

Top-cooling-solution-growth and characterization of piezoelectric $0.955\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.045PbTiO_3 [PZNT] single crystals

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A technique of top-cooling-solution-growth (TCSG) has been developed to grow the piezo-/ferroelectric perovskite single crystals of $0.955\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.045PbTiO_3 [PZNT95.5/4.5]. The flux composition and concentration, and the thermal parameters have been optimized, leading to the growth of high quality PZNT crystals with a size up to $20 \times 15 \times 10 \text{ mm}^3$. The perovskite crystals are found to form upon slow cooling down to 1020°C , while the undesirable pyrochlore crystals of $\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$ -type start growing upon further cooling from 1020°C to 950°C . By controlling the growth pathway, the formation of the pyrochlore phase can be avoided. The dielectric properties of the grown PZNT95.5/4.5 crystals have been measured as a function of temperature at various frequencies. Upon heating, the phase transition for the rhombohedral R3m to the tetragonal P4mm phase takes place at 132°C , while the tetragonal to cubic phase transition occurs at 160°C . The TCSG developed in this work provides an alternative technique to grow PZNT piezocrystals of medium size at low cost for transducer applications.

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1. Introduction

Relaxor ferroelectrics (relaxors) and the related materials have shown great interest both for fundamental solid state science and for advanced technology [1–3]. A complete solid solution forms in the system of relaxor $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ [PZN] and ferroelectric PbTiO_3 [PT]: $(1-x)\text{PZN} - x\text{PT}$ [PZNT]. A morphotropic phase boundary (MPB) between the rhombohedral R3m and the tetragonal P4mm phase appears near the composition $x \approx 0.09$ [4]. Single crystals of PZNT exhibit excellent dielectric and piezoelectric properties. The $(001)_{\text{cub}}$ -oriented crystals poled along $[001]_{\text{cub}}$ show a high dielectric constant, a large piezoelectric coefficients $d_{33} \approx 2,500$, an extremely high electromechanical coupling factors $k_{33} \approx 92\%$, and a very large strain ($\approx 1.7\%$) [4–9]. Such outstanding performance makes PZNT crystals one of the most promising materials of next generation for electromechanical transduction in a broad range of advanced applications, such as medical ultrasound imaging and underwater communication.

To meet the increasing need for piezocrystal resources in various applications, it is essential to develop effective techniques to grow large and high quality PZNT crystals. Intensive research was undertaken recently and important progress has been made on crystal growth. In contrast to the difficulties in synthesizing

polycrystalline perovskite phase, PZNT crystals can be grown by the flux method [10–13]. The optimized chemical, thermal and kinetic parameters have resulted in the growth of high quality PZNT91/9 crystals [13]. A modified Bridgman technique was developed by Yamashita and co-workers to grow large PZNT crystals using excess PbO as solution [7, 14–19], and PZNT91/9 crystal boules with dimension reaching about 50 mm (in diameter) \times 35 mm (in length) were successfully grown, providing large crystal wafers for transducer applications. However, the Bridgman method has a major disadvantage which is the high cost, because (i) it is difficult to separate the grown single crystals from crucibles, and thus the crucibles cannot be reused; (ii) the growth rate is very slow. Moreover, a non-uniformity in composition usually appears with a higher Ti^{4+} -concentration on the bottom and a smaller Ti^{4+} -rate on the top of the grown boules, resulting from a possible phase segregation.

When PZNT crystals are grown from the PbO flux, the perovskite phase is often accompanied with an undesirable pyrochlore phase of $\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$ -type [13, 20], the inclusion of which deteriorates the piezo- and ferroelectric properties of the perovskite crystals. A thermodynamic study indicates that PZNT91/9 crystals partially decompose into the pyrochlore phase above 1148°C and undergo an incongruent melting at 1226°C

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[20]. In spite of a number of reports on the formation of these two phases in the form of polycrystals and ceramics, the temperature ranges for the formation of pyrochlore and perovskite crystals are still not clear.

