

On the Feasibility of Growing $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.91}\text{Ti}_{0.09}]\text{O}_3$ Single Crystals**

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$\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.91}\text{Ti}_{0.09}]\text{O}_3$ (PZNT91/9) single crystals were grown by two methods: from solution using PbO as a self-fluxing agent (SC method) and directly from the melt without fluxing (MC method). In both growth methods, an allomeric $\text{Pb}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.69}\text{Ti}_{0.31}]\text{O}_3$ (PMNT69/31) single crystal was used as a seed. X-ray diffraction patterns of ground crystals showed that phase-pure perovskite PZNT91/9 single crystals were successfully fabricated by the above two methods. The composition of the crystals obtained by both the SC and MC methods was analyzed using X-ray fluorescence, which confirmed that the crystal composition is close to the nominal value, although volatilization of PbO and segregation during crystal growth are inevitable. The MC PZNT91/9 crystals exhibit excellent piezoelectric properties, with the piezoelectric constant, d_{33} , in the range of 1800–2200 pC N^{-1} . This value is comparable to that of the SC crystals. However, the MC crystals show an abnormal dielectric behavior. In contrast with the SC crystals, in the MC crystals a much broader dielectric peak appears in the dielectric response curves, accompanied by a much lower peak temperature of around 105 °C. Furthermore, frequency dispersion is apparent over a much wider temperature range (even more apparent than in pure relaxors), where a large, i.e., about 70 °C, full width at half maximum (FWHM) for the dielectric peaks is observed in the dielectric response. It is speculated that such an unusual phenomenon correlates with defects, microinhomogeneities, and polar regions in the as-grown MC crystals. The origins of this abnormality have not been interpreted in detail until now. However, optical observation of the domain structure confirms that both the SC and MC crystals possess complex structural states.

1. Introduction

Lead-based complex perovskite oxide $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PZNT) has attracted much attention due to, for instance, its excellent electrical properties in single-crystalline form, which makes it a promising candidate for high-performance ultrasonic transducers and related applications.^[1–3] Indeed, PZNT single crystals with a composition near the morphotropic phase boundary (MPB) were reported to exhibit very high electromechanical ($k_{33} > 90\%$) and piezoelectric ($d_{33} > 2000 \text{ pC N}^{-1}$) coefficients.^[4,5] PZNT is a relaxor-based complex oxide. When the PbTiO_3 (PT) content is less than the MPB content, a broad maximum appears in the temperature dependence of its dielectric properties, accompanied by an apparent frequency dispersion, i.e., a diffused phase transition is observable. The reason for this diffused phase transition is believed to be a distribution of Curie points in the material, resulting from compositional fluctuations, or microinhomogeneity (disorder) in the B-site cations of the perovskite structure.^[6]

The composition and the degree of ordering in the ion lattice of the complex perovskite structure greatly influence the physical properties of the oxides obtained, a fact which has also attracted intensive research in this area.^[7,8]

Compared with the conventional $\text{PbZrO}_3\text{--PbTiO}_3$ (PZT) system, PZNT single crystals are relatively easy to grow using a fluxing method over the whole composition range, which also makes PZNT a much better candidate for transducer materials than PZT for many advanced applications.^[5,9] Recently, intensive work has been undertaken on the growth and characterization of PZNT single crystals by the conventional fluxing method and by the solution Bridgman method.^[2,10] However, it is not easy to fabricate high-quality single crystals in a pure phase, partly a result of the high volatility of lead oxide and to severe segregation during crystal growth from flux. Furthermore, the fluxing method is usually unsuitable for growing large crystals because of its poor reproducibility and the occurrence of spontaneous nucleation. Heretofore, the results were barely reproducible, and the as-grown crystals were liable to contain inclusions of PbO flux and a pyrochlore phase. Harada et al., who reportedly used the solution Bridgman method, did not employ seed crystals during crystal growth; therefore their method is classed as another modification of the fluxing method.^[2] They could not effectively control the dimensions of the crystals obtained, and the crystals had an irregular shape and normal dielectric properties. By comparison, the Bridgman method has been used widely in crystal growth; by introducing a seed crystal, excellent reproducibility and large productivity have been obtained.

