performance makes the relaxor-based piezocrystals the next generation electromechanical materials in a broad range of advanced applications, such as high-resolution ultrasonic medical diagnostic equipment and undersea applications [2,5]. Compared with the conventional $Pb(Zr,Ti)O_3$(PZT) ceramics, PZNT are better because $(1-x)$PZN–xPT single crystals are relatively easily grown by a flux method over the whole composition range [6]. In addition, the PZNT crystals exhibit a low acoustic impedance that makes them ideal materials for array-type medical transducers with an improved resolution and a large bandwidth [5,7]. The MPB for the $(1-x)$PZN–xPT system is located at 8–10.5 mol% of $PbTiO_3$ content, which separated a rhombohedral phase from a tetragonal one, and the outstanding properties of the relaxor-based piezocrystals are related to the composition of the MPB and the

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related effects and the formation of engineered macrodomain states [8].

Recently, much work has been undertaken on the growth and characterization of the morphotropic PZNT single crystals by the flux method [2–4,6]. However, the flux method is unsuitable to grow large enough PZNT crystals for mass production because of its poor reproducibility and high volatilization of PbO at high temperature. Furthermore, the control of spontaneous nucleation has been one of the main issues. The growth results that have been reported so far contain inclusions of the PbO flux, a pyrochlore and other phases. Orita et al. have expanded the columbite method used for the synthesis of pure perovskite solid solutions [9]. In this letter, we used the B-site precursor synthesis method to presynthesize the raw materials used for the growth of PZNT single crystals in order to reduce the formation of pyrochlore phase. Also, we compared the electrical properties of the as-grown crystals by this method with those of PZNT crystals grown by other techniques with different pretreated methods of raw materials.

2. Experimental procedure

High purity starting agents (more than 99.9%) of PbO, ZnO, Nb_2O_5 and TiO_2 were dried before weighing. The mixture of those powders was justified in the ratios of PZN:PT = 91:9 and PZN–PT:PbO = 45:55 in molar percentage. PbO acted as flux. Single crystals of $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ (PZNT91/9) were grown by a modified Bridgman method with an allomeric $Pb[(Mg_{1/3}Nb_{2/3})_{0.67}Ti_{0.33}]O_3$ seed crystal. To prevent the formation of pyrochlore phase during crystal growth, the raw materials were presynthesized by B-site precursor synthesis method. Raw powders of ZnO, Nb_2O_5 and TiO_2 were precalcined at 950 °C for 1.5 h after those powders had been mixed and mortared in a "V"-type mixture equipment for 4–8 h. The resulting mixture was ground in a Al_2O_3 mortar and pestle. With the addition of stoichiometric PbO and mixed in the same equipment, the resultant mixture was postcalcined at 750 °C for 1.5 h. The resultant was mixed and mortared with the addition of PbO flux in a ball-milling equipment with ZrO_2 balls and pure water for 24 h. After parching and milling, the resulting mixture was pressed to prepare pellets 28 mm in diameter and 60 mm in length by the isostatic-pressing method. PZNT single crystals were fabricated in sealed platinum crucibles to control the uniformity of composition and to prevent the evaporation of PbO during crystal growth. The growth procedure was delineated in detail elsewhere.

The phase structure of the precalcined powders and the postcalcined ones was investigated by X-ray

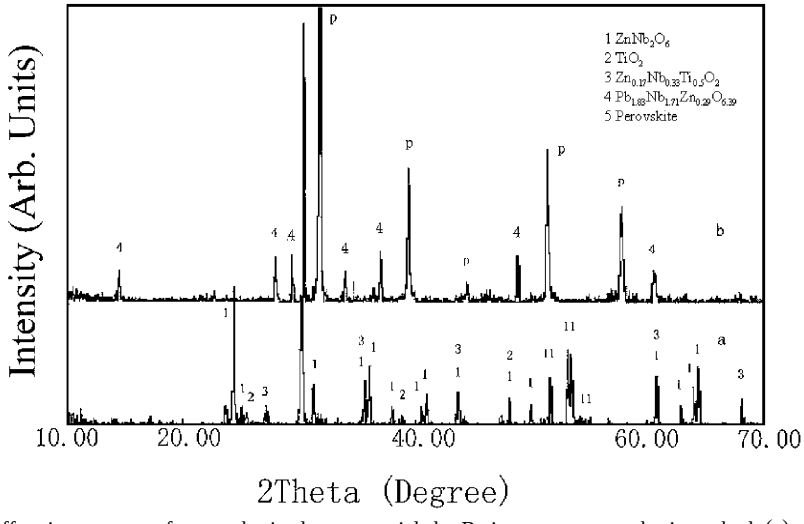

Fig. 1. X-ray powder diffraction patterns of presynthesized raw materials by B-site precursor synthesis method: (a) powders of ZnO, Nb_2O_5 and TiO_2 precalcined at 950 °C; (b) resulting powders of (a) with the addition of stoichiometric PbO postcalcined at 750 °C.