In terms of PZN-PT solid solutions, so far the major effort both on crystal growth and characterization has been focused on the morphotropic phase boundary composition 0.91PZN-0.09PT [PZNT91/9]. The MPB crystals have been shown to exhibit complex domain structures with coexistence of both the trigonal R3m and tetragonal P4mm phase at room temperature [13, 21]. Upon heating, the R3m to P4mm phase transition takes place in a large temperature interval above room temperature. This would result in unstable piezoelectric properties due to the changing rhombohedral/tetragonal domain structures in the crystals. On the other hand, PZNT crystals with lower Ti-concentration crystallize in the rhombohedral phase. An interesting composition is 0.955PZN-0.045PT [PZNT95.5/4.5], which is intermediate between the relaxor PZN and the MPB. Single crystals of PZNT95.5/4.5 show excellent piezoelectric performance [9]. They also allow us to investigate some intrinsic properties related to the rhombohedral phase, e.g. regarding the possible electric field-induced domain and polarization switching [9, 22].

In the framework of our continuous effort in the growth and characterization of relaxor-based piezocrystals, we have optimized the spontaneous solution growth and developed a new technique of top-cooling-solution-growth (TCSG) for the growth of PZNT95.5/4.5 crystals. This paper reports the growth results and the dielectric properties of the grown PZNT crystals, and discusses the temperature range for the formation of perovskite and pyrochlore phases.

2. Crystal growth by spontaneous nucleation method

2.1. Growth experimental

The flux method was used to study the phase formation and phase transition in the PZNT-PbO system. It is based on spontaneous nucleation by supersaturation upon slow cooling [23]. High purity (>99.9%) starting powders of PbO, ZnO, Nb₂O₅ and TiO₂ of PZNT 95.5/4.5 were mixed with different ratio of PbO as flux. The well-ground mixtures were put into a platinum crucible covered with Pt lid. The loaded Pt crucible was placed inside an alumina crucible, which was then

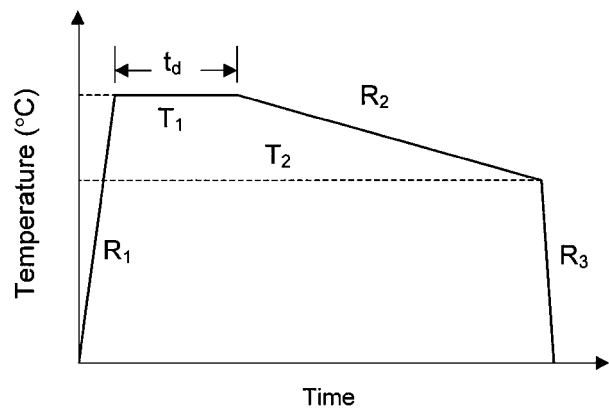


Figure 1 Typical temperature profile used for the growth of PZNT crystals. The parameters are given in Section 2.1 for flux growth and in Table II for TCSG.

sealed to an alumina cover by using refractory cement to prevent the PbO flux from volatilizing at high temperatures. Fig. 1 gives the typical thermal profile used, which consists of: (a) heating from room temperature to $T_1 = 1100^\circ\text{C}$ at a rate $R_1 = 200^\circ\text{C/h}$, (b) dwelling time $t_d = 5.0$ h. (c) cooling at $R_2 = 2^\circ\text{C/h}$ to 950°C and (d) cooling to room temperature at $R_3 = 500^\circ\text{C/h}$. The soaking temperature was limited to 1100°C in the study of phase formation. The grown crystals were separated from the flux by washing in dilute hot HNO_3 solution and then weighed to calculate the yield.

2.2. Optimum flux concentration

Five different flux concentrations with flux ratio = $\text{PbO}/(\text{PbO} + \text{PZNT95.5/4.5}) = 30, 40, 50, 55$ and 60 wt% were tried with the temperature profile given in Fig. 1. Table I gives the yields and size of the perovskite crystals grown by the spontaneous flux method. The optimum flux concentration is found to be 50 wt%, which leads to a maximum yield of the perovskite crystals.

