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Effects of Nb doping on the microstructures and electrical properties of $0.44Bi(Sc_{0.75}Co_{0.25})O_3–0.56PbTiO_3$ piezoelectric system

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ABSTRACT

The effects of Nb doping on the microstructures and electrical properties of $0.44Bi(Sc_{0.75}Co_{0.25})O_3–0.56PbTiO_3$ piezoelectric system were investigated. Our results indicate that a small amount of Nb ions can result in phase transition and improve the electrical properties. Enhanced ferroelectric–piezoelectric properties are obtained at low-level doping content with a slight reduction of transition temperature. The composition doped with 0.5 mol% Nb ions shows the optimal electrical properties with piezoelectric constant $d_{33} = 390$ pC/N, planar electromechanical coupling factor $k_p = 0.51$, and a high transition temperature ~351 °C, indicating a promising candidate for high-temperature applications.

1. Introduction

The current most important piezoelectric material, lead zirconate titanate (PZT) has been one of the most widely used piezoelectric ceramics since 1950s due to its excellent piezoelectric properties [1,2]. PZT has a Curie temperature T_c below 400 °C and shows thermal degradation at the temperature below 200 °C [2]. Higher Curie temperatures come at the expense of significantly reduced piezoelectric properties. However, there is an urgent need for piezoelectric devices used in the extreme conditions, especially high working temperature which is higher than that of current available PZTs, such as space exploration, oil or gas pipeline health monitoring, automotive smart brake, and so on [3]. Therefore, it is necessary and urgent to develop new high-temperature piezoelectric ceramics with excellent properties to meet the current needs.

Recent materials based on $BiScO_3–PbTiO_3$ (BS–PT) have been developed with a high Curie temperature T_c and optimal ferroelectric–piezoelectric properties compared to the current available PZTs [4–8]. It was anticipated that due to high T_c these materials are likely to have better thermal stability and resistivity up to higher temperatures than the low-T_c one. Enhanced properties and high transition temperature make BS–PT more promising for further investigations as a candidate of high-temperature piezoelectric systems. Extending the investigations of BS–PT perovskite compositions, the substitutions of Sc by the other metal ions (i.e. Fe, Sc, Co, Ga, In, etc.) were developed and found to show enhanced properties and/or higher transition temperatures. To enhance the room-temperature properties, one method of tailoring the performance is doping. Doping can result in “soft” or “hard” characteristics with the variation of corresponding properties; for example, improving electrical properties [9,10], and shifting the Curie temperature [11,12], improving mechanical character [13], and forming space charge field [14,15], etc.

In our study, we investigated the structure and electrical properties of the partially replacement of Sc by Co in the $(1-x)Bi(Sc_{0.75}Co_{0.25})O_3–xPbTiO_3$ ternary system. Our results indicated that the optimal electrical properties were obtained at the composition $0.44Bi(Sc_{0.75}Co_{0.25})O_3–0.56PbTiO_3$ near morphotropic phase boundary (MPB) with $d_{33} = 327$ pC/N, $k_p = 0.48$, and a high transition temperature ~465 °C. Here, extending the investigation of this composition, Nb ions were introduced to study the effects of donor-doping on the microstructure and electrical properties of $0.44Bi(Sc_{0.75}Co_{0.25})O_3–0.56PbTiO_3$ and the possible mechanism of doping was discussed.

2. Experimental

In this paper, the $0.44Bi(Sc_{0.75}Co_{0.25})O_3–0.56PbTiO_3 + z$ mol% $NbO_{2.5}$ (BSC–PT $z = 0$, 0.25, 0.50, 1.0, 1.5, and 3.0) ceramics were prepared by conventional mixed oxide ceramic processing techniques. The reagent-grade materials, Bi_2O_3, Sc_2O_3, PbO, Co_2O_3, TiO_2 and Nb_2O_5 powders were weighed as starting powders according to the nominal compositions, with 1 wt.% excess amounts of Bi_2O_3 and PbO to compensate the volatilization during sintering. The powders were mixed, dried, and then calcined at 850 °C for 2 h. After re-milling the powders, 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 1050–1200 °C for 2 h. To min-

