Ferroelectric phase transition in relaxor ferroelectric single crystals 0.76PMN-0.24PT

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Abstract The features of the single crystals 0.76PMN-0.24PT in dielectric, ferroelectric, pyroelectric properties and domain structures indicate that they are located between typical ferroelectrics and normal ones. The unpoled crystals present a transitional domain configuration between microdomains and typical macrodomains while the crystals on (001) cuts undergo field-induced phase transition under poling, showing two special temperature points T_d and T_m during the succedent heating procedure. The dielectric constant starts to decrease drastically at T_d

during cooling, or the transformation from induced macrodomain to transitional domain takes place at T_d during heating. Ferroelectric-paraelectric phase transition or depolarization continues within the whole temperature range of $T_d - T_m$, where ferroelectric phase in the form of transitional macrodomains coexists with paraelectric phase. Then the crystals macroscopically transoform into paraelectric phase containing ferroelectric microdomains at a temperature above T_m. However, owing to the influence of crystallite orientation on field-induced phase transition, the temperature T_d does not appear in the same temperature-electric field history in multicrystal ceramics with the same composition as the above single crystals.

Keywords: relaxor ferroelectrics, single crystals, ferroelectric phase transition, domain structure, PMNT.

It has been found that relaxor ferroelectric single crystals with perovskite structure exhibit much more excellent piezoelectric and electrostrictive properties than conventional PZTs ceramics[1,2]. Especially remarkable are the two systems of single crystals: $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PMNT) and $(1-y)Pb(Zn_{1/3}Nb_{2/3})O_3-yPbTiO_3$ (PZNT), whose piezoelectric constant $d_{33}>2\,000$ pC/N and whose electromechanical coupling factor k_{33} reaches up to 0.93—0.95 so that they can be put into important applications in medical ultrasonic imaging transducers, nondestructive defect inspections, sonars and solid actuators. Perfect single PMNT crystals have been grown by a modified Bridgman method recently. They have reached ϕ40 mm × 80 mm in size, with the maximum d_{33} value of 3 000 pC/N, k_{33} of 0.93, k_t of 0.64, ε of 5 300 and $\tan\delta < 0.6\%$[3, 4]. These large single PMNT crystals are very much favorable for the foundational researches for relaxor ferroelectrics.

As for the typical relaxor ferroelectrics PMN, a common review has not been achieved as yet on the essence of their ferroelectric phase transition. It is regarded as a diffuse phase transition by some authors, who ascribe the broad dielectric peak at T_m on ε-T curve to microregions with different Curie points resulting from the fluctuation in composition and structure[5]. But other authors[6,7] consider that the paraelectric-to-ferroelectric phase transition (PFPT) of PMN does not take place at T_m since no macro symmetry breaking occurs and the crystals keep cubic structure and optical isotropy free from spontaneous polarization while they pass through T_m or even are under the temperature far below T_m (4 K, for example)[8]. It is also found under HRTEM and TEM that there are ordered microregions (ordered domains) in nanometer order with nonstoichiometric Mg^{2+}:Nb^{5+}=1:1 in PMN whereas there are no macrodomains[9,10]. Therefore, in the view of the latter authors, the PFPT in PMN is "smeared"[6, 11], and can be induced below the temperature T_d ($T_d<T_m$) as long as the electric field exceeds the threshold strength E_{th}[7, 11, 12].

The phase diagram for PMNT ceramics under low temperature has been obtained by dielectric and pyroelectric characterization[13, 14]. No variation in the number of dielectric peaks was found after the PMNT ceramics with the PT content of 22.2—25 mol% were poled.

PMN-PT solid system consisting of PMN, a typical relaxor ferroelectrics, and PT, a typical normal ferroelectrics, is sure to have a transformation from the typical relaxor ferroelectrics behavior to the normal one with the variation in PMN-to-PT ratios. However, it is rare to study the features of ferroelectric phase transition in the compositional evolution as yet, and the studies on single crystals are even rarer for the lack of single crystals with series of components. In view of the differences between ceramics and single crystals in the grain size and structures, an interesting question can be put forward as well: Are the features of phase transition obtained from PMNT ceramics also completely tenable for PMNT single crystals?

1 Crystal growth and experimental

PMNT crystals were grown by a modified Bridgman method. The starting materials were PbO, MgO, Nb_2O_5 and TiO_2 and the compositions were designed as 0.76PMN-0.24PT and 0.65PMN-0.35PT. The obtained crystals have reached the size of ϕ40 mm × 80 mm and are good in perfection.

The structure of as-grown PMNT single crystals was measured by XRD while the composition was analyzed by the X-ray fluorescence spectrometry. The plate orientations were determined by X-ray orientation devices for single crystals and XRD and then the crystals were processed into the polished or thin plates. The domain configurations were observed under polarizing microscopes and their