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High composition uniformity of 4″ of PIN-PMN-PT single crystals grown by the modified Bridgman method

Zhenrong Li*, Kexin Song, Haisheng Guo, Yangbin Liu, Ming Ma, Shiji Fan, Zhuo Xu

Electronic Materials Research Laboratory, Key Laboratory of Education Ministry and International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, China

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Relaxor based ferroelectric single crystals $Pb(In_{1/2}Nb_{1/2})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PIN-PMN-PT) with composition near morphotropic phase boundary exhibit extraordinary piezoelectric properties. Due to the composition segregation during crystal growth, the composition and properties of PIN-PMN-PT single crystal boules are poor uniformity. In this work, uniformity of dielectric and piezoelectric properties of the crystal boules with 4″ diameter by 100 mm long were clearly improved along the crystal growth direction by the modified Bridgman method. For 70% length of the boule, T_{RT} and Tc were around 100 °C and 160–180 °C along the growth direction, respectively. The variety of piezoelectric constant d_{33} is about 1500-1800pC/N in the same range of the boule. So that PIN-PMN-PT crystals will be more cost-effective and beneficial for ultrasonic applications in higher temperature region.

1. Introduction

$Pb(In_{1/2}Nb_{1/2})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$(PIN-PMN-PT) relaxor-based single crystal with morphotropic phase boundary (MPB) composition have excellent piezoelectric properties of d_{33}~2000 pC/N and k_{33}~90%. As PIN-PMN-PT single crystals are mainly grown by the Bridgman technique, compositional segregation phenomena are inevitable, resulting in inconsistency of dielectric and piezoelectric properties [1–6]. Zhang and Luo [1,2] reported dielectric and piezoelectric properties of the crystal boule with [011] seed by dividing it into five parts, rhombohedral A, B, C, MPB and tetragonal region without referring to specific composition. 0.24PIN–PMN–PT and 0.33PIN–PMN–PT crystal boules with [011] seed [3,4] show similar composition change, with increasing PT and decreasing PMN along growth direction. The chemical composition analyzed by ICP method revealed that PIN content with a maximum variation of 1.7% was relatively stable throughout the crystal boule, meanwhile PMN 6.7% and PT 8.4%. Similarly, Wan et al. [5] also reported that the variation of PIN is less than 1.3% from bottom to top of the crystal boule along the growth direction of PIN-PMN-PT crystal. The variation of PMN and PT are 10.5% and 9.9%, respectively.

Although the &$2lt;001&$2gt;-oriented growth can produce desirable (001) wafers with high lateral uniformity in each wafer, it cannot eliminate the wafer-to-wafer variation. Usually, only a portion of each boule meets the desired piezoelectric and dielectric properties. In order to improve the homogeneity of relaxor-PT single crystal boules, the modified Bridgman method with continuous feeding growth (CFG) was used [7], in which powder or pellets are charged slowly into the melt during crystal growth. The challenge of this method is to minimize the thermal disturbance to the melt, as well as to prevent PbO evaporation during the feeding operation. This technique was demonstrated successfully by the growth of 80 mm diameter PIN-PMN- PT crystals and variation of Ti (PT) concentration in the crystal is reduced to +/- 2.5%. A modified Bridgman method using multiround growths and gradient composition raw materials were adopted to control the segregation and improve the compositional homogeneity [8]. However, it has very high risk of crucible leakage in the second run of the growth and no cost-effective in the practical of the growth.

In this paper, the modified Bridgeman method was used to grow 4″ (4 in.) in diameter PIN-PMN-PT single crystal along [110] direction in order to obtain high homogeneity of the crystal boule. The composition, dielectric and piezoelectric properties along growth direction were characterized.

2. Experimental

High purity oxide raw materials PbO, MgO, In_2O_3, Nb_2O_5 and TiO_2 were used. The feeding PIN-PMN-PT powders were synthesized by using columbite precursor procedure. The starting composition is

* Corresponding author.
E-mail address: zhrli@mail.xjtu.edu.cn (Z. Li).

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0.25PIN-0.44PMN-0.31PT. 4″ in diameter single crystals were grown along [110] direction by the modified Bridgman method. Resistance-heated multi-zone furnaces were used with soaking temperature 1380–1400 °C and soaking time 10–20 h and maintained at certain temperatures for growth. The crucible pulling down velocity is 3–8 mm/day. S-L temperature gradient was adjusted in the range of 10–25 °C/cm. The as-grown crystals were oriented along [001] direction based on the X-ray three-dimensional rotation orientation method. Then the crystal were cut into 5×5×3 mm^3 with the equal distance of adjacent samples numbered (1#~15#, in ascending order from the bottom to top of the boule in length of 100 mm) for the composition and electrical measurements. The composition analyses of all samples were performed by electron probe X-ray microanalyzer (EPMA, JEOL JXA-8230 superprobe). The six point positions on 5×5 mm^2 surface were chosen for test of each sample. The final composition of single crystal was determined to be the average value of six points [5]. For electrical properties measurements, silver electrodes were fired on both faces of the samples at 600 °C for 25 min. The samples were poled by a dc electric field of 10 kV/cm for 5 min at room temperature. The temperature dependence of dielectric permittivity (ε_r) and loss tangent (tanδ) were measured at frequencies of 1, 10, and 100 kHz using an impedance analyzer (HP4284A) in a temperature range from room temperature to 300 °C. The piezoelectric constant d_{33} was measured by a quasi-static piezo-d_{33} meter (ZJ-2 Model).

3. Results and discussion

The PIN-PMN-PT single crystal boule with 4 in. in diameter by 120 mm in length grown along [110] is shown in Fig. 1.