In order to grow large, high-quality PZNT crystals, we investigated the feasibility of growing PZNT single crystals by different

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methods. Due to the strong likelihood of the obtained perovskite phase decomposing, and to a longer growth time as compared with fabricating ceramics, it is more difficult to grow PZNT single crystals in a pure perovskite phase. According to some reports, when considering the structural stability and synthetic feasibility of different lead-based oxides, $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{-O}_3$ (PZN) complex oxide was the most difficult to synthesize in the perovskite structure.^[6,11] Although the addition of stabilized perovskite oxides with a higher electronegativity difference and a tolerance factor close to unity, such as BaTiO_3 , could stabilize perovskite PZN, we found that 9 mol-% PT was far too little to stabilize perovskite PZN;^[6] 30 mol-% was required. In other words, relaxor-based PZNT91/9 complex oxide was far more difficult to prepare in pure perovskite phase especially in the single-crystalline form. Based on the progress in PZNT crystal growth, we introduced an allomeric $\text{Pb}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.69}\text{Ti}_{0.31}]\text{O}_3$ (PMNT69/31) seed crystal during the crystal growth process. We adapted the solution Bridgman method by using conventional Bridgman equipment and PbO as a self-fluxing agent. Furthermore, we tried a novel method, where PZNT single crystals were grown directly from the melt. Although with both methods we successfully grew PZNT single crystals with a pure perovskite phase, there were astonishing differences in the electrical properties of the obtained crystals. In this paper, we report two methods for the growth of $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.91}\text{Ti}_{0.09}]\text{O}_3$ (PZNT91/9) single crystals: crystal growth from solution using PbO as a self-fluxing agent and crystal growth directly from melt without fluxing. Both above Bridgman methods used a PMNT69/31 crystal as a seed. We also compare the chemical and physical properties of the obtained PZNT91/9 crystals grown by these two methods.

2. Results and Discussion

Phase-pure perovskite PZNT91/9 single crystals were fabricated successfully by the above two methods. PZNT91/9 crystals grown from solution (SC crystals) have a dark-brown surface because of a thin coating of PbO flux. After flux removal by boiling in acetic acid, the crystal shows three faces, which deviate slightly in angle from the pseudocubic (001)_{cub} face, as determined by Laue X-ray diffraction measurements.^[12] By comparison, PZNT91/9 crystals grown directly from melt (MC crystals) are a light-brown color due to a thin coating of PbO or pyrochlore phase formed during crystal growth. (MC crystals are 15 mm in diameter and 55 mm in length.^[13]) They are similar to $\text{Pb}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.67}\text{Ti}_{0.33}]\text{O}_3$ (PMNT67/33) single crystals grown directly from the melt by a modified Bridgman method.^[14] Due to segregation and the high stability of the pyrochlore phase, both the SC and MC crystals exhibit a small amount of pyrochlore phase on their surfaces, which can be easily removed during the orientation process; thus, the impurities are not detrimental to the electrical properties of the crystals obtained. The red impurities on the surfaces of both the SC and MC crystals are composed mainly of a large amount of elemental lead and zinc, as determined by electron probe microanalysis (EPMA-8705). The composition of the obtained

SC and MC crystals was analyzed by X-ray fluorescence (Phillips PW2404 XRFA) using crystal plates cut from different parts of a crystal boule (Table 1). Due to segregation during crystal growth, the composition varies along the growth direc-

Table 1. Mean value of the compositions of the SC and MC PZNT91/9 single crystals measured by X-ray fluorescence analysis [XRFA results: x mol-%].