2.3. Phases in the PZNT95.5/4.5-PbO system

X-ray powder diffraction was used to determine the phases formed in the PZNT-PbO system. Two different phases were identified, the perovskite PZNT95.5/4.5 phase and the pyrochlore $\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$ -type phase, as shown in Fig. 2. It is found that the formation of these two phases depends upon the flux concentration and

TABLE I Yield and size of perovskite crystals grown by spontaneous method using different flux concentrations

Batch number	M1	M2	M3	M4	M5	M6 [†]
Flux ratio (%)	30	40	50	55	60	50
Size of Perovskite crystals	N/A	N/A	3–4 mm	3–4 mm	2–3 mm	1 mm
Yield of Perovskite crystals	N/A	N/A	25.7%	17.8%	9.23%	21.9%
Pyrochlore crystals	N/A	Yield $\approx 6.7\%$ Size $\sim 1\text{--}2$ mm	Present	Present	Present	Not present

[†]Using temperature profile of Fig. 4.

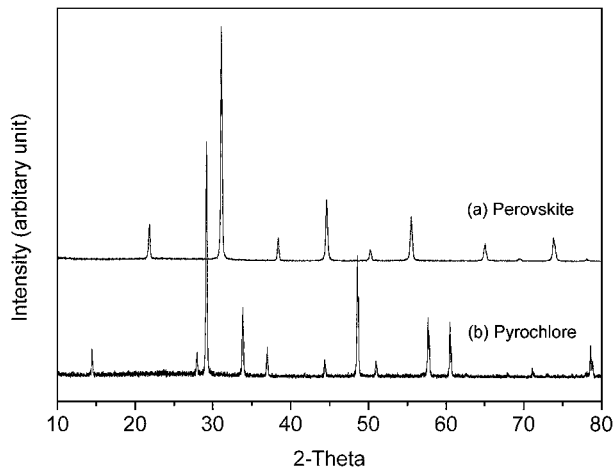


Figure 2 X-ray powder diffraction patterns of the perovskite PZNT95.5/4.5 phase (a) and the pyrochlore $\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$ -type phase (b).

the temperature profile used. When the flux ratio was smaller than 40 wt%, only the pyrochlore crystals were formed (Batch M2). With 50 wt% PbO flux (Batch M3), PZNT95.5/4.5 crystals were formed around the wall of the crucible (Fig. 3). The grown perovskite crystals show an irregular morphology, similar to the PZNT91/9 crystals [13]. Although the major phase formed is perovskite, some pyrochlore crystals are also found on the surface of solidified solution in the form of $(111)_{\text{cub}}$ -plates. There are also some small cubic perovskite crystals. A flux ratio higher than 50 wt% PbO led to the formation of pyrochlore crystals at the expense of the perovskite phase.

2.4. Effects of the thermal profile on the formation of phases

For growth batches M3, M4 and M5 in Table I, both the perovskite and the pyrochlore phases were formed. The

effects of thermal process on the formation of phases can be seen by comparing M3 with M6. These two batches had the same flux concentration but underwent different temperature profiles. M3 experienced a slow cooling from 1100°C down to 950°C (Fig. 1), but M6 was quenched from 1100°C to 950°C, followed by a slow cooling to 890°C, as shown in Fig. 4. The results are dramatically different. Both the perovskite and the pyrochlore phases were formed in M3. In M6, however, only very small perovskite cubic crystals appeared (Fig. 5), which were probably formed during the 5 hours soaking period at 1100°C and the following quenching process. This indicates that the pyrochlore phase is formed above 950°C.

3. Top cooling solution growth (TCSG)

3.1. Experimental for TCSG

One of the difficult issues in the flux growth is the formation of a large number of nuclei resulting from spontaneous nucleation. It is necessary to control and restrain the nucleation to grow larger piezocrystals. Based on the optimized flux growth conditions, a new growth process, the top-cooling-solution-growth (TCSG), has been developed for the growth of PZNT crystals. Stoichiometric 95.5%PZN-4.5%PT powders were mixed with PbO flux at the optimum ratio PZNT : PbO = 1 : 1 (50 wt% flux). The mixtures were ground homogeneously in acetone. The dried mixture was put in a platinum crucible (100 ml), and the crucible was placed inside an alumina crucible with a platinum wire hanged on the top, as shown in Fig. 6. The top cooling was ensured by the Pt wire, which triggers nucleation around it. The alumina crucible was then sealed to an alumina cover with refractory cement. The assembly was placed in a Muffle furnace with an open hole on the top. The thermal profile given in Fig. 1 was used with the thermal parameters described in Table II. The

