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Effects of Mn doping on the structure and electrical properties of high-temperature $BiScO_3$–$PbTiO_3$–$Pb(Zn_{1/3}Nb_{2/3})O_3$ piezoelectric ceramics

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ABSTRACT

The effects of Mn addition on the structure, ferroelectric, and piezoelectric properties of the $0.35BiScO_3$–$0.60PbTiO_3$–$0.05Pb(Zn_{1/3}Nb_{2/3})O_3$ ceramics were studied. The results demonstrate that the addition of small amounts of Mn did not cause a remarkable change in crystal structure, but resulted in an evident evolution in microstructure and ferro-piezoelctric properties. The addition of Mn can induce combinatory "hard" and "soft" piezoelectric characteristics due to aliovalent substitutions. The optimal electrical properties are obtained in the 0.25 mol% Mn-doped composition with a high Curie temperature, indicating that Mn doping contributes to the electrical properties of the ceramics. It can be expected that the improved piezoelectric material can be a promising candidate for high-temperature piezoelectric applications.

1. Introduction

Recently, both the industrial and scientific communities have expressed an urgent demand for the electronic devices using higher temperatures than the current commercially available $Pb(Zr,Ti)O_3$ (PZTs) due to their relatively low Curie temperatures T_c (~300 °C). Fortunately, a new Bi-based high-temperature piezoelectric ceramic system, such as $BiScO_3$–$PbTiO_3$ (BS–PT) has been developed with enhanced dielectric, piezoelectric properties, and high Curie temperature suitable for high temperature application [1,2]. Among these, many intensive studies were focused on BS–PT ceramics due to its excellent piezoelectric property and high Curie temperature (450 °C). Extending the investigation of bismuth and lead oxide based ternary solid solutions, a typical strategy of improved properties was to form new solid solution ceramics by adding the third component to BS–PT, such as BS–PT–PMNb [3], BS–PT–PMN [4], BS–PT–BST [5], $(K_{0.5}Bi_{0.5})TiO_3$ [6], and $LiSbO_3$ [7], and so on.

Doping is an effective and simple method to tailor electrical properties of piezoelectric ceramics. Doping can be either "hard" by addition of acceptor dopants (low valence state) creating anion vacancies or "soft" by addition of donor dopants (high valence state) eliminating oxygen vacancies [8]. For example, lead volatility in Pb-based perovskites produces Pb vacancies which are naturally compensated by oxygen vacancies leading to acceptor or "hard" characteristics. Intrinsic point defects and dopant reaction are believed to impact domain structure and domain wall stability in piezoelectric materials. So, the ultimate results of doping modification can lead to many variations, for example, improving electrical properties [9], shifting the Curie temperature [10,11], increasing mechanical character [12,13], and forming space charge field [14,15].

Mn is an effective additive being used widely in many perovskite piezoelectric ceramics to tailor the electrical characterization [16–18]. In the case, $MnCO_3$ was chosen as a modifier to be introduced into the ternary $0.35BiScO_3$–$0.60PbTiO_3$–$0.05Pb(Zn_{1/3}Nb_{2/3})O_3$ (BS–PT–PZN) high-temperature piezoelectric system. In our previous work, this studied composition near morphotropic phase boundary (MPB) exhibited excellent ferroelectric and piezoelectric properties with piezoelectric constant d_{33} = 490 pC/N, planar electromechanical coupling factors k_p = 57.4%, remanent polarization P_r = 40.1 μC/cm^2, coercive field E_c = 28.5 kV/cm, and a high Curie temperature T_c ~417 °C [19]. Here, we investigated the effects of Mn addition on the structure, ferroelectric, and piezoelectric properties of this ternary high-temperature piezoelectric system and possible doping mechanism was intensively discussed.

2. Experimental

In this paper, the $0.35BiScO_3$–$0.60PbTiO_3$–$0.05Pb(Zn_{1/3}Nb_{2/3})O_3$ + z mol% $MnCO_3$ (BS–PT–PZN, z = 0, 0.25, 0.50, 0.80, 1.00, and 1.50) ceramics were prepared by conventional mixed oxide ceramic processing techniques. The reagent-grade materials, Bi_2O_3, Sc_2O_3, PbO, TiO_2 and $ZnNb_2O_6$ precursor were weighed as starting powders according to the nominal compositions, with

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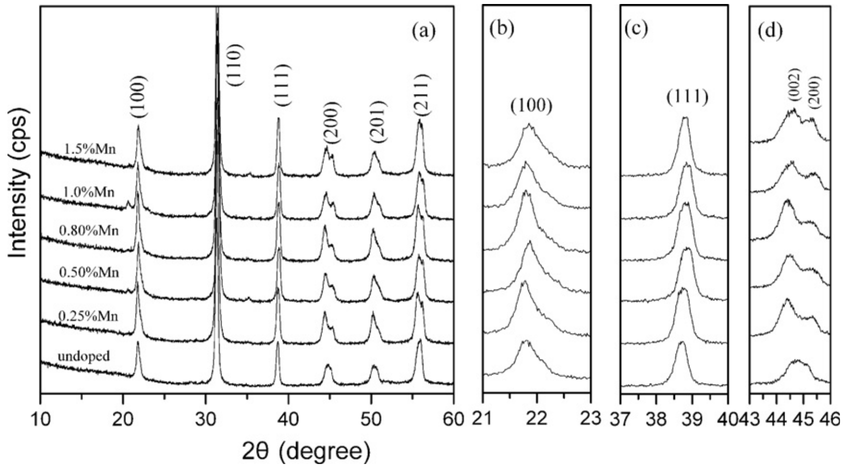

Fig. 1. XRD spectra of pure and Mn-doped BS–PT–PZN ceramics.

