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Ferroelectric Properties and Transmission Response of PZN-PT Single Crystals for Underwater Communication

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ABSTRACT

Single crystal of $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ (PZN-PT) at the composition of morphotropic phase boundary (MPB) shows a very high electromechanical coupling coefficient, piezoelectric coefficient, and dielectric constant compared to conventional PZT ceramics. These exceptional properties of these single crystals find enormous applications in medical ultrasound imaging and underwater communication (Sonar). The growth of PZN-PT single crystals has been carried out by bottom-supported flux Bridgman method. There are many growth issues to be addressed during the process of growth. The grown crystals are oriented and cut along <001> direction with the crystal dimension of 8 x 6 x 1.5 mm^3 for further analysis. The oriented crystals were poled at a rate of 1 kV/mm. The poled crystals have been characterised for dielectric, strain and piezoelectric values. Further, the poled specimen were tested for transmitting response at various frequencies in acoustic test facility and the difficulties in their growth.

Keywords: Crystal growth, sonar, piezoelectric coefficient, transducer, underwater communication, PZN-PT single crystal, electromechanical coupling factor, dielectric constant, ferroelectric constant

1. INTRODUCTION

Compared to the conventional PZT ceramics, PZN-PT single crystals exhibit extremely high piezoelectric constant, a very high electromechanical coupling factor, and high dielectric constant with loss less than 1 per cent (k_{33} > 90 %, d_{33} > 2000 pC/N, and ε_r > 2000) at morphotropic phase boundary (MPB) composition of (1-x) PZN and x PT between x = 0.08 to x = 0.10. The MPB at x = 0.09 separates the rhombohedral and tetragonal phases at 25 °C. These properties employ PZN-PT single crystal as an excellent material for underwater communication and medical ultrasound imaging applications. $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) with rhombohedral symmetry has diffuse-phase transition around 140 °C and $PbTiO_3$ (PT) with tetragonal symmetry has typical long-range ferroelectric properties with phase transition at 490 °C. But the combined solid solution has the advantages of both the relaxor PZN and ferroelectric PT properties. PZN-PT crystal of compositions near MPB can be grown by conventional flux method[1] and flux Bridgman method[2]. Flux method has the demerits like the poor size of the obtained crystals, reproducibility, PbO volatilisation at higher temperature and is unfavourable for the effective size harvest. Bridgman method can produce good size crystals, but it has some demerits like

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the phase stability of the grown crystal remains with pyrochlore. To overcome this problem, the synthesis of PZN-PT powder before the growth process, becomes necessary. The removal of crystals from the platinum crucible without damaging both the crystal and the platinum crucible is very difficult.

2. EXPERIMENTAL PROCEDURE

In this study, PZN-PT powder of desired composition was synthesised by double calcinations method. In the first stage ZnO, Nb_2O_5 and TiO_2 were weighed stoichiometrically and were grinded well in a mortar and the mixture was soaked at 1000 °C for 4 h. Then the powder was thoroughly mixed with stoichiometric PbO and subjected to post-calcination at 750 °C for 2 h. Then X-ray diffraction (XRD) was carried out on the post-calcined powder and it showed the presence of both perovskite and pyrochlore phases. The pyrochlore phase found in synthesised powder disappears during the growth process. This intermediate phase helps a lot more in minimising the PbO evaporation.

This synthesised PZN-PT powder materials was used for the growth of PZN-PT single crystals by bottom-supported flux Bridgman method. A three-zone resistive heating SiC furnace with a gradient of 7 °C/cm was used for the crystal growth. The synthesised PZN-PT powder was taken in a 50 cc platinum crucible, which was supported by an alumina crucible. Refractory zirconia powder was taken in between the two crucibles to support the platinum crucible at high temperature and minimise the PbO evaporation. The synthesised PZN-PT charge was soaked at 1200 °C for 4 h and then lowered at a rate of 1 mm/h through a translation length of 40 cm. After completion of the crucible lowering, the furnace was cooled down to room temperature at the rate of 100 °C/h. The crystals were separated from the flux by boiling in 30 per cent of HNO_3 for several hours.

3. RESULTS AND DISCUSSION

3.1 Piezoelectric and Ferroelectric Studies

PZN-PT crystals grown by the above method, were subjected to XRD to confirm the perovskite phase (Fig. 1) and it was found that the results obtained were in good agreement with the previous results[3]. Grown PZN-PT single crystals were brown (Fig. 2). Grown crystals were oriented along <001> direction using X-ray diffractometer technique. The oriented crystals were cut along the <001> direction with the crystal dimension of 8 x 6 x 1.5 mm^3 for further analysis. Further confirmation on the orientation of crystals was done with Laue-back reflection technique.

