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THERMAL STABILITY AND FERROELECTRIC PROPERTIES OF $Pb[(Zn_{1/3}Nb_{2/3})_{0..91}Ti_{0.09}]O_3$ SINGLE CRYSTAL FOR ULTRASONICS TRANSDUCER APPLICATIONS

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ABSTRACT

Single crystal of $Pb[(Zn_{1/3}Nb_{2/3})_{0..91}Ti_{0.09}]O_3$ (PZN-PT) is very attractive for its better performance compared to that of conventional PZT ceramics. PZN-PT at Morphotropic Phase Boundary (MPB) shows a very high electromechanical coupling coefficient, piezoelectric coefficient and dielectric constant. These single crystals are being attracted the field of medical ultrasound imaging and underwater communication (SONAR) applications. Single crystals of PZN-PT are grown by bottom-supported flux Bridgman method with PbO flux. The obtained crystals are in light brown colour. The X-ray powder diffraction of powdered PZN-PT single crystal confirms the perovskite phase of the grown crystal. The growth problems are addressed to get good size crystals suitable for the devices. Thermal stability of the grown crystal is done by DTA/TG analysis. XRF studies have been carried out to confirm composition of the grown crystal respectively. The results are discussed in detail.

Keywords: Single crystal, Morphotropic phase boundary, piezoelectric coefficient

1. INTRODUCTION

Lead Zinc Niobate with typical relaxor behavior and Lead Titanate with long range ferroelectric order with ferro/para electric transition at 398^0C forming a solid solution by retaining their respective advantages is attracted for it applications in ultrasonic devices such as medical ultrasonic imaging and SONAR applications. PZN-PT(91/9) at MPB exhibits an exceptionally high piezoelectric constant of d_{33}>2000pC/N, electromechanical coupling coefficient k_{33}>90%[1]. PZN-PT single crystal can be grown by various techniques such as conventional flux method, top-seeded solution growth, modified Bridgman method and vertical gradient freeze-solution growth method. Among the various methods flux method and modified Bridgman method is widely preferred by many researchers for its possibility of harvesting bulk size crystals and better reproducibility of growth runs. Also it is difficult to grow these crystals by Czochralski method, which is widely used method for mass-production, because PZN-PT changes to pyrochlore crystal at temperatures greater than 800^0C[2]. In the present report, PZN-PT crystals are grown by bottom supported Bridgman method, which is suitable for the growth of heavier crystals. Moreover, this method is more suitable to flow O_2 gas to induce single nucleus, where crystals can be grown in larger size by avoiding multinucleation. Whereas, this is difficult to employ in hanging Bridgman method.

2. EXPERIMENT

High purity powders of PbO, ZnO, TiO_2¸ Nb_2O_5 (99.9% purity) were mixed well using a mortar and the mixture is taken in a platinum crucible. The platinum crucible is suitable closed by platinum lid to avoid PbO evooparation. The platinum crucible is placed in a Al_2O_3 crucible and Al_2O_3 powder is taken in between the crucibles to support the platinum crucible at high temperatures. A mixture of these powders in the ratio of PZN-PT at 91:9 mol% is calcined at 800^0C for 4 h in a 3 zone furnace and the temperature was increased to 1180^0C and melt is allowed for homogenization for 4 hrs. The platinum crucible with melt was driven through the 3 zones at a speed of 1 mm/h. When the crucible reaches 900^0C the furnace is cooled down to room temperature at a faster rate of 100^0C/h. Then, the platinum crucible is removed from the furnace and allowed to boil in HNO_3 solution for several hours to extract the crystals from the residual flux. The grown crystals are brown in colour [2,3]. The resulted crystals were subjected to powder X-ray diffraction to confirm the phase of the grown crystal and XRF analysis at different parts to study the compositional inhomogeneity. Other basic characterization studies like DTA/TGA, UV-Visible and dielectric studies were also performed on unpoled crystals.

3. RESULTS AND DISCUSSION

3.1 CRYSTAL GROWTH RUNS

The growth results show that the multinucleation problem faced initially was efficiently controlled in bottom supported Bridgman method by optimizing the various parameters mainly the furnace gradient and translation rate. Fig 1 Shows the schematic diagram of the bottom supported Bridgman Setup. The furnace gradient 15°C/cm and translation of 0.6-1 mm/hr is found to be optimum to induce one nucleus and growth of that particular nucleus. Initially when the furnace gradient was less (7 °C/cm) and the translation rate was high (2mm/hr) and resulted with more number of crystals with poor size crystals. The growth runs with two different soaking temperature 1180°C and 1200 °C have no effect on the size of the harvested crystal rather the colour obtained is light orange and brown colour respectively. Initially the growth runs were performed with 85 g total charge to optimize the growth runs. Fig 2 shows the harvested crystals with the platinum crucible. The optimized growth runs end up with two crystals alone with a larger size of 14x10x8 mm^3. Also attack of platinum crucible by PbO at higher temperature was another serious problem and hence a crucible with thickness greater 1mm is preferable for growth of these crystals. Fig 3 shows the harvested crystals from a single growth run. Attempts were being taken to flow O_2 from bottom to induce a large gradient at a single point at the bottom of the crucible.