	PbO	ZnO	Nb ₂ O ₅	TiO ₂	Zn _{1/3} Nb _{2/3}	X
SC crystal	101.27	29.00	29.43	9.83	87.86	0.1006
MC crystal	101.15	28.34	29.72	9.88	87.78	0.1012
Stoichiometry	100.00	30.33	30.33	9.00	90.99	0.09001

tion of the obtained SC and MC crystals and Table 1 lists an arithmetic mean value for the compositions of three plates. Measurements were taken at 5 mm intervals along the growth direction. The results are consistent with the X-ray powder diffraction (XRD) measurements of samples taken from different parts of a boule, which confirms the existence of segregation. In both SC and MC methods, because PZNT91/9 single crystals were grown from PMNT69/31 seeds, the PT content is slightly higher at the initial part. From Table 1 we can see the actual compositions of the SC and MC crystals are close to the nominal ones; therefore, the notation PZNT91/9 is still used to indicate the compound composition.

The lattice structure of the SC and MC PZNT91/9 crystals was investigated by XRD using ground crystals (Rigaku D/MAX-3C, Cu K α radiation). XRD patterns show that both the SC and MC crystals exist in a pure perovskite structure without detectable impurities.^[12,13] To check the degree of segregation and the amount of decomposition of the as-grown perovskite structure during the crystal growth process, XRD measurements were also taken along the growth direction of samples of MC crystals cut from different parts of a boule. The distance between the two measurements was 45 mm. No obvious difference can be seen in the XRD patterns of samples cut from different parts, except for a slight difference in the intensity of some diffraction peaks. (200) diffraction peak splitting appears in the XRD patterns of both crystals, which indicates the coexistence of rhombohedral and tetragonal phases. XRD data confirm that segregation and decomposition are not severe during the above two crystal-growth methods. Further structure refinement is needed, since the microstructure greatly influences the physical properties of the perovskite oxides obtained.

Although XRD diffraction confirms that the SC and MC crystals exist in the pure perovskite phase, their electrical properties exhibit astonishing differences. Figure 1 shows the temperature dependence of the dielectric constant, ϵ_r' , and the dielectric loss tangent, $\tan \delta$, at a frequency of 1 kHz of the MC and SC crystals (HP4192A precision LCR meter). The dielectric response of the MC crystal is very different from that of the SC crystal. PZNT91/9 crystals grown from PbO flux (FC crystal) usually exhibit two anomalies, which are generally ascribed to the phase transitions from the rhombohedral ferro-

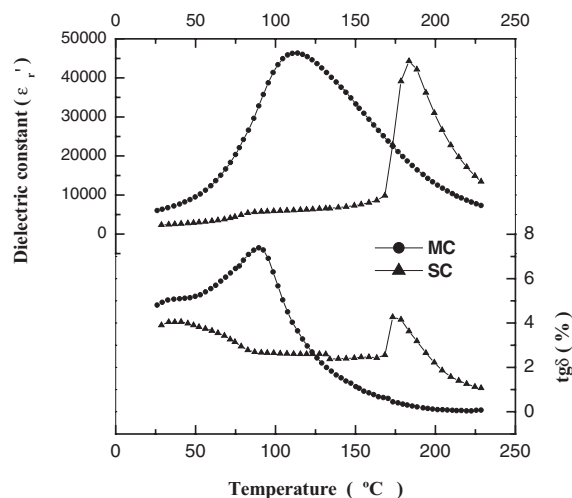


Figure 1. Temperature dependence of the dielectric constant (ϵ_r) and dielectric loss tangent ($\tan \delta$) of the MC and SC crystals ((001) plates) at 1 kHz during the heating process.

electric (FE) phase to the tetragonal FE phase and then to the cubic paraelectric (PE) phase with increasing temperature.^[2,4] In our experiment, the dielectric anomalies in the SC crystal that appear at about 65 °C and 180 °C agree well with the results reported earlier.^[2,4] However, for the MC crystal, there is just one unique anomaly, where the maximum temperature of the dielectric constant appears at rather lower values of about 105 °C. Dielectric measurements at different frequencies show an apparent frequency dispersion; that is, the dielectric peak temperature increases with frequency, and the value of the dielectric maximum decreases with frequency. The frequency dispersion is even more obvious than in the pure PZN relaxor. Furthermore, the full width at half maximum (FWHM) of the dielectric peaks (of around 70 °C) is much broader, which has not, to the best of our knowledge, been reported before, even in systems for which diffused phase transitions are typical.

