Japanese Journal of Applied Physics

Growth of $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ Single Crystals Directly from Melt

Jpn. J. Appl. Phys. Vol. 40 (2001) pp. L 1377–L 1379
Part 2, No. 12B, 15 December 2001

Growth of $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ Single Crystals Directly from Melt

Bijun FANG, Haosu LUO*, Haiqing XU, Tianhou HE and Zhiwen YIN

The State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 215 Chengbei Rd., Jiading, Shanghai 201800, China

(Received October 15, 2001; accepted for publication October 24, 2001)

Piezoelectric $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ (PZNT 91/9) single crystals were grown directly from melt by a modified Bridgman method. X-ray diffraction confirms that the crystals are of pure perovskite structure. The obtained crystals have piezoelectric constant d_{33} in the range of 1800–2000 pC/N, which is comparable to that of the PZNT crystals grown from flux. However, compared with the flux-grown PZNT 91/9 crystals, there is a broad diffused peak on the curve of temperature dependence of the dielectric constant, and a lower dielectric peak at 105°C. Domain observation shows that both the rhombohedral and tetragonal orientation states coexist in the morphotrpic PZNT 91/9 crystals.

KEYWORDS: Bridgman method, lead zinc niobate, lead titanate, dielectric constant, frequency dispersion, domain

The relaxor ferroelectric $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) is characterized by a diffuse maximum of the dielectric constant associated with a strong frequency dispersion. On the other hand, $PbTiO_3$ (PT) shows a typical long-range ferroelectric property with a ferroelectric (FE)-paraelectric (PE) phase transition at $T_C = 490$°C. The solid solution of $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PZNT) is expected to combine the advantages of both relaxor FE PZN and FE PT. Indeed, single crystals of PZNT have been reported to exhibit a very high electromechanical coefficient ($k_{33} > 90\%$) and piezoelectric coefficient ($d_{33} > 2000$ pC/N).[1] Such excellent performance has triggered much research on this material, and also makes PZNT a much better candidate for transducer materials than the $PbZrO_3$–$PbTiO_3$ (PZT) solid-solution system for a broad range of advanced applications.[2,3] Compared with the growth of PZT single crystals, PZNT single crystals are relatively easily grown from PbO flux over a wide composition range. Recently, intensive work has been undertaken on the growth and characterization of PZNT single crystals by the conventional flux method and the flux Bridgman method.[4,5] However, it is difficult to grow large PZNT crystals using the flux method due to its poor reproducibility and spontaneous nucleation during crystal growth. In this letter, we will report a novel method for the growth of $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ (PZNT 91/9) crystals directly from melt without flux by a Bridgman technique.

Single crystals of PZNT 91/9 were grown by a modified Bridgman method with an allomeric $Pb[(Mg_{1/3}Nb_{2/3})_{0.69}$-$Ti_{0.31}]O_3$ (PMNT 69/31) seed crystal without any flux. The size of the PMNT 69/31 seed crystal is 15 mm in diameter and 35 mm in length. The seed crystal was orientated along the $\langle 111\rangle_{cub}$ direction. To prevent the formation of the pyrochlore phase during crystal growth, the raw materials were precalcined by the B-site precursor synthesis method.[6] High-purity PbO, ZnO, Nb_2O_5 and TiO_2 powders were mixed in a mortar according to the ratio of PZN : PT = 91 : 9. The highest temperature of the Bridgman furnace is more than 1380°C. The temperature gradient is about 30–50°C/cm at the solid-liquid interface. To control the decomposition of PZNT crystals during crystal growth, the growth rate was relatively fast, about 0.5–1.0 mm/h. The procedure was similar to that for growing the $Pb[(Mg_{1/3}Nb_{2/3})_{0.67}Ti_{0.33}]O_3$ (PMNT 67/33) single crystals directly from melt.[7]

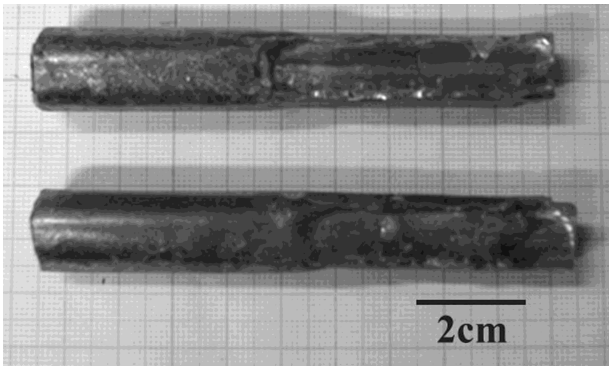

Fig. 1. As-grown $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ crystal boules grown directly from melt by a modified Bridgman method without flux.