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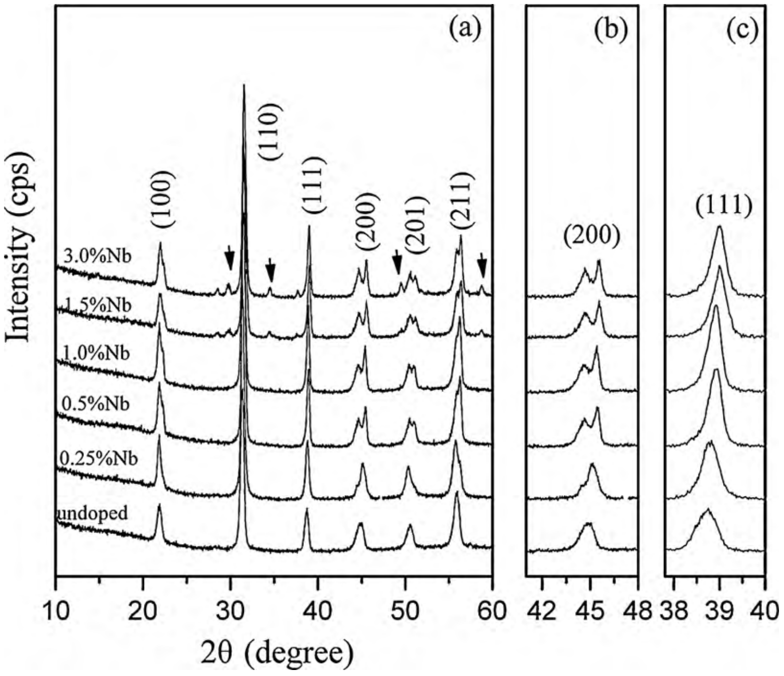

Fig. 1. XRD spectra of the Nb-doped BSC–PT ceramics sintered at 1150 °C for 2 h.