1 wt.% excess amounts of Bi_2O_3 and PbO to compensate the volatilization during sintering. Here, $ZnNb_2O_6$ precursor was prepared by columbite method [20] with the mixture of ZnO and Nb_2O_5 powders sintered at 1250 °C for 2 h. The powders were mixed, dried, and then calcined at 850 °C for 2 h. After re-milling the powders, the binder was added and then the powders were pressed into pellets with 12 mm in diameter and 1.2 mm in thickness at 200 MPa. The pellets were sintered at 1000–1100 °C

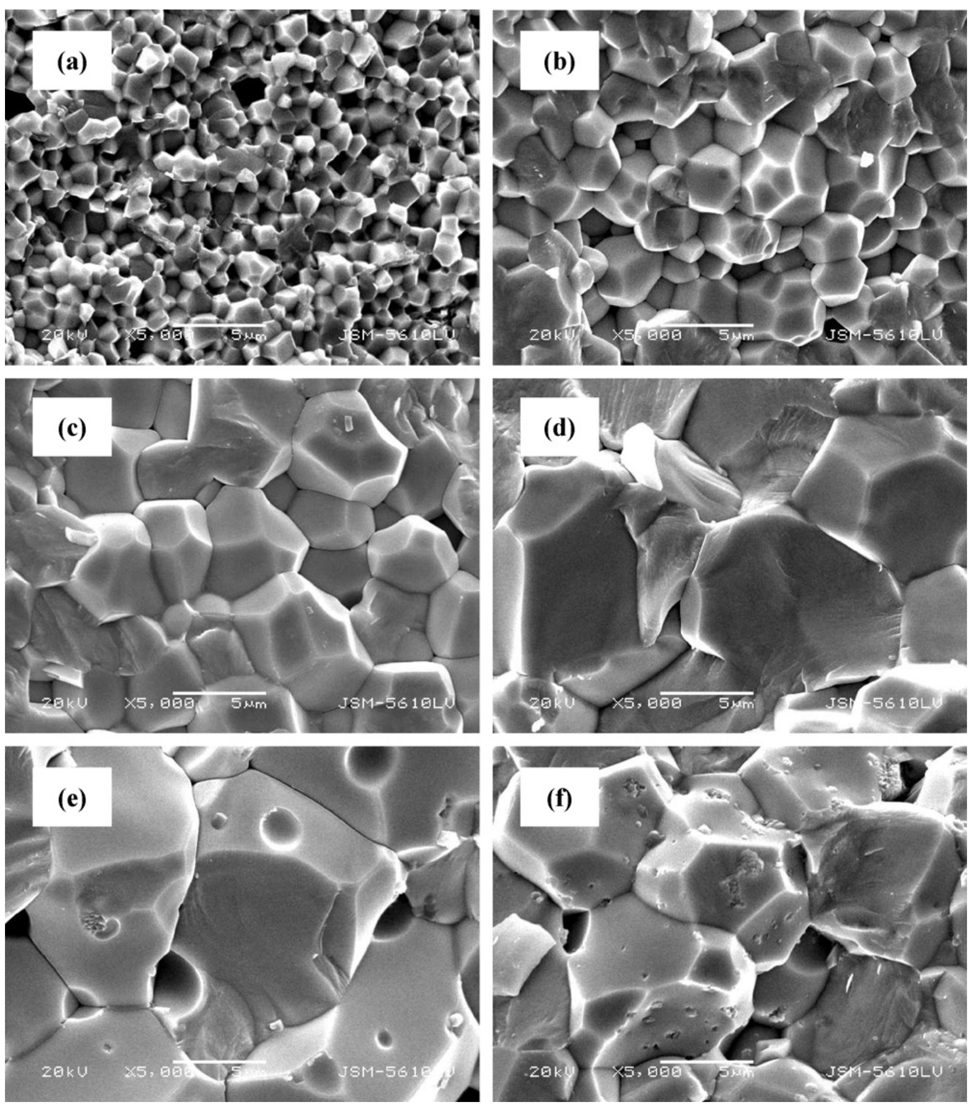

Fig. 2. SEM pictures of the fresh fractured surfaces of undoped and doped BS–PT–PZN ceramic samples sintered at 1080 °C for 2 h: (a) undoped sample; (b) 0.25 mol% Mn; (c) 0.50 mol% Mn; (d) 0.80 mol% Mn; (e) 1.0 mol% Mn; (f) 1.5 mol% Mn.