PZN-PT sample of 1 mm thickness was electroded with silver paste and poling was performed at the

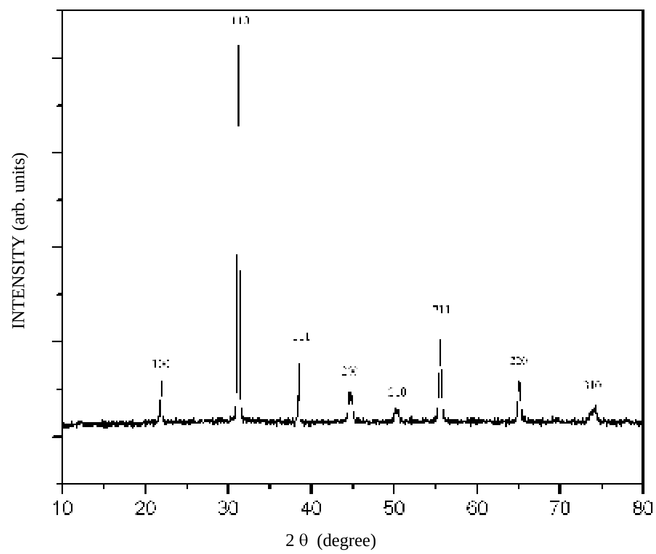

Figure 1. X-ray powder diffraction pattern of PZN-PT (91-9) single crystal.

Figure 2. Grown PZN-PT (91-9) single crystal by bottom-supported flux Bridgman method.

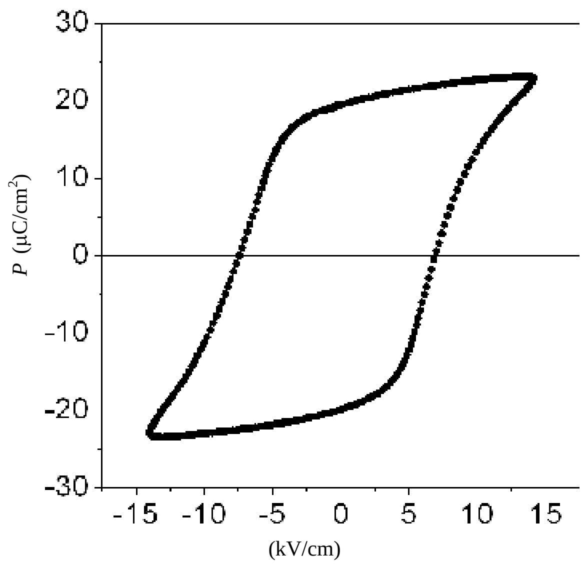

Figure 3. P-E hysterisis analysis loop for PZN-PT <001> oriented single crystal.

rate of 1 kV/mm. Piezoelectric coefficient of the poled sample was found to be 1200 pC/N. The polarisation as a function of electric field for the PZN-PT single crystal was analysed and is shown in Fig. 3. The value of remanent polarisation, P_r is 19.7 μC/cm² and the value of coercive field E_c is 7.2 kV/cm. The amount of strain developed as a function of E unipolar field for <001> oriented PZN-PT single crystals reaches 0.28 per cent for an electric field of 25 kV/cm. The electromechanical coupling coefficient of the poled crystal is found to be 45 per cent in the thickness mode.

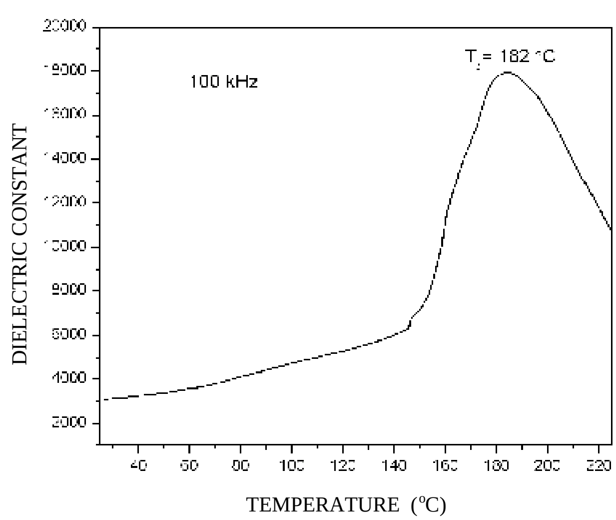

Figure 4. Dielectric spectrum for as grown PZN-PT (91-9) single crystal at 100 kHz.