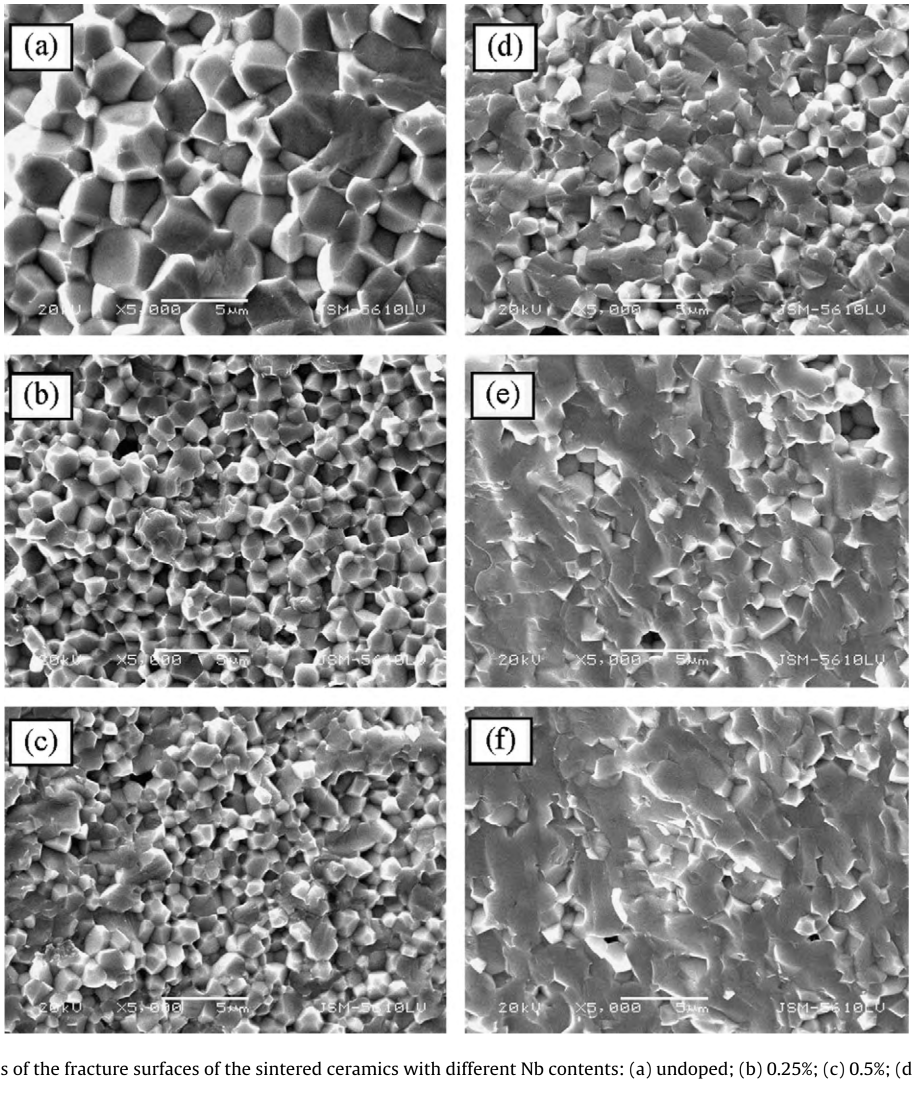

Fig. 2. SEM photographs of the fracture surfaces of the sintered ceramics with different Nb contents: (a) undoped; (b) 0.25%; (c) 0.5%; (d) 1.0%; (e) 1.5%; (f) 3.0%.

imize weight loss due to PbO and Bi_2O_3 volatility, a source powder of the same composition was put inside the crucible.

Phase structures were detected by a Philips vertical X-ray diffractometer (XRD, PW3050/60, MPSS) using Cu Kα1 radiation confirmed the formation of perovskite-type phases without any impurities, 2θ in the range of 10–60° with a step of 0.02°. The microstructure observations of the fresh fractured surfaces of sintered specimens were examined using a scanning electron microscopy (SEM, Akashi Seisakusho JSM-5610LV). The dielectric and piezoelectric properties were measured on pellets with silver electrodes printed and fired at 500 °C for 20 min. Temperature frequency dependence of dielectric properties was measured using an LCR meter (HP 4284A) from room temperature to 550 °C. The specimens were poled under a field of 3–4 kV/mm for 15 min at 120 °C. The piezoelectric constant d_{33} of poled samples were measured using a quasi-static piezoelectric d_{33} meter (Model ZJ-3D, Institute of Acoustics Academic, Beijing, China). The electromechanical coupling factor k_p of poled samples were measured using an impedance analyzer (HP4294A) by the resonance and anti-resonance technique on the basis of IEEE standards. The hysteresis loops of polarization of unpoled samples were performed using RT66A test system (Radiant Technologies) in silicon oil at room temperature under a field of 4 kV/mm.

3. Results and discussion

Fig. 1 shows XRD spectra of the Nb-doped BSC-PT ceramics sintered at 1150 °C for 2 h. All the compositions show single perovskite phase except for the highest doping one, indicating the limit of solubility. Here, we can identify the structure symmetry by the (1 1 1) splitting for rhombohedral and (2 0 0)/(1 0 0) for tetragonal symmetry. The MPB corresponds to a mixed phase region of rhombohedral symmetry and tetragonal symmetry for the undoped composition. As the Nb content increases, the splitting of (2 0 0) peak becomes stronger, indicative of the increase of tetragonality.

Fig. 2 shows SEM photographs of the fresh fracture surfaces of the sintered Nb-doped BSC–PT ceramics with different Nb contents. It can be seen that the average grain size for the undoped sample is about 2.5 μm, while it is less than 1 μm for all the doped compositions, indicating the function of Nb ions as a grain-growth inhibitor. Similar results were reported by D. Hennings on the La-doping PT ceramics [16] and by Chen et al. on Nb doping BS–PT [17]. Donor dopants, those of higher charge than that of the ions they replace, are compensated by cation vacancies, whereas acceptor dopants, ions of lower charge than that of replaced ions, are compensated by oxygency vacancies. Nb addition can induce donor characteristic which form cation vacancies due to its high valence state. These cation vacancies can accumulate in the grain boundary and lead to the formation of cation vacancies pair under the actions of Coulomb force. The enhanced cation vacancies pair accumulates in the grain boundary which decreases the mobility of grain boundary when sintering and inhibits grain growth [18,19]. Therefore, the func-