Single crystals of PZNT 91/9 were obtained with the size about 15 mm in diameter and 50 mm in length (Fig. 1). The growth interface angle deviates slightly from the pseudocubic $(111)_{cub}$ face. The as-grown crystals exhibit a light brown color on their surface due to a thin coat of the PbO or pyrochlore phase resulting from segregation during crystal growth. This is similar to that in the growth of PMNT 67/33 single crystals directly from melt by the Bridgman method.[7] Due to segregation, there is a small amount of the pyrochlore phase on their surface. The impurity of red color on the surface of the crystals is composed of a large amount of lead and zinc elements, which was determined using an electron probe microanalyzer (EPMA-8705). The lattice structure of the PZNT 91/9 crystals was investigated by X-ray diffraction (XRD) at different regions (Fig. 2), where the length of the crystal boule was 45 mm. The index numbers of the X-ray diffraction peaks are indexed referring to the results of powder X-ray diffraction for PZN and PT. There are no apparent differences in XRD patterns from the top to bottom parts, except for the relative intensity of some diffraction peaks. The shifting and widening of some diffraction peaks were observed, which indicates structural imperfection of the PZNT crystals. We can also observe slight splitting of the (200) diffraction peak, which indicates the coexistence of rhombohedral and tetragonal phases. Lattice constant $a_r = 4.054$ Å and distortion angle $\alpha = 89.90°$ have been reported for the rhombohedral PZNT 92/8 single crystal,[8] whereas the powder diffraction data show the average lattice constants $a_t = 4.036$ Å and $c_t = 4.146$ Å, which deviates slightly from those of the pseu-

*Corresponding author. E-mail address: hsluo@public3.sta.net.cn

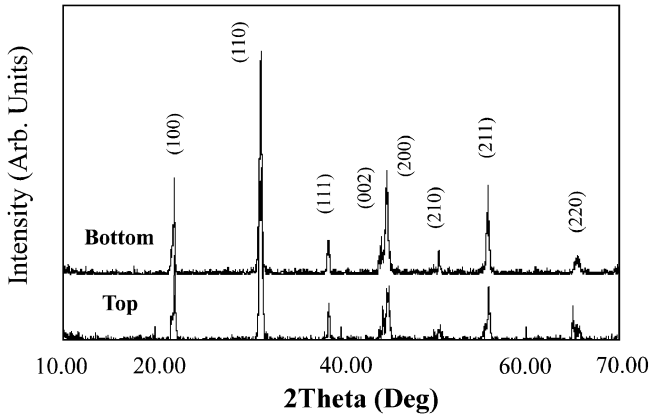

Fig. 2. X-ray diffraction patterns of initial part and ending part of $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ crystal.

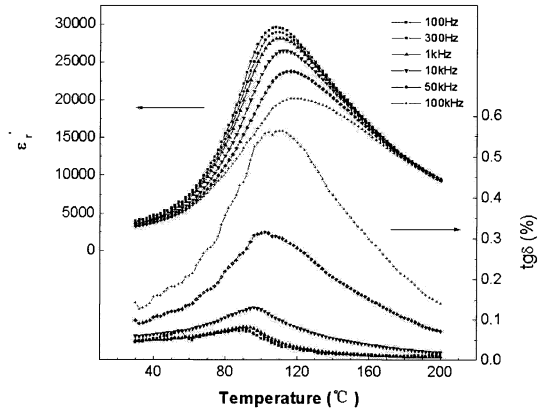

Fig. 3. Temperature dependence of real part of dielectric constant and dissipation factor of unpoled (001) PZNT 91/9 plane crystal at different frequencies upon heating.

docubic structure.

Figure 3 shows the temperature dependence of the dielectric constant and dissipation factor of an unpoled PZNT 91/9 (001) plane crystal at different frequencies upon heating (HP4192A). The measured plane crystal was $12 \times 12\,mm^2$. Silver electrode paste was formed on the specimen and then fired in the air at 550°C for 1 h. Compared with PZNT crystals grown by the flux Bridgman method, the relationship between the dielectric constant and temperature is abnormal. The former has two obvious anomalies at about 75°C and 180°C, corresponding to phase transitions from the rhombohedral FE phase to the tetragonal FE phase and the cubic PE phase with increasing temperature. However, for the PZNT 91/9 crystals grown directly from melt, there is only one anomaly at a rather low temperature, about 105°C, where frequency dispersion is apparent. The temperature where the maximum dielectric constant appears increases with frequency; at the same time, the value of the dielectric maximum decreases with frequency in the dielectric response. The peaks of dielectric response are much broader, and the full-widths at half-maximum (FWHM) of the dielectric peaks are round 70°C. The detailed of the reason for this phenomenon are not yet clear. We propose that there may be a small amount pyrochlore mixed in the perovskite phase, although it was not detected by XRD due to the sensitivity limitation of X-ray diffraction. The existence of a pyrochlore

