Effect of valence state and incorporation site of cobalt dopants on the microstructure and electrical properties of 0.2PZN–0.8PZT ceramics


Abstract

A CoCO$_3$-added Pb(Zn$_{1/3}$Nb$_{2/3}$)$_{0.20}$(Zr$_{0.50}$Ti$_{0.50}$)$_{0.80}$O$_3$ (0.2PZN–0.8PZT) system was prepared and investigated. The results reveal that Co ions are present in the mixed valence form of +2 and +3, and their relative mole ratio depends on doping content. Co doping induces a phase transformation from the MPB to the tetragonal phase side, and the corresponding domain size increases accordingly. The solubility limit of Co ions in the perovskite matrix is near 0.2 wt.% in CoCO$_3$ form. Below the solubility limit, Co ions enter the B sites of the oxygenic octahedral center, and the charge-compensating oxygen vacancies accelerate mass transport, which assists in the densification of the specimens. Above the solubility limit, excess Co ions gather in the grain boundaries and triple junctions, which facilitate the formation of a liquid phase with excess PbO and lead to remarkable grain growth. The resulting size effect plays a dominant role in improving the piezoelectric properties, which compensates for the hardening effect of acceptor doping. The optimum piezoelectric parameters are obtained at 0.8 wt.% CoCO$_3$-doped 0.2PZN–0.8PZT system: $d_{33} = 310$ pC N$^{-1}$, $k_p = 0.66$, and $e_{max} = 14,600$.

Keywords: Perovskites; Ferroelectricity; Phase transformations; Grain growth; Grain-boundary structure

1. Introduction

Pb(Zr,Ti)O$_3$ (PZT)-based ceramics are an important piezoelectric material widely applied in the electronic industry, mainly in the manufacture of actuators and sensor devices [1–3]. By introducing various additives to the PZT matrix, piezoelectric and dielectric properties can be tailored to a wide extent [4–7]. The effect of dopants is a complex matter. However, a number of important generalizations have been proposed regarding aliovalent substituents in perovskites. Donor dopants (e.g., La$^{3+}$ [8], Nb$^{5+}$ [9] and W$^{8+}$ [10])—those with higher charges than the ions they replace—are compensated by cation vacancies, whereas acceptor dopants (e.g., Fe$^{3+}$ [11], Cr$^{3+}$ [12], Li$^{+}$ [13] and Mn$^{3+}$/Mn$^{2+}$ [14])—ions with lower charges than the ions they replace—are compensated by oxygen vacancies. Donor doping in PZT could be expected to reduce the concentration of oxygen vacancies, leading to a reduction in the concentration of domain-stabilizing defect pairs. The resulting increase in wall mobility causes an observed increase in dielectric constant and loss, piezoelectric coefficients and coupling factors, and a reduction in the mechanical quality factor $Q_m$, while the acceptor doping increases the concentration oxygen vacancies, pinning the domain wall and causing an observed contrary effect compared with the donor doping. The two types of substitution behaviors result in the “softening” and “hardening” effect, respectively. In addition, the dopants are also known to be important factors influencing microstructural development. Some works indicate that the addition of dopants above the solubility limit can strongly reduce grain size [15–17]. The solid solution impurity drag mechanism has
been proposed to explain this phenomenon, but without any corroborating evidence [18–20]. Conversely, in other works [21–23], gradual increase in grain size has been observed in the doped ceramic system, even with the dopant level above the solubility limit. However, the related mechanism is still lacking. Hence, although doped PZT-based ceramics have been explored for many years, the doping mechanism remains debatable. Related substantial supporting evidence, especially at the nanoscale, is rare.

In a previous work [24], a ternary solid solution consisting of PZT and a complex perovskite-type compound, Pb(Zn$_{1/3}$Nb$_{2/3}$)$_3$O$_5$ (PZN), was developed. The discovered composition of 0.2PZN–0.8PZT was near the morphotropic phase boundary (MPB), showing super piezoelectric properties. In the present paper, as an extension to the research on doping behavior, CoCO$_3$ was selected as a representative of dopants to modulate the microstructure and the electrical properties of the 0.2PZN–0.8PZT system. A systematic research was conducted to clarify the confused views on Co doping in previous works [17,23,25,26]. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM), in conjunction with energy-dispersive X-ray detection (EDX), were applied to investigate the domain structure evolution and the liquid-phase sintering behavior induced by Co doping. Emphasis was placed on the valence state distribution and the incorporation sites of Co ions within the sample, as well as the formation of secondary phases when doping above the solubility limit. The influence of Co doping on electrical response (i.e., dielectric relax behavior, ferroelectric and piezoelectric properties) was also investigated and analyzed in correlation with the microstructure.