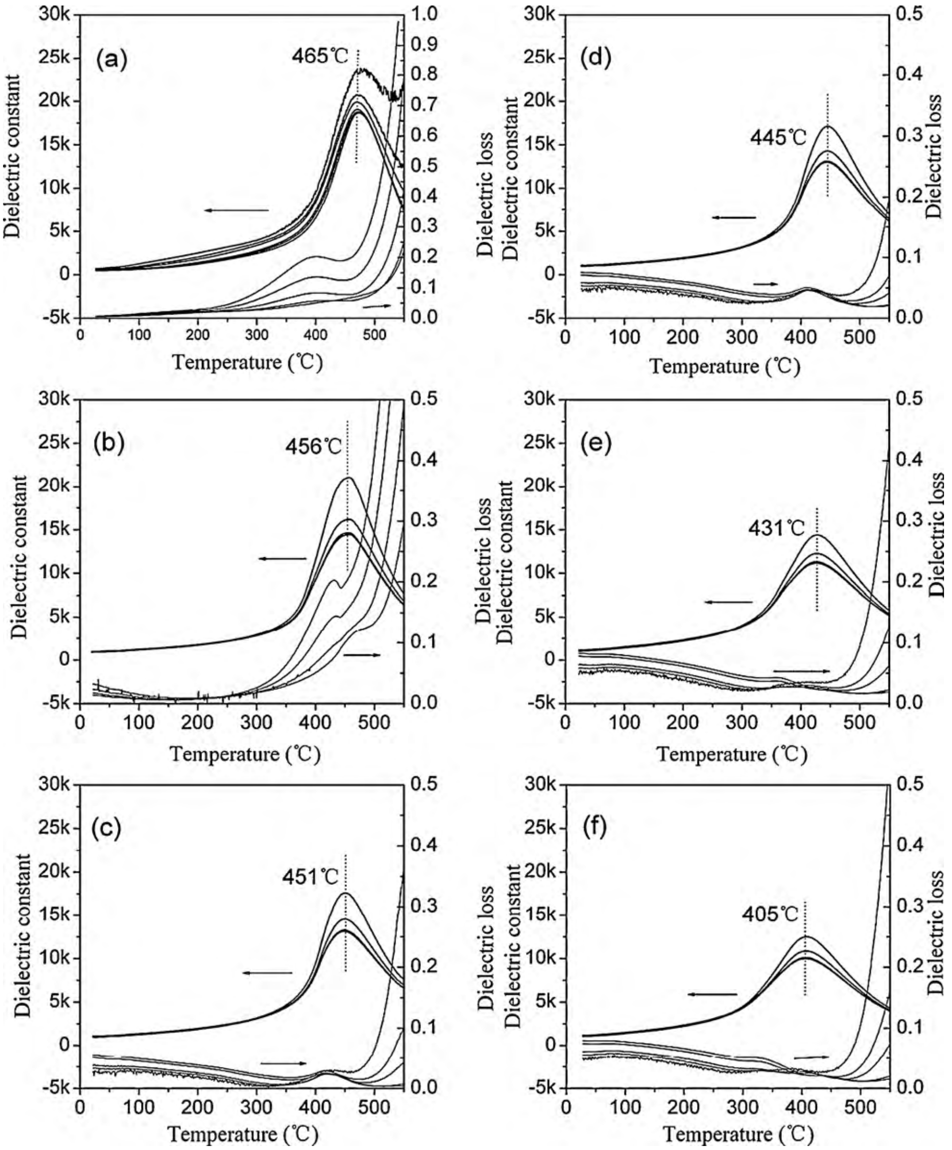

Fig. 3. Dielectric temperature spectra of the sintered samples with different Nb contents (100 kHz to 1 MHz): (a) undoped; (b) 0.25%; (c) 0.5%; (d) 1.0%; (e) 1.5%; (f) 3.0%.

tion of Nb ions as a grain-growth inhibitor can be ascribed to the accumulation of cation vacancies in the grain boundary.

Fig. 3 shows dielectric temperature spectra of the sintered samples with different Nb contents. In general, the introduction of an additive into a ferroelectric material with a perovskite structure can result in a decrease in the temperature of maximum dielectric constants, the dielectric constant at T_c, and the existence of a more diffuse phase transition in the vicinity of T_c. Thus, the temperature of maximum dielectric constant at T_c decrease and T_c also decreases from 465 °C to 405 °C with the addition of Nb ions. The dielectric peaks become suppressed and broader due to the presence of diffuse characteristics.