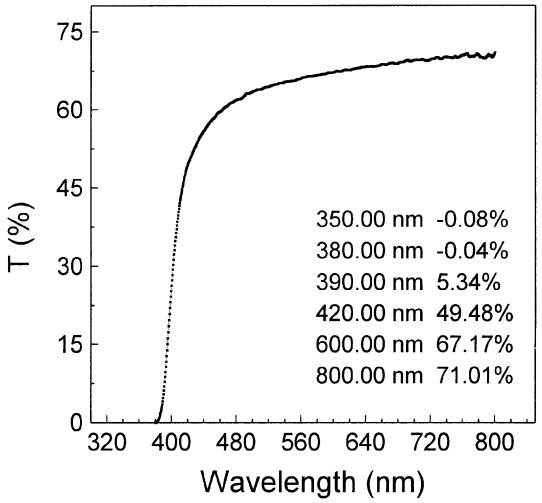

Fig. 4. Transmittance spectra of an unpoled (001) PZNT plane crystal (360 μm).

phase may influence the dielectric performance of the PZNT crystals. Furthermore, the lattice structure may not be perfect. Figure 4 shows transmittance spectrum of the unpoled (001) PZNT plane crystal (360 μm in thickness) recorded on a Shimadzu UV-2501PC spectrophotometer. It shows the crystal has rather high transparency, and the cut-off edge appears at about 390 nm. Piezoelectric performances were measured, and the results show that the piezoelectric coefficient d_{33} is about 1800–2000 pC/N within a wafer, which is comparable to that of PZNT 91/9 crystals grown from flux.

Observed under a polarizing light microscope, PZNT 91/9 plates of (001) cut from the top of a crystal boule exhibit no obvious extinction regions, but there are alternately arranged domain stripes. However, the plates cut from the bottom exhibit obvious extinction, but where no macrodomains are observed. From the viewpoint of crystal symmetry and the laws of extinction, the results indicate that rhombohedrally and tetragonally orientated domains coexist in the PZNT 91/9 crystals. Such domain configurations have also been observed in the PZNT 91/9 crystals grown from flux.[9)]

In conclusion, $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ single crystals with piezoelectric constant d_{33} of about 1800–2000 pC/N were grown directly from melt. Because of the little structure difference between PMNT and PZNT crystal, the PMNT seed crystals can effectively prevent spontaneous nucleation. The faster growth rate can effectively control the decomposition during PZNT crystal growth, which leads to the formation of pyrochlore and segregation of PbO. The allomeric PMNT seed crystals and faster growth rate are advantages for the PZNT crystals grown directly from melt, however, the quality of the PZNT crystals must be further improved.

The authors would like to thank the National Sciences Foundation of China (Grant Nos. 59995520 and 59872048) and the Shanghai Municipal Government (Grant No. 99XD14024) for financial support.

1) J. Kuwata, K. Uchino and S. Nomura: Jpn. J. Appl. Phys. **21** (1982) 1298.
2) S. Saitoh, T. Kobayashi, K. Harada, S. Shimanuki and Y. Yamashita: Jpn. J. Appl. Phys. **37** (1998) 3053.
3) S. Saitoh, T. Kobayashi, K. Harada, S. Shimanuki and Y. Yamashita: IEEE Trans. Ultrason. Ferroelectr. Freq. Control **45** (1998) 1071.

4) K. Harada, S. Shimanuki, T. Kobayashi, S. Saitoh and Y. Yamashita: J. Am. Ceram. Soc. **81** (1998) 2785.
5) S. Shimanuki, S. Saitoh and Y. Yamashita: Jpn. J. Appl. Phys. **37** (1998) 3382.
6) M. Orita, H. Satoh and K. Aizawa: Jpn. J. Appl. Phys. **31** (1992) 3261.
7) H.-S. Luo, G.-S. Xu, H.-Q. Xu, P.-C. Wang and Z.-W. Yin: Jpn. J. Appl. Phys. **39** (2000) 5581.
8) B. Noheda, D. E. Cox, G. Shirane, S.-E. Park, L. E. Cross and Z. Zhong: Phys. Rev. Lett. **86** (2001) 3891.
9) Z.-G. Ye, M. Dong and L. Zhang: Ferroelectrics **229** (1999) 223.