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Growth and properties of $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ ($x=0.07$–0.11) ferroelectric single crystals by a top-seeded solution growth method

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Abstract

The relaxor-based single crystals of complex perovskite solid solutions, $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ [PMN–PT] and $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ [PZN–PT], exhibit extraordinary piezoelectric performance: displaying extremely high piezoelectric coefficients, very large electromechanical coupling factors, and exceptionally high strain. These materials outperform the currently used $Pb(Zr_{1-x}Ti_x)O_3$ [PZT] ceramics, making them the materials of choice for the next generation of electromechanical transducers for a broad range of advanced applications. In this article, the PZN–xPT ($x=0.07$–0.11) single crystals near the morphotropic phase boundary were prepared using the top-seeded solution growth technique. Ferro-/dielectric and piezoelectric properties, crystal chemistry, domain structure, and electromechanical coupling properties were systematically characterized. It is showed that the top-seeded solution growth method is an effective alternative technique for preparing the high quality PZN–xPT ferroelectric crystals, which is effective in controlling nucleation/growth of the PZN–xPT single crystals and suppressing the undesired Pb deficient pyrochlore phase by providing a Pb rich environment.

Keywords: C. Dielectric properties; C. Ferroelectric properties; C. Piezoelectric properties; PZN–PT crystals; Crystal growth

1. Introduction

Relaxor-based ferroelectrics have attracted much attention in recent years, in terms of studying the mechanism that explains their exceptional properties, and their practical applications. In particular, single crystals of these perovskite solid solutions exhibit a piezoelectric effect 10 times larger than conventional ceramics, which makes them promising end members for the next generation of piezoelectric materials and devices [1–3]. $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) are typical relaxors, the temperature dependences of real and imaginary parts of the complex dielectric permittivity show high and broad maxima (T_m) that shift to higher temperatures with increasing the measurement frequency. Presently, it is generally accepted that strong dielectric dispersion of T_m is a consequence of the dynamics of polar nanoregions (PNRs) [2]. Their solid solution single crystals with normal ferroelectric $PbTiO_3$, such as $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PMN–xPT) and $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PZN–xPT), are the most important relaxor-based perovskite ferroelectrics. When it was poled properly along the [001] orientation, it would present ultrahigh piezoelectric coefficients and electromechanical deformations,

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which is one order-of-magnitude larger than those of conventional high piezoelectric $(1-x)PbZrO_3$–$xPbTiO_3$ (PZT) ceramics [1,3]. Therefore, the growth of practical PMN–*x*PT and PZN–*x*PT ferroelectric crystals and understanding the mechanism of ultrahigh piezoelectric response have attracted much attention in recent years.

In 1959 and 1961, relaxors PMN and PZN crystals were first grown from the flux of PbO [4], and their relaxor behaviors were first reported in 1961 [5]. So far, many researchers always focused on relaxor-based ferroelectric single crystal growth using a flux method [6–9]. In 1997, Park and Shrout also reported that ferroelectric solid solutions PMN–*x*PT (x=0.33) and PZN–*x*PT (x=0.09) single crystal exhibited ultrahigh piezoelectric response d_{33} and electromechanical coupling factors k_{33}, which achieved 1500–1570 pC/N and 90%–92% near the MPB regions, respectively [10–12]. The orientation of rhombohedral PMN–*x*PT and PZN–*x*PT crystal with optimized d_{33} is along the [001] direction rather than its spontaneous polarization [111] direction [13]. Moreover, their excellent ferroelectric, electric-field induced strain, pyroelectric, and electric-optic properties were also discovered [1,3].