Fig. 4 shows the ferroelectric *P*–*E* hysteresis loops for Nb-doped ceramics under 4 kV/mm measured at 10 Hz. This measurement was performed under the condition that samples were poled to full saturation under electric fields without electrical breakdown of the samples. Remnant polarization P_r and coercive field E_c as a function of Nb content are shown in Fig. 5. It can be observed that P_r increases until it reaches a peak value at $z = 0.50$, then decreases for higher Nb concentration. Simultaneously, E_c decreases obviously

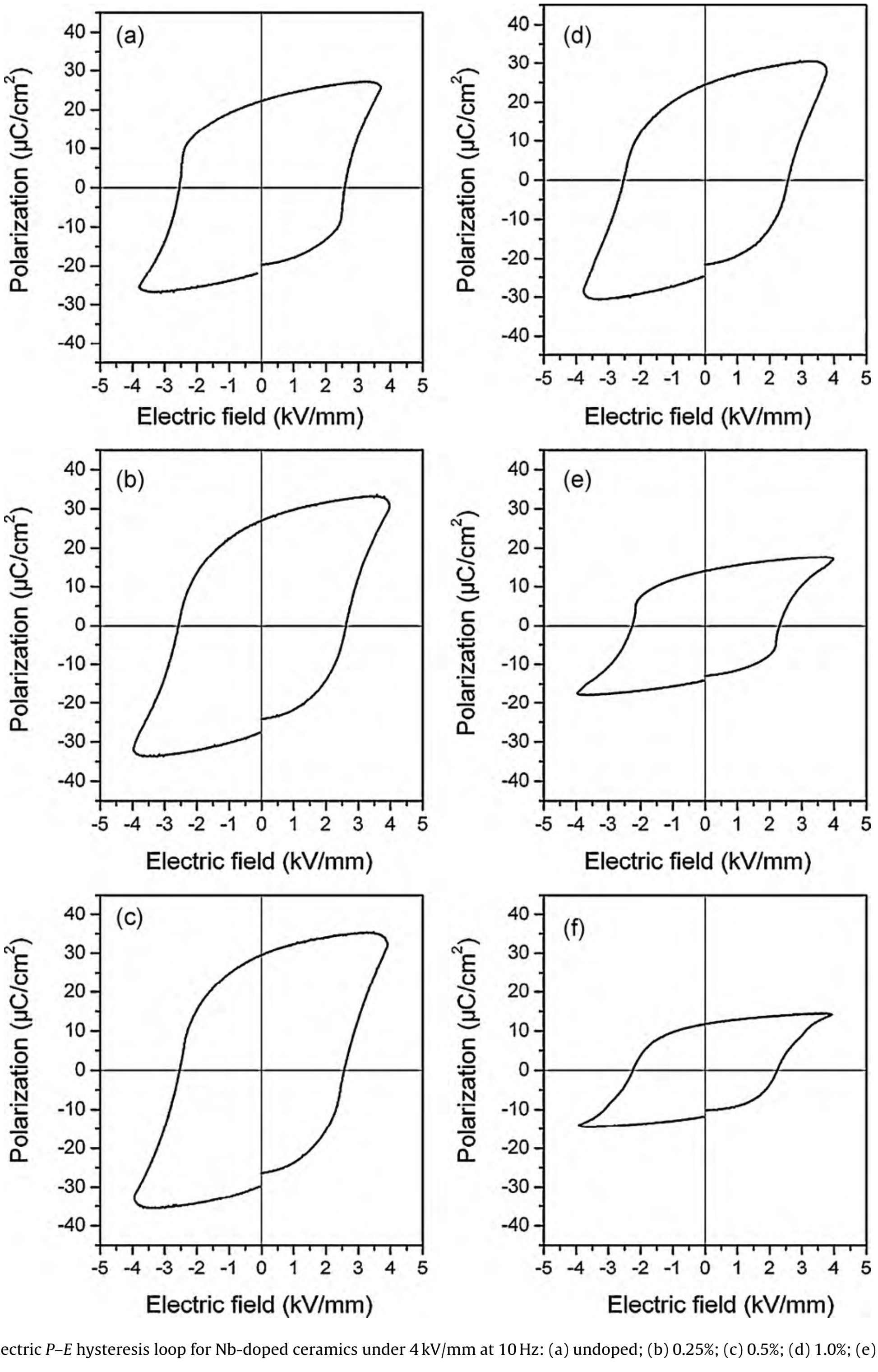

Fig. 4. Ferroelectric *P*–*E* hysteresis loop for Nb-doped ceramics under 4 kV/mm at 10 Hz: (a) undoped; (b) 0.25%; (c) 0.5%; (d) 1.0%; (e) 1.5%; (f) 3.0%.

