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Structures and electrical characterizations of high-Curie temperature $(Na_{0.5}Bi_{0.5})TiO_3$–$PbTiO_3$ low-lead single crystals with compositions near the morphotropic phase boundary

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Abstract

A series of $(Na_{0.5}Bi_{0.5})TiO_3$–$PbTiO_3$ (NBT–PT) single crystals with compositions near the morphotropic phase boundary (MPB) region were grown by the modified Bridgman technique. The dependence of structure on composition was measured, and the MPB region of the NBT–PT system was confirmed. The dielectric properties of the NBT–PT single crystals were investigated, and the phase transition behaviour of the NBT–PT single crystals during heating was examined. With increasing addition of PT, the coercive field of the NBT–PT crystals decreased to levels much lower than that of the pure NBT system; such a change allowed easy poling of the NBT–PT crystals and the resultant piezoelectric properties were significantly enhanced. The electromechanical coupling factor of the crystals showed relatively constant thermal stability at the depolarization temperature (T_d). Finally, studies of the domain evolution of NBT–0.09PT showed the disappearance of domains at the T_d, which indicates that phase transition at the T_d is related to changes in domain structures.

Keywords: C. Dielectric properties; C. Ferroelectric properties; D. Perovskites

1. Introduction

Perovskite relaxor ferroelectric systems, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN–PT) and $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PZN–PT), have recently gained increased attention because of their excellent piezoelectric properties and electromechanical coupling factors. These properties endow the systems with great potential applicability in various devices [1–6]. However, the relative low temperature usage range of these systems, which is influenced by their low Curie and ferroelectric rhombohedral to tetragonal phase transition temperatures, limits their applications in harsh environments [7,8]. Furthermore, these systems contain large amounts of lead, which raises environmental safety concerns particularly during sintering, when lead evaporation occurs [9,10]. In this regard, finding low-lead or lead-free piezoelectric ceramics with high Curie temperatures and good piezoelectric properties is a worthwhile endeavour.

Since sodium bismuth titanate $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT), an A-site complex rhombohedral perovskite relaxor ferroelectric, was first discovered by Smolenskii et al. in the 1960s, this lead-free system has attracted considerable attraction as a potential material for various device applications because of its high Curie temperature (T_C=320 °C), large remnant polarization (P_r=38 μC/cm^2) and high coercive field (E_C=7.3 kV/mm) [11–15]. Previous research reveals the phase transition sequence of NBT during heating: (i) a phase transformation from the rhombohedral ferroelectric phase to the antiferroelectric tetragonal phase occurs at 220 °C; (ii) the antiferroelectric tetragonal phase transforms

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into a paraelectric tetragonal phase at 320 °C, where a diffuse maximum of dielectric permittivity can be observed and (iii) the paraelectric tetragonal phase transforms into the cubic phase at 520 °C with no visible change in dielectric response [16–18]. Unfortunately, relatively large leakage currents and high E_C cause difficulties when poling NBT [19]. Therefore, recent investigations have concentrated on NBT-based solid solutions with compositions near the morphotropic phase boundary (MPB), such as $(Na_{0.5}Bi_{0.5})TiO_3$–$PbTiO_3$ (NBT–PT), $(Na_{0.5}Bi_{0.5})TiO_3$–$BaTiO_3$ (NBT–BT) and $(Na_{0.5}Bi_{0.5})TiO_3$–$(K_{0.5}Bi_{0.5})TiO_3$ (NBT–KBT), to achieve improved piezoelectric properties [20–25].

Amongst the NBT-based solid solution systems currently under study, $(1-x)(Na_{0.5}Bi_{0.5})TiO_3$–$xPbTiO_3$ (NBT–xPT) is a system that possesses a rhombohedral–tetragonal MPB region located at x=0.13–0.15 [26–28]. The phase diagram proposed by Hong and Park [26] indicated that the T_C of this system has a minimum value of 280 °C at a composition of around $x=0.10$. However, to date, research on the crystal growth of NBT–PT systems is limited, and the electrical properties of NBT–PT systems, including their piezoelectric and ferroelectric properties, and their temperature–property relationships have rarely been reported. To facilitate the synthesis of single crystals with good quality, the modified Bridgman technique has been adopted to improve the crystal growth. This technique is reported to be an effective method for growing single crystals in ferroelectric systems such as PMN–PT, PZN–PT, and NBT–BT [7,29,30]. In the present study, low-lead-containing NBT–PT single crystals with compositions near the MPB region are successfully grown, and the dependence of NBT–PT crystal properties, including compositional segregation and structural and electrical properties, on composition are investigated systematically.