3.2 POWDER X-RAY DIFFRACTION

Powdered grown crystals were subjected X-ray powder diffraction and the results confirm that the grown crystals are in perovskite phases. This result is in good agreement with JCPDS data and the reports already available in literature[4]. Moreover, the pyrochlore phase with poor ferroelectric properties were not observed in the grown crystal. Fig 4 shows the X-ray powder diffraction spectrum of the grown crystals.

3.3 COMPOSITIONAL ANALYSIS

The composition of the grown crystal was verified with X-ray fluorescence spectrometer. The chemical inhomogeneity is very common in these types of ferroelectric solid solutions[5]. XRF was performed at two selected regions and the results were compared with the theoretical values. The result given in table 1 shows that the grown crystals with sight variation in chemical composition at different parts. But the more lead content and less Zn, Nb oxide is found to be common in two different parts. So to overcome this problem, growth runs can be performed with excess of respective oxides at their starting.

3.4 DTA/TG AND DIELECTRIC ANALYSIS

DTA/TGA analysis of PZN-PT 91: 9 single crystals was performed in static air atmosphere. One strong broad endothermic peak was observed around 1225°C and a small peak was observed at 1150°C. The broad peak shows that a major incongruent melting takes place at this temperature and the minor peaks found around 1150°C confirm the decomposition of perovskite phase. The TGA results show that the weight loss of PZN-PT crystal is less than 5 % till 1100°C and it is around 30% on further increase in temperature till 1400°C[5]. The dielectric analysis was performed for a unpoled PZN PT single crystal. The relaxor behavior is retained and T_c is found to be at 200°C and the dielectric loss is less than 1%. Matsushita et al have observed that the Ti^{4+} variation may occur radially even in single wafer and this may also be a reason for slightly higher T_c value[6]. UV – Visible transmission study was performed for a well-polished unpoled grown crystal and the transmittance of the crystal increases from 5-15% in visible range.

4. CONCLUSION

The single crystals of PZN-PT solid solution were grown by bottom supported Bridgman method. The grown crystals were found to be of pure perovskite phase. Attempts were made to grow large size crystals by bottom cooling method. Due to various reasons like compositional in homogeneity, Pb loss at high temperature, growth method, particularly for the crystals grown at Morphotropic Phase Boundary (MPB) will affect the properties drastically even with small change in composition[6]. The PT composition is found to be non-uniform within the different parts of a single crystal. This was confirmed from XRF results. Such chemical inhomogeneity is very common in these types of ferroelectric solid solutions. The thermal stability of the grown crystals were measured using simultaneous thermo-gravimetric analysis (TG) and differential thermal analysis (DTA). Dielectric studies were performed on the as grown unpoled crystals. The reproducibility of crystal grown by modified flux Bridgman method is good; this method can be effectively used for the growth of large size single crystals and also for mass production.

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TABLES

Table 1. Comparision of XRF data with theoretical values.

Oxides	Theoretical value (%)	Sample 1 (%)	Sample 2 (%)
1. PbO	66.49	67.90	67.59
2. Nb_2O_5	24.02	23.14	23.40
3. TiO_2	2.14	2.01	2.02
4. ZnO	7.35	6.95	7.00

FIGURES

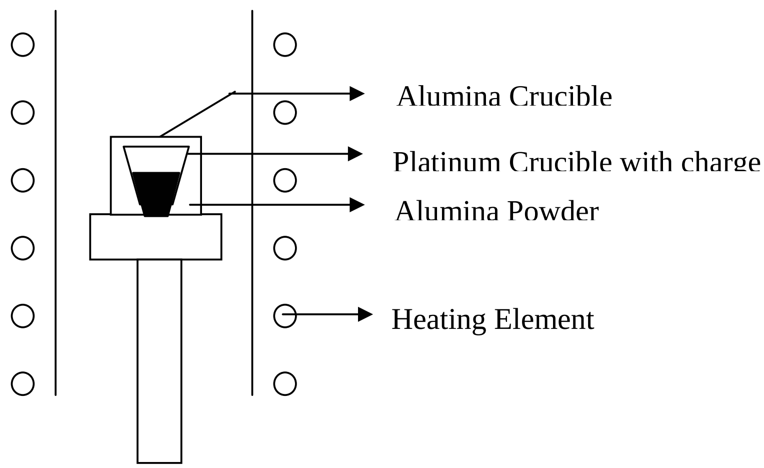

Fig.1 – Schematic diagram of Buttom supported Bridgman method for growth of PZN-PT single crystal

Fig.2 - Grown PZN-PT single crystal with platinum crucible

Fig.3 - Grown PZN-PT single crystal by bottom supported Bridgman method

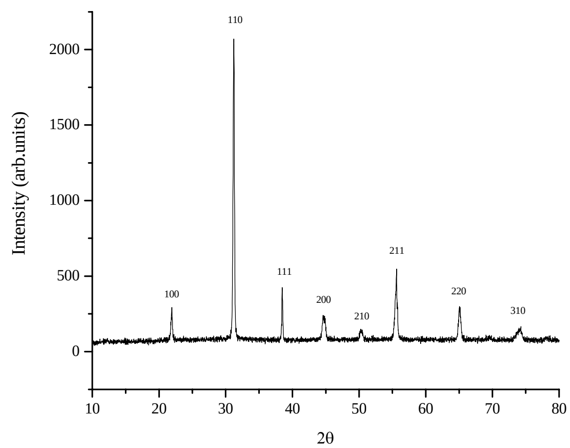

Fig.4 - X-ray powder diffraction pattern of grown PZN-PT single crystal