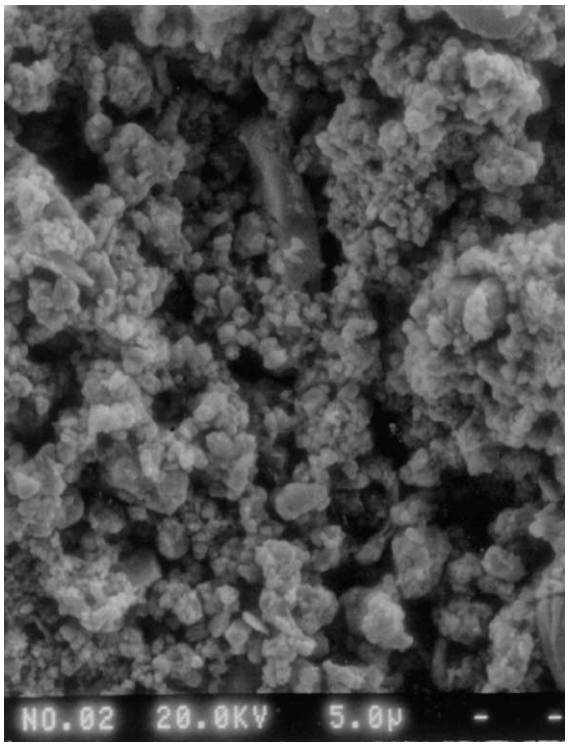

Fig. 2. The morphology of the raw materials presynthesized by B-site precursor synthesis method (SEM 2000×).

powder diffraction (Rigaku D/MAX-3C X-ray diffractometer). In order to improve the homogeneity of the as-grown single crystals, ensuring the uniformity of the presynthesized raw materials used for the crystal growth was very important. The morphology of the postcalcined powders was examined by Scanning Electron Microscope (SEM, EPMA-8705 QHz) and the particle size distribution of the presynthesis powders was analyzed by Mastersizer 2000 (Malvern Instruments, Malvern, UK). After removal of the PbO flux by boiling acetic acid, the phase structure of the obtained PZNT crystals was also measured by XRD measurement. The crystal direction was determined by Laue X-ray diffraction method combing with XRD pattern. The electrical properties of the PZNT single crystals were studied in detail, and we compared the results with PZNT crystals grown by other techniques with different pretreated methods of raw materials.

3. Results and discussion

Fig. 1 is the X-ray diffraction patterns of the precalcined powders and postcalcined powders by B-site precursor synthesis method. From what we can see after precalcination at 950 °C of the mixed ZnO, Nb_2O_5 and TiO_2 powders, the main phase is $ZnNb_2O_6$ with columbite structure. There are also little $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ with rutile structure and trace TiO_2 with anatase structure. The relative content of these compounds could be calculated by the half width of the main diffraction peak with each phase. The structures of the above substances are based on oxygen octahedron, which is similar in structure with the perovskite phase and is sure able to effectively reduce the formation of pyrochlore phase during crystal growth. The XRD pattern of the

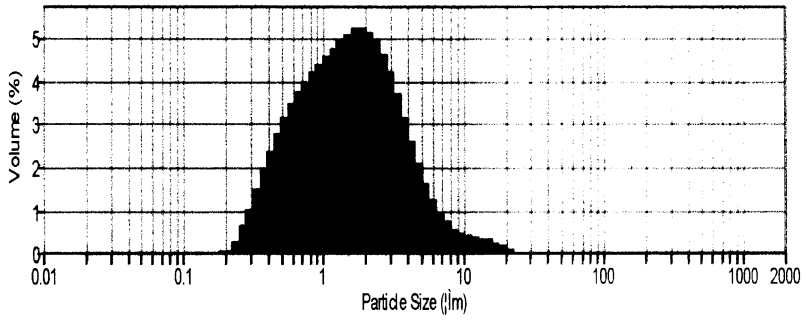

Fig. 3. The particle size distribution of the raw materials used for the growth of PZNT91/9 single crystals presynthesized by B-site precursor synthesis method.

