Ferroelectric and piezoelectric properties of novel relaxor ferroelectric single crystals PMNT

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Abstract Relaxor ferroelectric single crystals PMNT with the size of ϕ40 mm×80 mm have been grown by a modified Bridgman method and their ferroelectric and piezoelectric properties have been characterized. The properties varied with the compositions and cut types. On the (001) cut, PMNT76/24 single crystals exhibited a dielectric constant ε of about 3 400, a dielectric loss of tanδ <0.7%, a piezoelectric constant d_{33} of 980 pC/N, an electromechanical coupling factor k_t of 0.55 and T_c of about 110℃. Whereas the properties of PMNT67/33 single crystals on (001) cut were better: ε of about 5 300, tanδ<0.6%, d_{33} up to 3 000 pC/N, k_t 0.64, k_{33} 0.93 and T_c of about 150℃. The piezoelectric properties on other cuts such as (110) and (111) were much lower than those on the (001) cut. The rhombohedral PMNT crystals grown by this method showed more excellent piezoelectric properties than those grown by high temperature solution method and higher value of k_t than the rhombohedral PZNT single crystals. It has also been found that the fluctuation in ferroelectric and piezoelectric properties was related to such factors as composition uniformity and poling degree.

Keywords: relaxor ferroelectrics, single crystals, PMNT, piezoelectric properties, ferroelectric properties.

Medical B-type ultrasonic transducers with greatly enhanced resolution and broad bandwidth will come out before long, which should be attributed to the significant renovation of their probe materials, i.e. the replacement of conventional PZT series piezoelectric ceramics by novel relaxor ferroelectric single crystals (1-x)$Pb(Mg_{1/3}Nb_{2/3})O_3$-x$PbTiO_3$ (PMNT) and (1-y)$Pb(Zn_{1/3}Nb_{2/3})O_3$-$y$$PbTiO_3$(PZNT). The enormous enhancement of piezoelectric and electrostrictive properties in these single crystals marks an exciting breakthrough and has attracted great attention in the international ferroelectric field[1]. They will be applied noticeably to nondestructive defect inspections, sonars and solid actuators as well.

PMNT single crystals belong to solid solutions with ABO_3 complex perovskite-type structures, and their growth is difficult. The growth methods were kyropoulos[2], or predominantly, high temperature solution method[3—5]. The optimum piezoelectric properties of PMNT single crystals grown by high temperature solution method were: piezoelectric constant d_{33} = 1 500 pC/N, dielectric constant ε =4 000[4], dielectric loss tan δ = 0.014, electromechanical coupling factors k_t = 0.568 and k_{33} = 0.923[5]. In comparison with PZNT single crystals grown by the same method, PMNT crystals still dropped behind a little in piezoelectric properties. For example, the maximum value of d_{33} of PZNT crystals reached up to 2 500 pC/N[6]. However, the previous experiments demonstrated that it might be more difficult to grow PZNT single crystals for all their excellent piezoelectric properties.

As for the methods used to grow PZNT crystals, some problems yet remained unresolved. In these methods, the addition of flux (PbO) to starting materials was necessary and unavoidable as in the case of high temperature solution[6,10,11] or Bridgman method[12]. Since PZNT had poor thermal stability, it could grow in a stable or metastable state only in solutions containing flux (for example PbO) or under high pressure. It was difficult for high temperature solution methods to enlarge the crystal sizes without crystal seeds and to control crystal defects effectively[13]. On the other hand, the problems in composition uniformity and property stability became eminent after the PbO flux, which could reach 55% (molar percent) of the solution, was added in Bridgman methods[12]. When excess PbO flux was used, the solution saturation and crystallizing temperature would vary with the descending of crucibles, making it difficult to maintain stable shape and position of solid-liquid interfaces. Therefore, it is necessary to seek a more adaptive method to grow this type of single crystals, PZNT or PMNT.

In this note, a modified Bridgman method has been adopted to grow PMNT single crystals to overcome the disadvantages in conventional methods. The modifications in this method included: (i) crystal seeds were used to control spontaneous nucleation and to enlarge the single crystal sizes quickly by means of geometric washout; (ii) PMNT powders were pre-synthesized from starting materials PbO, MgO, Nb_2O_5 and TiO_2 powders to enhance the composition uniformity of PMNT crystals; (iii) pure PMNT melt was directly used and no excess PbO as flux added to keep almost unchanged the freezing temperature and the shape or position of solid-liquid interfaces during descending of Pt crucibles. This is the key for the growth of high-perfect and high-quality single crystals in Bridgman techniques; (iv) some measures were taken to suppress volatilization of PbO and leak of Pt crucibles, which were often encountered due to the erosion of crucibles by PbO. The piezoelectric and electromechanical coupling properties of PMNT acquired by this method will be reported and reviewed. Furthermore, the factors leading to property fluctuations will be discussed for reference in adjustment of material structures and the optimization of piezoelectric properties.

1 Crystal growth and experiment

A modified Bridgman method was adopted to grow PMNT crystals. The compositions of PMNT crystals were designed as PMNT76/24~PMNT65/35 near the morphotropic phase boundary (MPB) of PMN-PT pseudo-binary system to obtain optimum piezoelectric properties. The PMNT single crystals grown by the above method reached the size of ϕ40 mm$\times$80 mm, which could meet the needs of the probes with various sizes in medical ultrasonic transducers.

The structure of PMNT crystals was measured by XRD and the plate orientations were determined by X-ray orientation devices combined with XRD. The domain configurations and crystal defects were observed under optical microscopes, and the crystal compositions analyzed by X-ray fluorescence spectrometry. The square plates 0.3—0.5 mm thick, 10—20 mm wide with a ratio larger than 10 of width to thickness were used for the measurement of ferroelectric and piezoelectric properties. The poling electric field was 10 kV/cm. The dielectric properties were measured by an impedance analyzer (HP4192A) at frequencies from 100 Hz to 100 kHz while the ferroelectric hysteresis loops were tested by a Sawyer-Tower type meter at a frequency of about 1 Hz, and piezoelectric constant d_{33} was measured by a quasi-static d_{33} meter of Berlincourt type at about 55 Hz. The electromechanical coupling factors of thickness mode k_t and longitudinal bar mode k_{33} were calculated from resonance and anti-resonance frequencies.

2 Results and discussions

(i) Ferroelectric properties. The ferroelectric hysteresis loops of PMNT76/24 single crystals indicated that their coercive field E_c was 1.8 kV/cm, remanent polarization P_r 22.5 μC/cm^2. The measurement of their dielectric properties showed that their dielectric constant at room temperature ε_{RT} was about 3 400, their maximum dielectric constant ε_{max} = 29 000 and dielectric loss tanδ lower than 0.7%, meanwhile their dielectric constant showed a peak of a certain breadth at temperature T_m of about 110℃, and certain frequency dispersions (fig. 1).

The ferroelectric hysteresis loops of PMNT67/33 single crystals indicated that their E_c was 3.5 kV/cm, P_r 31 μC/cm^2. Their ε_{RT} was about 5 300, tanδ lower than 0.6%, ε_{max} 32 000, and T_m about