Such an unusual phenomenon introduces great confusion into the understanding of the mechanism of ferroelectric phase transitions. Considering the stability of complex perovskite structures and taking into account the effect of B-site ordering in perovskite, addition of PbTiO_3 should greatly stabilize the compounds obtained with a perovskite structure, as well as increase the degree of ordering in B-site positions, which would lead to a ferroelectric phase transition from diffused to normal.^[6–8,15,16] A broad dielectric peak for the MC crystal as shown in Figure 1, which indicates great disorder in the lattice sites or a severe inhomogeneity in the microstructure and composition, or both, contradicts the above speculation. The origins of this eccentric phenomenon are not yet totally clear; further work on this observation deserves much attention.

As mentioned above, although XRD data of different parts of the MC crystal did not exhibit any differences, the dielectric response in different parts varied greatly. Figure 2 shows the electrical character of MC crystal plates cut from different parts of a boule. Great differences in the dielectric response ap-

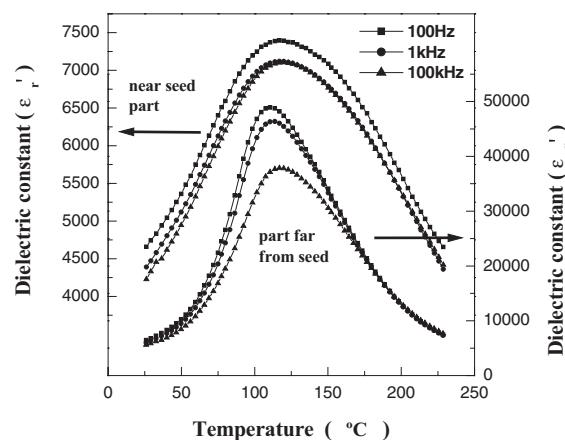


Figure 2. Temperature dependence of the dielectric constant (ϵ_r) in different parts of a MC crystal ((001) plane), measured at different frequencies.

pear: the upper part, i.e., the part near the seed crystal, shows extremely low values of the maximum dielectric constant compared with similar relaxor-based perovskites, and the temperature of the dielectric peak is independent of the frequency. The dielectric constant varies with frequency over the entire temperature range studied, and the curve of the temperature dependence of the dielectric constant can be divided into two nearly symmetrical, linear sections. This phenomenon, where the typical relaxor to the normal phase transition also disappears, has not been reported before. The FWHM is wider, covering around 125 °C. The dielectric loss decreases readily with temperature, except at high frequencies (more than 100 kHz), where it increases abruptly at higher temperatures (to over 200 °C, not shown here). The end part, i.e., the part far away from seed crystal, exhibits a different dielectric character, which was discussed before. Such tremendous differences indicate the existence of a severely inhomogeneous microstructure and microcomposition, or a variation of the degree of ordering in lattice sites. By X-ray fluorescence analysis, we ruled out the existence of magnesium impurities in the as-grown MC crystal, which could be introduced during crystal growth by diffusion from the PMNT69/31 seed.

Defects and undetected impurities could explain in part the abnormally wide dielectric response observed in the MC crystals. Figure 3 shows the substructure of dislocations observed in the MC crystals by transmission electron microscopy (TEM; JEM-3010). Due to the difference in the lattice parameters of the PMNT seed and the as-grown PZNT crystal, as well as to the large thermal stress resulting from crystal growth directly from the melt at such a high temperature, dislocations are easily formed during crystal growth. Furthermore, there may be a little pyrochlore mixed in the perovskite phase, (although it was not detected by X-ray diffraction), since a pyrochlore phase is easily formed and the obtained perovskite phase decomposes quickly.^[6] The possibly present pyrochlore phase would deteriorate the dielectric performance of the obtained MC crystal.