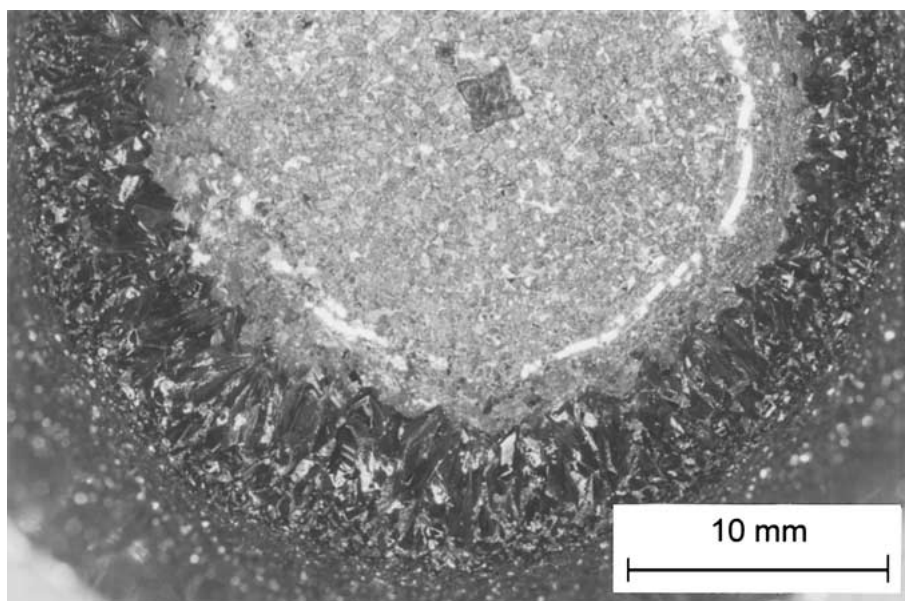


Figure 3 Top view of an as-cooled crucible from a spontaneous nucleation growth with 50 wt% PbO as flux (Batch M3) showing numerous perovskite PZNT95.5/4.5 crystals grown around the wall of crucible.

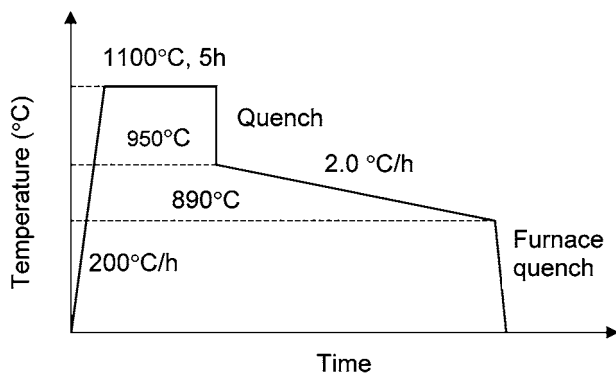


Figure 4 Temperature profile used for growth batch M6 with a quenching from 1100°C to 950°C upon cooling, which prevents the formation of the pyrochlore phase.

grown crystals were separated from the solidified flux using dilute hot HNO_3 solution.

3.2. TCSG results

By carefully adjusting the airflow for top-cooling, single crystals of PZNT95.5/4.5 were successfully grown. Fig. 7a shows the top view of an as-cooled crucible (Batch S2). It can be seen that a primary single nucleation actually took place around the Pt-wire by top cooling, resulting in the growth of a large single crystal of PZNT95.5/4.5 at the center of crucible. In contrast to the spontaneous flux growth, only very few small crystals were formed around the crucible wall. The small cubic crystals on the surface of solidified flux resulted from the secondary nucleation during further cooling process. Fig. 7b shows the grown crystal separated from the flux. The main facets developed are parallel to $\{001\}_{\text{cub}}$ planes. The size of the PZNT crystals reaches $20 \times 15 \times 10 \text{ mm}^3$ grown from a crucible of moderate volume (100 ml).