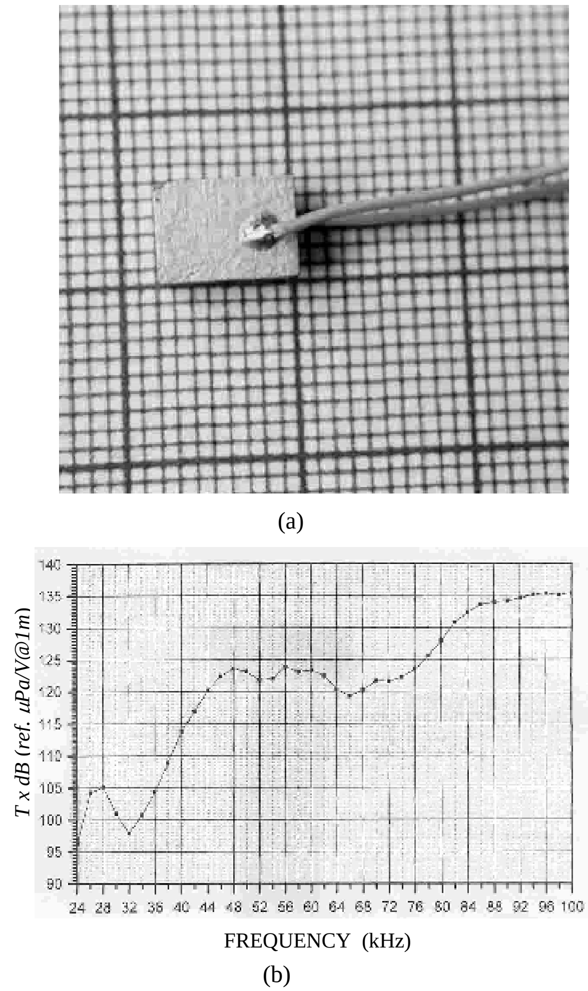

Figure 5. (a) Oriented PZN-PT (91-9) single crystal with electrical contacts and (b) transmitting response of <001> oriented PZN-PT (91-9) single crystal.

3.2 Dielectric and Transmitting Response Analyses

Figure 4 shows the dielectric spectrum as a function of temperature carried out for the grown crystal and the T_c value was found to be 182 °C and was in good agreement with the previous reports[4,5]. Figure 5 (a) shows the sample, where the electrical contacts were given to the <001> oriented crystal for transmitting response analysis. The sample was moulded with sound-transparent material and kept for curing at room temperature. After 48 h curing, the sample was tested in the Naval Science and Technological Laboratory's acoustic tank facility for its transmitting response. The transmitting response is the ratio of pressure produced at 1 m from the acoustic centre of the transducer in the direction of maximum response axis to the voltage applied across the electric input terminals of the transducer. Figure 5 shows the transmitting response of <001> oriented PZN-PT (91-9) single crystal. It is observed from the figure, that there is an increasing trend in the transmitting response with frequency except at lower frequency region. It shows a maximum value of transmitting response at 100 kHz (135 dB). Studies have been taken up to further improve the transmitting response with modification of the material.

4. CONCLUSION

Growth of PZN-PT(91–9) crystals from *PbO* flux has been carried out by bottom-supported flux Bridgman method. The issues related to growth were discussed in detail. Grown crystals were oriented along <001> direction and various analyses like piezoelectric coefficient hystersis, dielectric and transmitting response analysis were carried out and results presented. Piezoelectric coefficient of the poled sample is found to be 1200 pC/N. P-E loop trace shows that the remanent polarisation value, P_r is 19.7 μC/cm^2 and the value of coercive field, E_c is 7.2 kV/cm. Strain measurements and piezoelectric coefficients show lower values and these may be due to the compositional inhomogeneity along the grown crystals which is more common in these types of relaxor crystals. The electromechanical coupling coefficient of the poled sample was found to be 45 per cent in thickness mode. Though there are some basic problems like effective achievable crystal size in growth of these crystals and phase stability of grown crystal, etc. The interesting results on PZN-PT single crystals confirms that these crystals can be the best sonar transducers in the near future.

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