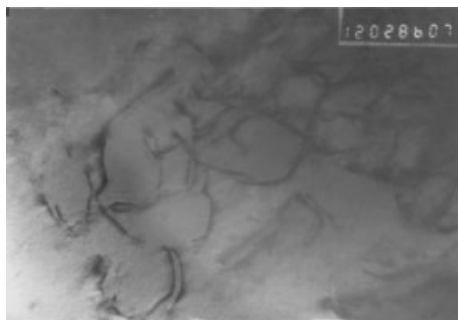


Figure 3. Substructure of dislocations observed in the MC crystal imaged by TEM.

An imperfect crystal structure was further verified by measurements of the ferroelectric properties. The frequency dependence of the admittance and impedance of a MC (001) plane crystal exhibits several spurious resonance peaks, which are detrimental to the efficiency of the conversion of electrical energy to mechanical work. Strain induced by electric fields in the same sample also introduces great non-symmetry, which is partly attributed to a space-charge field caused by defects, or micropolar regions, or both (Figs. 4,5). However, the piezoelectric performance of the MC crystal is excellent, with a piezoelectric constant, d_{33} , of about 1800–2200 pC N⁻¹ within a wafer, which is comparable to that of the SC crystal.

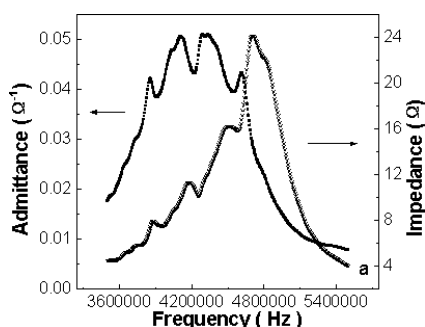


Figure 4. Frequency dependence of the admittance [Ω^{-1}] and impedance [Ω] observed in a MC (001) plane crystal.

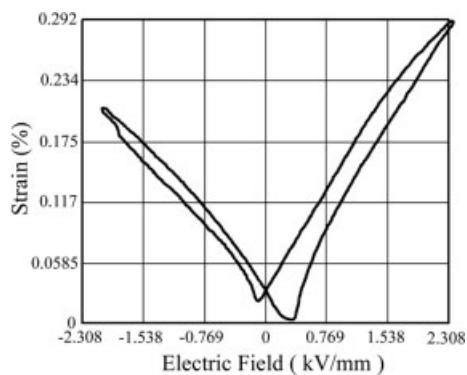


Figure 5. Hysteresis loop of the strain dependence on the electric field at room temperature of a MC (001) plane crystal.

The electrical properties indicate the existence of defects, or impurities, or both, and thereby an instability of the perovskite structure. However, the MC crystals possess better thermal stability. Figure 6 illustrates a simultaneous thermogravimetry/differential thermal analysis (TG/DTA) of ground powder of MC crystals (Netzsch STA429 analyzer). Three endergonic peaks appear in the curve, accompanied by weight loss. Usually, the

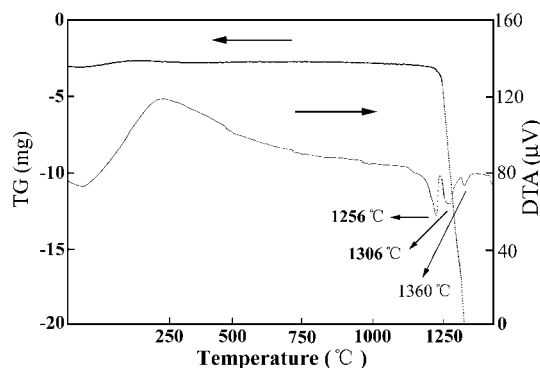


Figure 6. Simultaneous TG/DTA analysis of ground powder of the MC crystal.

“ λ ”-type peak appearing at 1256 °C is regarded as the melting point of the crystal, and at 1306 °C the crystal has become completely liquid. Such results agree well with those of the FC crystal. However, the temperature at which the perovskite phase decomposed into the pyrochlore phase is much higher, 1360 °C, which is around 200 °C higher than in the FC crystal.^[17] Such results indicate that there are some special factors, which cannot be interpreted now, that improve the thermal stability of the MC crystal in the perovskite structure.