3.3. Crystal morphology

The crystal morphology was examined by optical microscopy. The surface micrograph of a grown

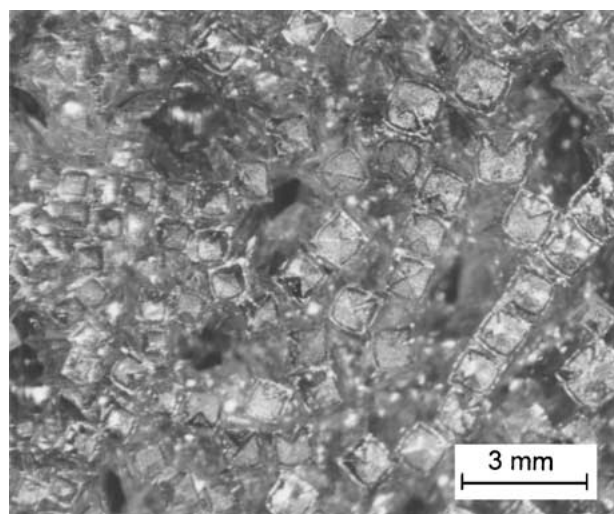


Figure 5 Cubic morphology of the perovskite crystals grown from Batch M6.

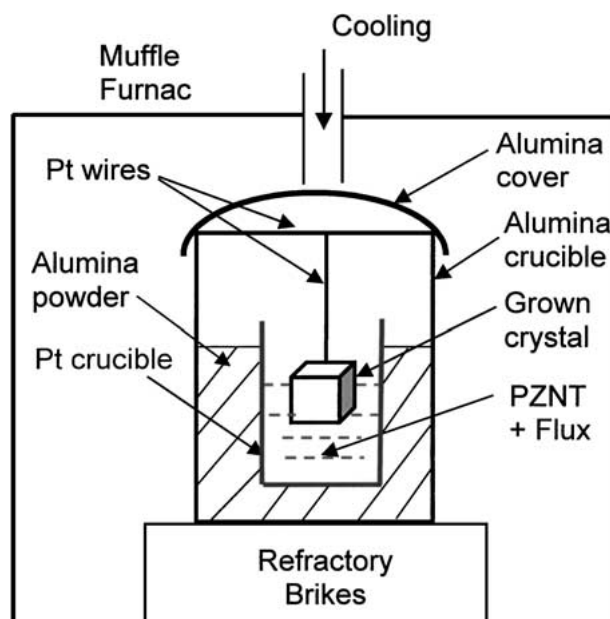


Figure 6 Set-up for the top-cooling-solution-growth (TCSG) of PZNT single crystals.

PZNT95.5/4.5 crystal (Fig. 8) reveals a degenerated morphology with growth steps parallel to $(001)_{\text{cub}}$ plane, indicating a dominant layer growth mechanism for the $\{100\}_{\text{cub}}$ faces which are the so-called F (flat) faces, as defined by Hartman and Perdok [24–26]. This suggests that the growth of PZNT crystals is controlled by two-dimensional growth starting from a primary nucleation around the Pt-wire. This growth mechanism is similar to the one deduced for the flux growth of PZNT91/9 [13] and PMNT65/35 [27] piezocrystals.

3.4. Effects of thermal profile on the phase formation in TCSG

For growth batch S1 (Table II), the primary crystal grown from TCSG and most of the small crystals from spontaneous nucleation are found to be the perovskite phase, but some brown pyrochlore crystals are also found near the central large single crystal. For growth bathes S2 and S3, the crystals grown from TCSG belong to the perovskite phase, so do the small crystals formed around the wall of the crucible and on the surface of the flux, and no pyrochlore crystals are found in these two batches. The main difference between S1 and S2/S3 lies in the temperature profile: S1 underwent a slow cooling from 1170°C to 1000°C, while S2 and S3 were cooled from 1170°C to above 1020°C. It is clear that the pyrochlore phase is formed below 1020°C and it is more favorable for the perovskite crystals to grow at the temperature range above 1020°C.