2. Experiment procedure

2.1. Crystal growth

NBT–PT crystals were grown directly from melts by the modified Bridgman technique. High purity (>99.5%) Na_2CO_3, PbO, Bi_2O_3, TiO_2 were used as starting materials and mixed according to the nominal formulas of NBT–0.05PT, NBT–0.09PT, NBT–0.12PT and NBT–0.16PT. Mixed powders were first calcined at 700 °C for 6 h and then placed in a platinum crucible that was sealed at the top to prevent evaporation of PbO and Bi_2O_3. NBT or NBT–PT crystals grown along the [1 1 0] direction were selected as seed crystals to inhibit spontaneous nucleation.

The furnace used for crystal growth is similar to that described in Ref. [7]. The furnace was set to 1400 °C during crystal growth. After soaking for about 10 h, the crucible was pulled down at a rate of 0.1–0.3 mm/h, and the temperature gradient was controlled to about 40–100 °C/cm. After crystal growth, the furnace temperature was decreased to room temperature at a rate of 10–40 °C/h.

2.2. Characterizations procedures

Structural characterization of the crystals was performed by X-ray diffractometry (XRD, Bruker Advance D8 diffractometer).

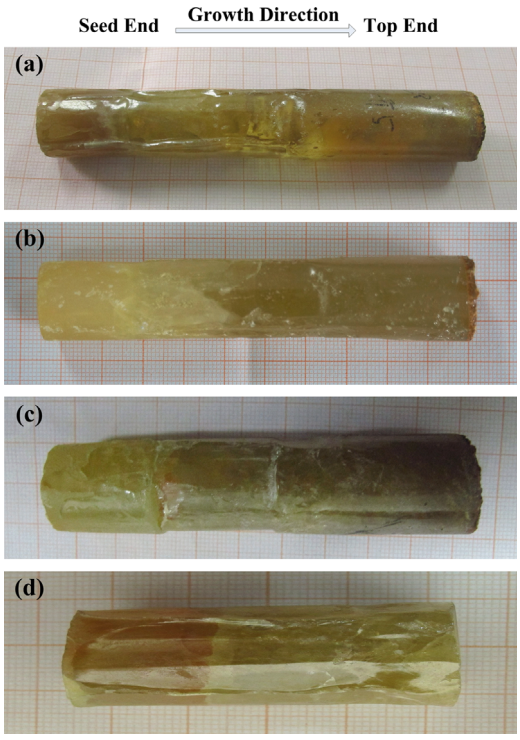

Fig. 1. As-grown NBT–xPT single crystals: (a) NBT–0.05PT, (b) NBT–0.09PT, (c) NBT–0.12PT and (d) NBT–0.16PT.

Table 1
Compositions and effective segregation coefficients of the NBT–xPT crystals and raw powders.

Crystals	Nominal composition of Pb^{2+} in raw powders	Real composition of Pb^{2+} in as-grown crystals	K_{eff}
NBT–0.05PT	0.05	0.061	1.22
NBT–0.09PT	0.09	0.074	0.82
NBT–0.12PT	0.12	0.106	0.88
NBT–0.16PT	0.16	0.143	0.89

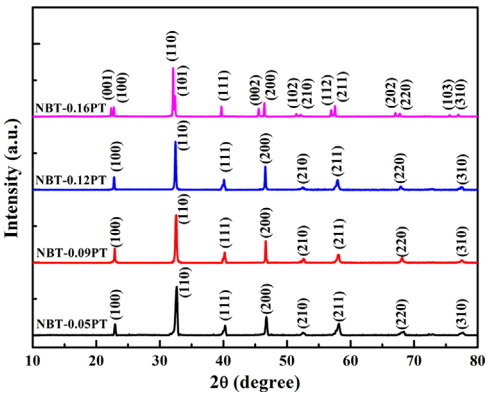

Fig. 2. X-ray diffraction patterns of the NBT–xPT single crystals.