Table 1
Summary of the pretreated method of raw materials and electrical properties of the crystals grown by different methods

	Vertical Bridgman method [3]	Conventional flux method [2]	Modified Bridgman method (this work)
Pretreated method of raw materials	calcined at 800 °C for 2 h, sintered at 1000 °C for 4 h	pre-melt at 1100 °C for 2 h	B-site precursor synthesis method
Morphology of as-grown crystals	irregular shape	arrow-head shape	cylindrical shape with three appearing faces
Dielectric constant (unpoled)	3500–11,800	–	2500–5000
Dielectric constant (poled)	2100–3700	3000	2000–3000
Dissipation factor ($tg\delta$%)	1.5	2.8	1.3–3.5
Curie temperature (°C)	175–185	~ 175	172–186
Electromechanical coupling factor (k_t%)	35–57	54	55–64

postcalcined mixed powders confirmed our hypotheses. Fig. 1(b) shows that after postcalcining, the main structure is already perovskite $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$. There is still some pyrochlore phase, which is $Pb_{1.83}Nb_{1.71}Zn_{0.29}O_{6.39}$, not $Pb_3Nb_4O_{13}$ as reported by some authors, but the content is small. There may also be a trace content of unreacted TiO_2, but we are not certain because of the sensitivity limitation of the conventional X-ray diffraction. Although the presynthesized raw materials would wholly melt before crystal growth, the powder morphology and the particle size distribution will greatly affect the composition homogeneity of the obtained crystals, which means fine uniform presynthesized raw powders would improve the homogeneity of crystal properties. The powder morphology and the particle size distribution of the presynthesized raw materials by B-site precursor synthesis method are shown in Figs. 2 and 3, respectively. We can see that the powder morphology is homogenous and the average grain size of the presynthesized powder is 1.508 μm, which are great advantageous factors for the growth of high quality PZNT91/9 single crystals.

The typical size of the $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ single crystals grown by the modified flux Bridgman technique is 28 mm in diameter and 25 mm in length. After removal of PbO flux, the obtained crystals show dark yellow color. The as-grown crystals have three appearing faces, which deviates a slight angle from the pseudo-cubic (001) direction. The phase structure of the obtained PZNT91/9 crystals was analyzed by XRD measurement. XRD pattern shows that the as-grown crystals are of pure perovskite structure and there is no pyrochlore phase within the sensitivity of the X-ray powder diffraction, which means $Pb(Zn_{1/3}Nb_{2/3})O_3$ and $PbTiO_3$ have formed a perfect perovskite structure solid solution. XRD patterns of the samples cut from different parts of the same boule also show that due to the composition segregation, the phase structure transforms from the rhombohedral phase into the tetragonal phase along the growth direction during the crystal growth. We discussed this phenomenon and advanced reasonable explanation in detail elsewhere.

Based on the results discussed above, the mechanism of formation of perovskite PZNT91/9 from PbO flux environment can be delineated as follows:

Presynthesized stage:

$$\begin{aligned} &0.303ZnO + 0.303Nb_2O_5 + 0.09TiO_2 \\ &\quad \rightarrow 0.303(1-x)ZnNb_2O_6 \\ &\qquad + 1.811\,xZn_{0.17}Nb_{0.33}Ti_{0.5}O_2 \\ &\qquad + (0.09 - 0.906\,x)TiO_2(\text{trace}) \end{aligned} \tag{1}$$

$$\begin{aligned} &0.303(1-x)ZnNb_2O_6 \\ &\qquad + 1.811\,xZn_{0.17}Nb_{0.33}Ti_{0.5}O_2 \\ &\qquad + (0.09 - 0.906\,x)TiO_2(\text{trace}) \\ &\quad \rightarrow (1 - 1.83y)Pb\left[\left(Zn_{1/3}Nb_{2/3}\right)_{0.91}Ti_{0.09}\right]O_3 \\ &\qquad + yPb_{1.83}Nb_{1.71}Zn_{0.29}O_{6.39} + 0.265\,yZnO \\ &\qquad - 0.2999\,yNb_2O_5 + 0.165\,yTiO_2 \end{aligned} \tag{2}$$