TABLE II Parameters of the temperature profiles used for the TCSG (Referring to Fig. 1)

Batch number	R_1 (°C/h)	T_1 (°C)	t_d (h)	R_2 (°C/h)	T_2 (°C)	R_3 (°C/h)
S1	200	1170	10	2.0	1000	500
S2	200	1170	10	1.0	1020	500
S3	200	1170	10	1.0	1030	500

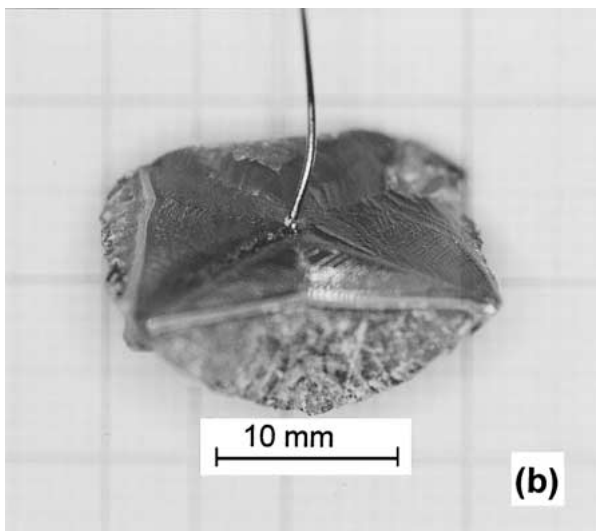
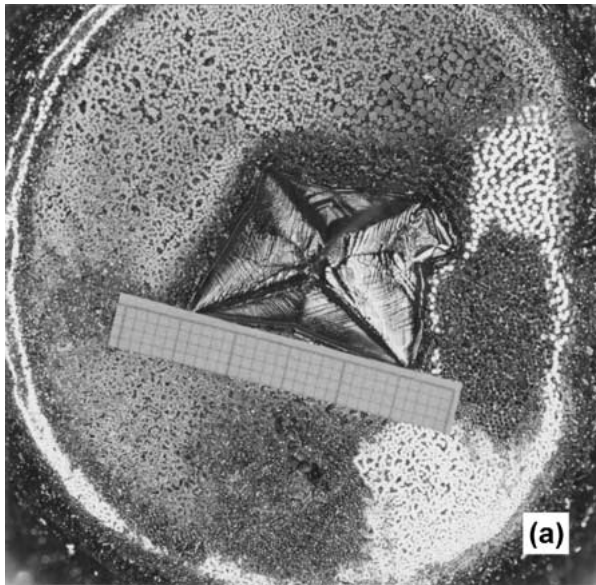


Figure 7 (a) Top view of an as-cooled crucible from top cooling solution growth of PZNT95.5/4.5 single crystals (scale in mm); (b) A single crystal grown from a primary nucleation by top-cooling.

Based on the above observation and the discussion in Section 2.4, it can be concluded that the perovskite phase is formed at higher temperature range. During the cooling process down to $T \geq 1020^\circ\text{C}$, only the perovskite crystals are formed. Upon further cooling, the pyrochlore phase is formed in the temperature interval $\sim 950^\circ\text{C} < T < \sim 1020^\circ\text{C}$. Therefore, in order to grow the perovskite crystals and to avoid the formation of the pyrochlore phase, it is necessary to end the slow cooling process at above 1020°C , followed by a rapid cooling down to room temperature.