Although the exact structure of the MC crystal needs further investigation, optical observation by polarized light microscopy has shown its complex structural character. (001)_{cub} plates cut from the end part of the MC crystal have no obvious extinction regions, but there are macroscopic, alternately arranged domain stripes; plates cut from the upper part have obvious extinction regions, where no macroscopic domains appear. From the viewpoints of crystal symmetry and the laws of extinction, the above results show that rhombohedrally and tetragonally oriented domains coexist in the MC crystal. Such domain configurations are also observed in the SC and FC crystals.^[18]

3. Conclusion

Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O₃ (PZNT91/9) single crystals were grown successfully by two Bridgman methods: from solution using PbO as a self-fluxing agent (SC method) and directly from the melt without fluxing (MC method). In both cases, an allomeric Pb[(Mg_{1/3}Nb_{2/3})_{0.69}Ti_{0.31}]O₃ (PMNT69/31) crystal was used as a seed. High piezoelectric performance PZNT91/9 crystals with a piezoelectric constant, d_{33} , of about 1800–

2200 pC N^{-1} were grown by the MC method. The results were comparable to those obtained by the SC method.

Although the PZNT complex oxide was instable in the perovskite structure, we successfully synthesized PZNT91/9 for the first time in single crystalline form with a pure perovskite phase directly from the melt. We ascribe our success in part to the slight difference in crystal structure between the PMNT69/31 seed and the as-grown PZNT91/9 crystal and the relatively fast growth rate in our experiments. The perovskite PMNT69/31 seed effectively prevented spontaneous nucleation, and the relatively fast growth rate suppressed decomposition of perovskite obtained during crystal growth, which leads to the formation of pyrochlore and to the segregation of PbO.

However, the dielectric properties of the MC crystal were quite unexpected when compared with the SC crystal. The MC crystal shows an extremely broad dielectric-response peak at a relatively low temperature, accompanied by an apparent frequency dispersion over a wide temperature range. In other words, using the allomeric PMNT69/31 seed crystal and relatively fast growth rate is advantageous for PZNT91/9 crystal growth directly from melt; however, the quality of the MC crystal needs to be improved further.

4. Experimental

PZNT91/9 single crystals were grown by two Bridgman methods. High-purity PbO , ZnO , Nb_2O_5 , and TiO_2 oxides were used as raw materials. Due to the poor stability of the PZNT perovskite structure, the raw materials were precalcined by the columbite precursor synthetic method [19]. We modified the method slightly by adding TiO_2 to the prereaction of the B-site refractory oxides. Columbite and other oxides with complex structures were presumed to form, which bypassed effectively the formation of the pyrochlore phase, leading to the direct formation of PZNT perovskite. The preparation of the raw materials by this method provided a substantial increase in the amount of perovskite phase formed compared with former process, i.e., this modified method suppressed, to some extent, the formation of the pyrochlore phase during crystal growth [20]. For the SC method, PZNT crystals were grown at a temperature of 1150 °C. Other conditions included a temperature gradient of about 30–50 °C cm^{-1} , a decreased rate of 0.2–0.5 mm h^{-1} , and PbO acting as fluxing agent. For the MC method, the highest tem-

perature of the Bridgman furnace was more than 1380 °C. The temperature gradient was about 40–80 °C cm^{-1} at the solid–liquid interface. To suppress decomposition of obtained PZNT perovskite at such a high growth temperature, the growth rate was relatively fast, about 0.5–1.0 mm h^{-1} . Such a fast growth rate inevitably introduced some impurities into the as-grown crystal, although these may not be detectable due to the detection limit of the X-ray equipment. The growth procedure was similar to that of the PMNT67/33 single crystals grown directly from melt [14]. For both Bridgman methods, an allomeric PMNT69/31 single crystal was used as a seed, and the growth face was oriented perpendicular to the $\langle 111 \rangle_{\text{cub}}$ direction.

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