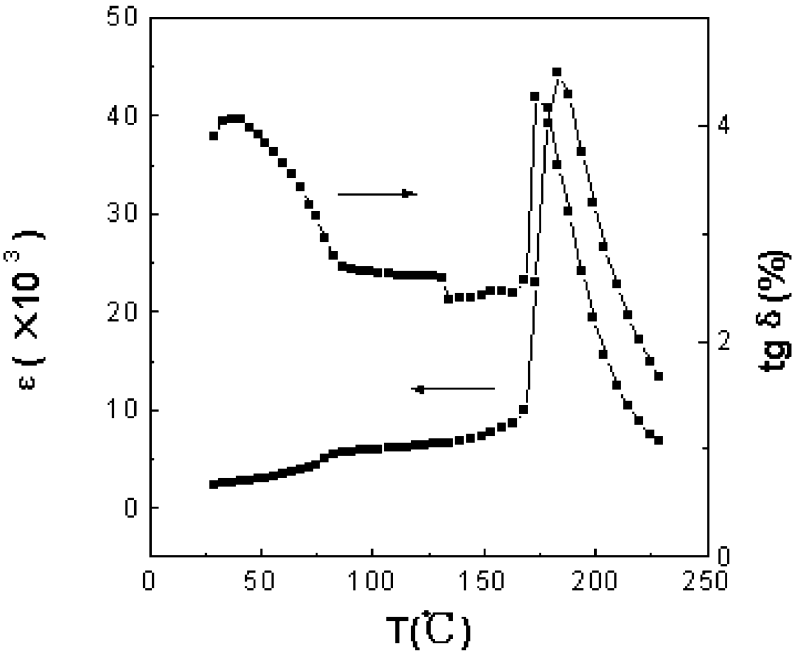

Fig. 4. Temperature dependence of dielectric constant and dissipation factor at 1 kHz measurement frequency during heating process of a (001) PZNT91/9 plane crystal.

Crystal growth stage:

$$(1-1.83y)\mathrm{Pb}\left[\left(\mathrm{Zn}_{1/3}\mathrm{Nb}_{2/3}\right)_{0.91}\mathrm{Ti}_{0.09}\right]\mathrm{O}_3 + y\mathrm{Pb}_{1.83}\mathrm{Nb}_{1.71}\mathrm{Zn}_{0.29}\mathrm{O}_{6.39} + 0.265y\mathrm{ZnO} - 0.2999y\mathrm{Nb}_2\mathrm{O}_5 + 00.165y\mathrm{TiO}_2 \xrightarrow{\text{PbO flux environment}} 1.0\mathrm{Pb}\left[\left(\mathrm{Zn}_{1/3}\mathrm{Nb}_{2/3}\right)_{0.91}\mathrm{Ti}_{0.09}\right]\times\mathrm{O}_3(\text{perovskite}) \quad (3)$$

These reaction schemes justify all the necessary requirements of mass balance and explain the results of XRD patterns.

The electrical properties of the obtained PZNT91/9 single crystals were measured systematically. We compared the results with those of PZNT91/9 single crystals grown by other techniques with different pretreated methods of raw materials. The results indicate that the electrical properties are as well as or better than the Vertical Bridgman method PZNT91/9 single crystals and the Conventional Flux method (Table 1).

Fig. 4 shows the temperature dependence of the dielectric constant ($\varepsilon_{33}/\varepsilon_0$) and dielectric loss at 1 kHz measurement frequency during heating process of a (001) PZNT91/9 plane crystal. Two anomalies are observed at 85 and 183 °C, corresponding to the phase transition from rhombohedral ferroelectric phase to tetragonal ferroelectric phase and to cubic paraelectric phase with increasing temperature. Further studies of large PZNT crystals with high homogeneous quality are progressing. We will report the results in the near future.

4. Conclusions

1. Single crystals of $\mathrm{Pb}[(\mathrm{Zn}_{1/3}\mathrm{Nb}_{2/3})_{0.91}\mathrm{Ti}_{0.09}]\mathrm{O}_3$(PZNT91/9) 28 mm in diameter and 25 mm in length were grown by a modified flux Bridgman method with an allomeric seed crystal using B-site precursor synthesis method.
2. B-site precursor synthesis method can effectively reduce the formation of pyrochlore phase during crystal growth and the obtained crystals by this method were pure perovskite structure.

3. The electrical properties of the as-grown PZNT91/9 crystals are as well as or better than the Vertical Bridgman method PZNT91/9 single crystals and the Conventional Flux method.
4. Homogeneous presynthesized raw powder morphology and fine distribution of particle size would have great effects in improving the uniform quality of PZNT91/9 single crystals.

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