Since PIN-PMN-PT is a complete solid-solution system, it inevitably exhibits an inhomogeneous composition distribution along the boules grown by the Bridgman method, resulting in the variation of dielectric and piezoelectric properties along growth direction. PIN is least sensitive to chemical segregation during crystal growth. PT increases and PMN decreases along crystal growth direction [2–5].

The composition variation along the PIN-PMN-PT single crystal growth direction is illustrated in Fig. 2. There are two regions in the boule obviously. For the first region of the boule (sample 1#–5#), the PIN content changed in the range of 23–26 mol%, while PMN content decreased from 50 mol% to 45 mol% and PT content increased from 26.8 to 31.6 mol%. The trend of composition segregation is similar to our previous works except for a little big PIN variation [5]. The compositions of the first region of the boule was effected by the seed composition because of melting of top of the seed during seeding, so changes of them are here often. For the second region of the boule (6#–15#), PIN, PMN and PT content was almost constant about 24 ± 1 mol%, 44 ± 1 mol% and 32 ± 1 mol%, respectively, in proportion of 70% in the boule. Composition segregation of the boule was obviously weakened and the homogeneity of composition is effectively improved. It is well known that the MPB composition in PIN-PMN-PT is around PT 31–32 mol%, so 70% length of the boule has MPB composition.

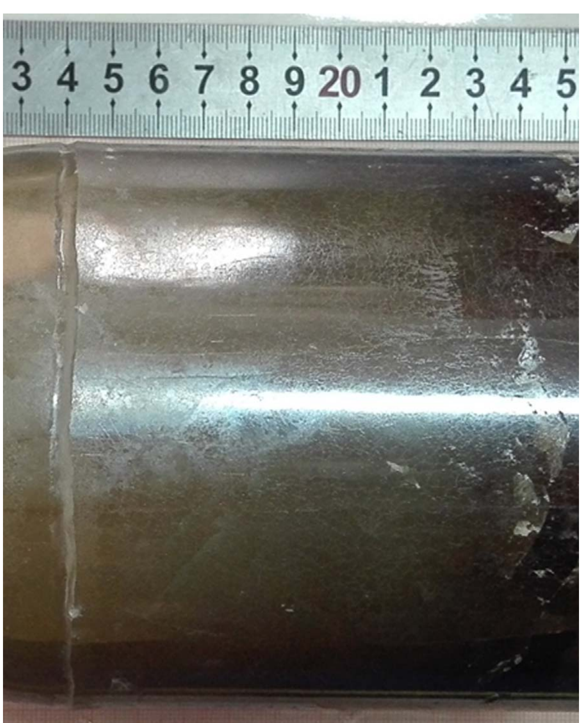

Fig. 1. 4" PIN-PMN-PT single crystal boule.

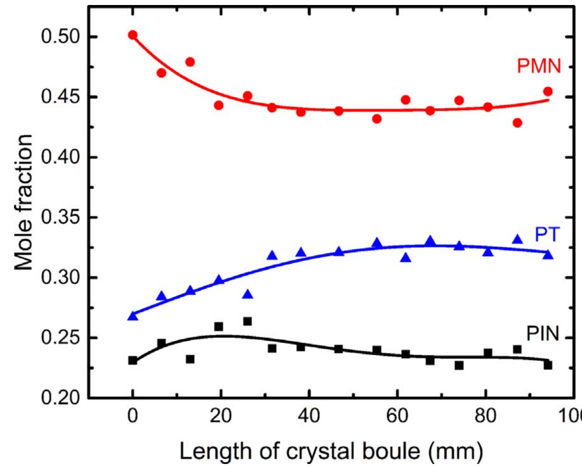

Fig. 2. The composition variation of PIN-PMN-PT single crystal along growth direction.

PIN content was relatively stable, PMN content decreased and PT content increased from bottom to top of PIN-PMN-PT crystal boule along the crystal growth direction [3,4]. So the composition variation results in that one third of the whole boule with high piezoelectric properties could be used for piezoelectric devices. Our previous results are also similar and the variation of d_{33} is from 1000 to 2000 pC/N along the crystal growth direction [5]. During crystal growth process, the content variation of each composition depends on its effective segregation coefficient k_{eff}. The k_{eff} is related to, besides its natural character, the temperature gradient on the interface of solid-liquid (S-L) and in the liquid phase, crystal growth direction and its growth speed et.al.. The temperature gradient on the interface of solid-liquid (S-L) will affect the diffusion layer thickness of S-L front end. The temperature gradient in the liquid phase will affect the concentration gradient for each composition due to its thermal diffusivity. The variation of growth speed will change their k_{eff}. Based on above factors, in order to keep the stability of k_{eff}, we try to change S-L temperature gradient (10–25 °C/cm), to control the growth speed (3–8 mm/day) and to change the each composition diffusion velocity through adjusting the temperature gradient in the liquid phase during crystal growth. The results show that the composition homogeneity of the boule was improved, as shown in Fig. 2.

Temperature dependence of the dielectric properties for 1–15# poled single crystal samples are shown in Fig. 3. For all of the samples, two dielectric peaks are presented, which are related to phase transition temperature T_{RT} (rhombohedral to tetragonal phase) and Tc (ferroelectric to paraelectric phase). From 1# to 5# sample, we can find that the phase transition temperature T_{RT} is gradually decreases from about 110–100 °C and T_c is gradually increases from about 130–160 °C. From 6# to 15# sample, T_{RT} is stable around 100 °C for all the samples and Tc changes in the range of 160–180 °C, as shown in Fig. 4. The dielectric relaxation characteristics of ferroelectric to paraelectric phase transition are clear for 1#–5# samples resulting from low PT