However, the size of PMN–*x*PT and PZN–*x*PT crystals were not large enough to characterize systematically until 1990s [14,15]. From then on, the crystal growth and characterization became the key issues in the field of ferroelectrics and piezoelectrics. In 1997, PMN–*x*PT single crystals were grown using a modified Bridgman method in SICCAS, and the size reached Φ40 mm × 80 mm [16,17]. At the same time, flux method was improved to grown PZN–*x*PT crystals, and the size of as-grown crystal reached 43 × 42 × 40 mm^3[18]. Unfortunately, the undesired pyrochlore phase is another crucial difficulty in preparation of PZN–*x*PT ferroelectric single crystals which hindered the development of growing large size PZN–*x*PT single crystals near MPB region. In 2002, Bijun Fang et al. grew PZN–*x*PT single crystals with a size up to Φ28 mm × 25 mm using a modified Bridgman method [19]. However, it was difficult to achieve high quality PZN–*x*PT single crystals in a reproducible and productive manner. The macroscopic properties of the crystals with the same chemical composition vary significantly according to different research groups. For instance, the piezoelectric coefficient d_{33} of PZN–0.07PT crystals showed deviations up to 23% from the average value [20,21], which produced difficulties for practical applications and theoretical investigations. Such a property discrepancy was always attributed to the solute segregation during the crystal growth process. Up to now, the mass production of PZN–*x*PT single crystals has not been realized by various methods, although PZN–*x*PT single crystals are the most promising for the applications of next-generation transducers and other piezoelectric devices [3,22].

To obtain large size, high-quality single crystals, we have developed a top-seeded solution technique as an alternative to realize controlled growth of large PZN–*x*PT crystals using in-lab made flux furnace. In this article, we will introduce the crystal preparation, crystal chemical, phase structure, domain structure, and related electrical properties of binary PZN–*x*PT (x=0.07–0.11) single crystals.

2. Experimental procedure

2.1. Crystal growth

The PZN–*x*PT (x=0.07–0.11) single crystals were grown by the top-seed solution method. The starting materials, PbO (99.9%), TiO_2 (99.9%), ZnO (99.9%), Nb_2O_5 (99.9%), were weighed according to the desired stoichiometric composition of PZN–*x*PT. Here, the molar ratio of ZnO/Nb_2O_5 is 1.08 which can suppress undesired pyrochlore phase effectively. A mixture of PbO and H_3BO_3 (with a molar ratio of PbO:H_3BO_3=10:1) was used as high-temperature flux. The molar ratio of the flux to solute was chosen as 3:1. The detailed growth process is as follows: The weighed chemicals were thoroughly mixed and loaded into a platinum crucible with size of Φ40 × 50 mm^2, which were then placed into a vertical tube furnace equipped with an automatic temperature controller to melt. The furnace

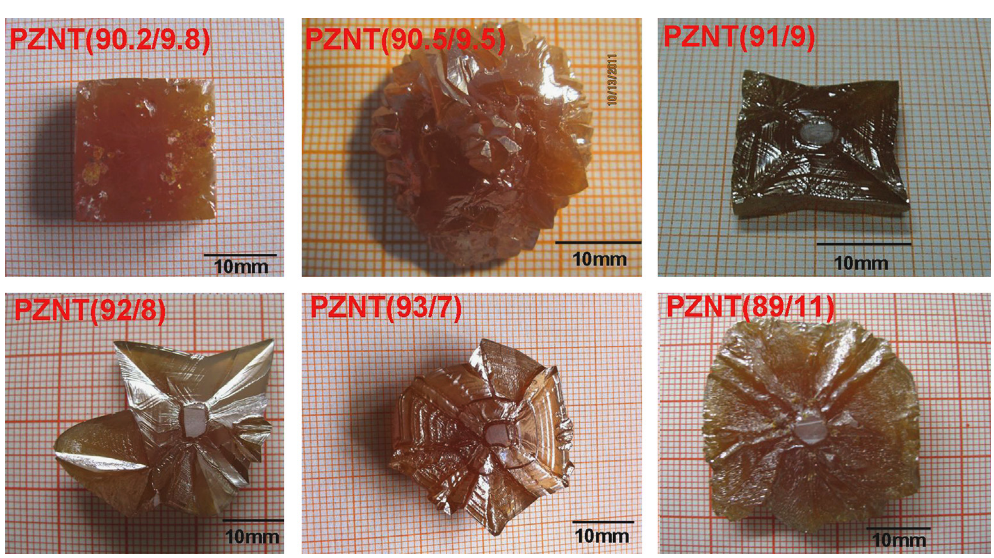

Fig. 1. As-grown PZN–*x*PT (x=0.07–0.11) ferroelectric single crystals obtained by the TSSG method.