4. Dielectric properties of the PZNT95.5/4.5 crystals

The dielectric properties of the PZNT95.5/4.5 crystals were measured as a function of temperature at various frequencies. A crystal plate with an area of 11.32 mm^2 and a thickness of 0.75 mm was cut from a sample of S2 and finely polished. The polished parallel surfaces were covered with a layer of Ag-paste (about $100 \mu\text{m}$ thick) and connected with a pair of Au-wire ($40 \mu\text{m}$ diameter). The platelet covered with electrodes was then fired at 150°C in an oven for 30 min. The dielectric properties were measured using a Solartron 1260 Impedance Analyzer in conjunction with a Solartron 1296 Dielectric Interface. An ac voltage of $1 V_{\text{rms}}$ was applied, and no electric field poling was performed. Fig. 9 gives the variation of the real part of permittivity (ϵ') and the dissipation factor ($\tan \delta$) versus temperature. The dielectric properties show that two phase transitions take place in PZNT95.5/4.5, one at $T_{\text{RT}} = 132^\circ\text{C}$, corresponding to the rhombohedral to tetragonal transition, another at $T_{\text{C}} \approx 160^\circ\text{C}$, corresponding to the tetragonal to cubic transition. A weak relaxation behavior appears at $T > T_{\text{C}}$ with a maximum of dielectric loss at 240°C for 1 kHz (Fig. 9b). The dielectric constant (ϵ') of the crystal is about 2,250 at room temperature, which is smaller than the value measured along

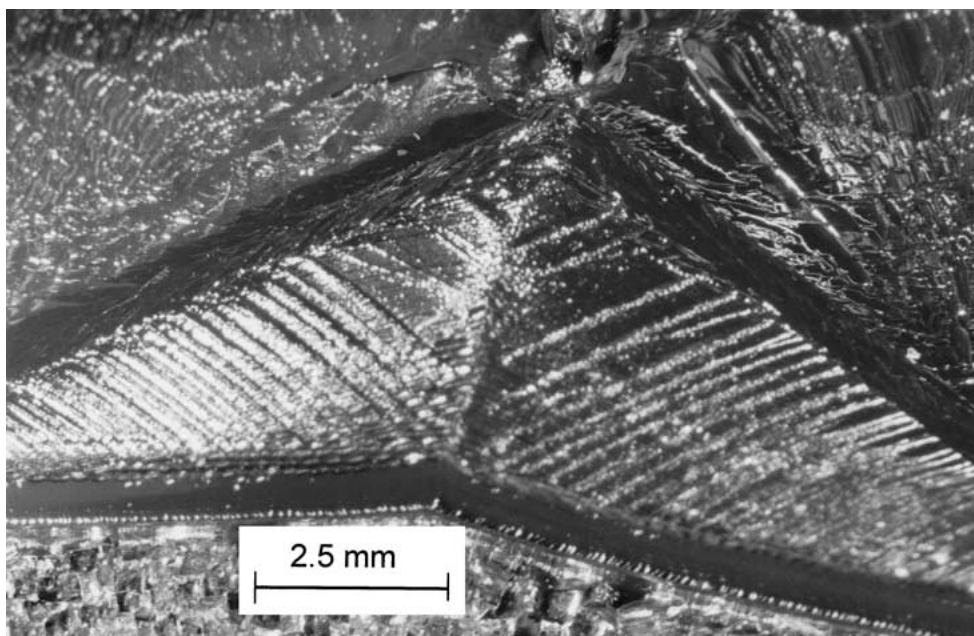


Figure 8 Surface micrograph of an as-grown PZNT95.5/4.5 crystal by TCSG showing degenerated growth steps parallel to $\{001\}_{\text{cub}}$ planes.