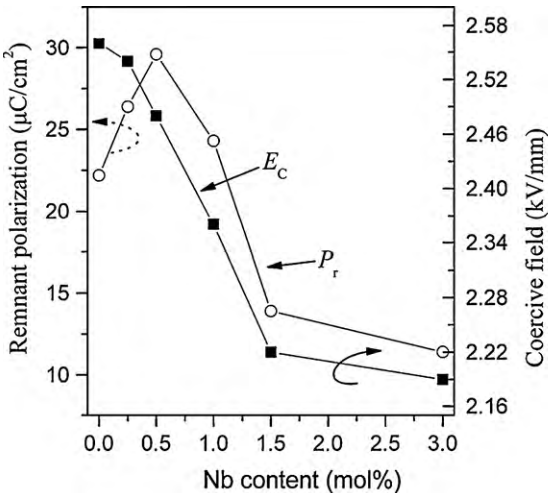

Fig. 5. Remnant polarization P_r and coercive field E_c of the sintered ceramics with different Nb contents.

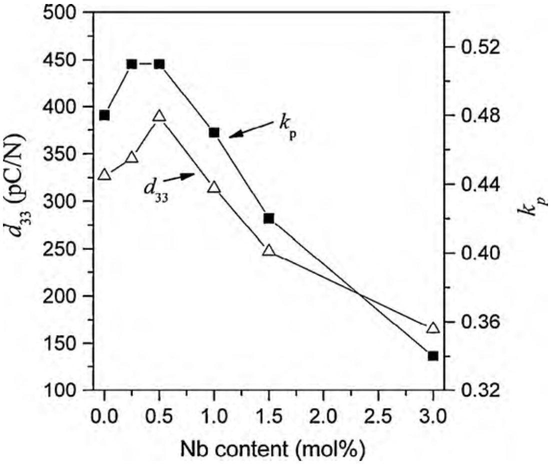

Fig. 6. Piezoelectric properties of the sintered ceramics with different Nb contents.

with increasing Nb content. Generally, ferroelectric parameters are very sensitive to doping effects. For instances, increasing the oxygen vacancies introduces space charges for acceptor doping, which restricts the domain motion and produces a slim loop, whereas donor-doping produce metal ion vacancies to maintain the charge neutrality, which increases the squareness of the P–E hysteresis loop and decreases the coercive field [20–27]. Therefore, the decrease of E_c can be ascribed to the soft characteristic due to the donor-doping.

The piezoelectric properties of ferroelectric materials may be influenced by a great variety of factors such as a crystal structure, the kind of dopants, the condition of fabrication, microstructure, etc. In this case, the dopant can lead to the changes of microstructures and phase evolution which can vary the piezoelectric characterization of this system. Here, the effects of Nb content on the piezoelectric properties are shown in Fig. 6. The values (d_{33} and k_p) are increased in a narrow composition range from $z = 0$–0.5, then decreased with further doping. The values d_{33} and k_p exhibit maxima at $z = 0.5$, which are 390 pC/N and 0.51, respectively. This is consistent with the results of P–E characteristics. The degradation of d_{33} and k_p for higher doping level may be due to the accumulation of excess Nb ions in the grain boundary resulting in the decrease of ferroelectricity.

4. Conclusion

The Nb ions were introduced into the $0.44\text{Bi}(\text{Sc}_{0.75}\text{Co}_{0.25})\text{O}_3$–$0.56\text{PbTiO}_3$ composition near MPB and the effects of Nb doping were investigated. The dopant can lead to the changes of microstructures and phase evolution which can vary the piezoelectric properties of this system. The phase structure transfers gradually to tetragonal symmetry as Nb content increases. The additions of Nb ions are introduced as a grain-growth inhibitor due to the accumulation of cation vacancies in the grain boundary. Enhanced ferroelectric–piezoelectric properties are obtained at low-level doping content due to the donor-doping characteristic, whereas the transition temperature slightly decreases. The composition $0.44\text{Bi}(\text{Sc}_{0.75}\text{Co}_{0.25})\text{O}_3$–$0.56\text{PbTiO}_3$ + 0.5 mol% Nb ions shows the optimal electrical properties with $d_{33} = 390$ pC/N, $k_p = 0.51$, and a high transition temperature ~351 °C, which is comparable to the pure BS–PT ceramics.

Acknowledgements

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