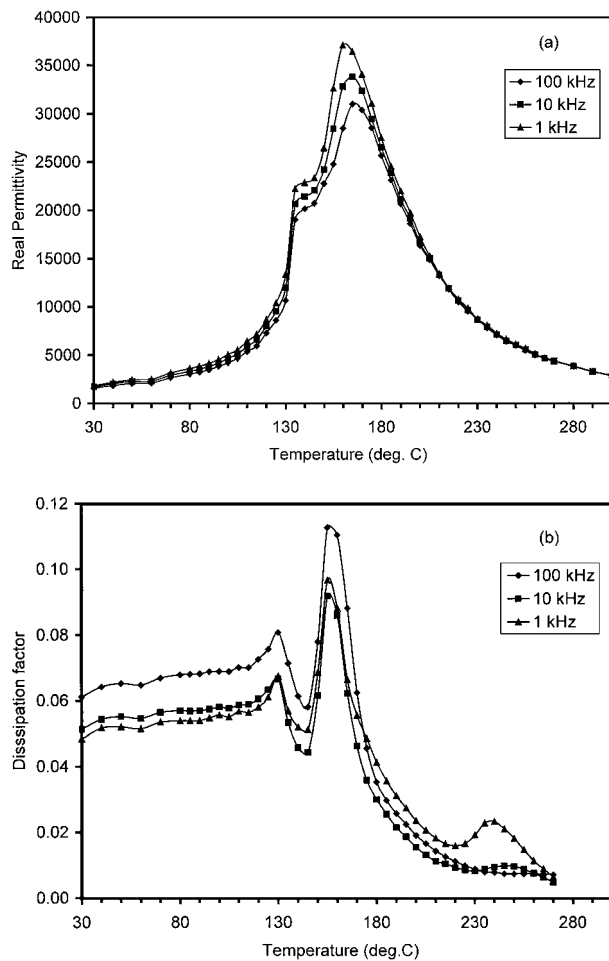


Figure 9 Variation versus temperature of (a) the real part of dielectric permittivity (ϵ') and (b) the dissipation factor ($\tan \delta$) at frequencies 1, 10 and 100 kHz for an unpoled PZNT95.5/4.5 crystal plate of intermediate orientation between $\langle 001 \rangle_{\text{cub}}$ and $\langle 111 \rangle_{\text{cub}}$.

$\langle 001 \rangle_{\text{cub}}$ -direction ($\epsilon' = 5,000$), but larger than the one along $\langle 111 \rangle_{\text{cub}}$ ($\epsilon' = 640$) of a poled crystal [9]. This is due to the fact that the crystal under investigation had an intermediate orientation between $\langle 001 \rangle$ and $\langle 111 \rangle$ and was not poled (a detailed study of the anisotropic properties of the grown PZNT crystals is underway). Nevertheless, the dielectric constant reaches a maximum value of 37,000 around T_C at 1 kHz, indicating the good quality of the grown PZNT95.5/4.5 crystals.

5. Conclusions

1. A new process by top-cooling-solution-growth has been developed to grow the perovskite crystals of 95.5PZN–4.5PT. Single crystals up to $20 \times 15 \times 10 \text{ mm}^3$ size were successfully grown from a crucible of 100 ml. A single nucleation can be achieved by TCSG without using any seed crystals. Compared with the Bridgman growth, the TCSG technique presents some advantages: (i) no seed crystals are needed; (ii) the grown crystals show more regular morphology with principal facets oriented to $\{001\}_{\text{cub}}$, hence are easier to be handled in transducer applications; (iii) it is expected that the grown crystals are less stressed, thus the residual internal strain could be minimized; (iv) it is

easier to separate the primary grown crystals from the solidified flux, and (v) the Pt crucibles can be reusable. Therefore, the TCSG provides an alternative solution to the Bridgman method to grow medium size piezocrystals at very low cost.

2. The chemical conditions for the growth of PZNT95.5/4.5 crystals by spontaneous nucleation (flux) method has been optimized. A flux ratio of 50 wt% PbO has been shown to result in a maximum yield of the perovskite crystals.

3. The thermodynamic conditions for the formation of the perovskite and pyrochlore phase have been clarified. The perovskite crystals primarily grow upon cooling from 1170°C down to above 1020°C , while and the pyrochlore crystals are formed between $\sim 1020^\circ\text{C}$ and 950°C . Therefore, it is necessary to rapidly cool the crucibles from 1020°C down to below 950°C at the end of slow cooling process in order to grow the perovskite crystals and to avoid the formation of the pyrochlore phase.

4. The temperature dependence of the dielectric properties indicates clearly two phase transitions in PZNT95.5/4.5 at $T_{\text{RT}} = 132^\circ\text{C}$ and $T_C = 160^\circ\text{C}$, corresponding to the rhombohedral to tetragonal and the tetragonal to cubic transition, respectively. In comparison with the PZNT91/9 crystals of MPB composition, T_C is slightly decreased from 175 to 160°C , but T_{RT} is significantly increased from about 70°C to 132°C in the PZNT95.5/4.5 crystals, giving rise to more stable rhombohedral domain states and thereby a higher stability of piezoelectric properties against temperature change for transducer applications.

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