2. Experimental procedure

The specimens were prepared using a conventional mixed-oxide process. The compositions used in this study are as follows: Pb(Zn$_{1/3}$Nb$_{2/3}$)$_3$O$_5$(Zr$_{0.50}$Ti$_{0.50}$)$_{0.80}$O$_3$ + $x$CoCO$_3$, where $x$ = 0–1.5 wt.%. Reagent-grade oxide powders (Pb$_3$O$_4$, ZrO$_2$, TiO$_2$, ZnO, Nb$_2$O$_5$ and CoCO$_3$) were used as starting materials. The powders were weighed and mixed by ball milling in alcohol for 24 h, with partially stabilized zirconia balls as media. After drying, the mixture was calcined in a covered alumina crucible at 850 °C for 2 h. The calcined powders were remilled for 24 h and then pressed into disks 11.5 mm in diameter at ~100 MPa. The green disks were sintered at 1000 °C for 2 h in a sealed alumina crucible. To minimize PbO loss, a PbO-rich atmosphere was maintained by placing powders of PbZrO$_3$ used as packing powders inside the crucible.

Specimen density was measured by the Archimedes method. The crystal structures of the samples were examined by XRD (Bruker D8 Advance, Karlsruhe, Germany) in the $\theta$–$2\theta$ configuration using Cu Kα radiation. The valence state of the Co ions was determined by XPS (ESCALAB 250, Thermo Electron, Waltham, MA). Micromorphology was detected on a thermally etched surface by SEM (Hitachi S4800, Japan). The mean grain size was calculated by the line intercept method. HRTEM was carried out using an instrument (Hitachi FEI Tecnai F20, Japan) equipped with an EDX detector operated at an accelerating voltage of 200 kV. Specimens for the TEM studies were prepared by the standard procedure of mechanical thinning, dimpling and ion milling towards electron transparency before TEM observation. Ar$^+$ ion beam milling was applied to prepare the specimens, using a 5 kV potential combined with a gun current of 2.2 mA at an incidence angle of 15° to the rotating sample.

To measure the electrical properties, silver paste was coated on both sides of the sintered pellets and then fired at 560 °C for 30 min to form electrodes. The dielectric property and its dependence on temperature were measured using a multi-frequency inductance capacitance resistance (LCR) analyzer (Agilent E4980A, Santa Clara, CA) with an automated temperature controller. Ferroelectric behavior was studied using a ferroelectric tester (Premier II, Radiant Technologies Inc, Albuquerque, NM) at 1 Hz. Prior to the testing of piezoelectric properties, the specimens were poled in a silicone oil bath at 120 °C by applying a DC field of 35 kV cm$^{-1}$ for 30 min and then aged for 24 h. The piezoelectric constant $d_{33}$ was measured using a piezoelectric $d_{33}$ meter (ZJ-6A, Institute of Acoustics, Academic Sinica, China) at 100 Hz. The electromechanical coupling factor $k_p$ was determined by a precision impedance analyzer (4294A; Agilent Technologies, Santa Clara, CA) through the resonance–anti-resonance method based on IEEE standards.

3. Results and discussion

3.1. Crystal structure and microstructure

The XRD patterns of 0.2PZN–0.8PZT ceramics with different CoCO$_3$ additions in the 20 range of 20–60° are
shown in Fig. 1a. A complete perovskite structure is formed, and no detectable traces of the pyrochlore or other impurities are observed as the CoCO3 addition increases. Further observation of the XRD patterns reveals obvious changes in diffraction peaks near $2\theta = 45^\circ$, indicating that Co doping induces a structural transition. To determine the phase evolution, fine scanning was carried out in the diffraction angle range $2\theta = 43-46^\circ$, and the results are shown in Fig. 1b. The diffraction peaks are separated by fitting the Gaussian–Lorentz line shape, and the positions of the reflections are fixed using the least squares method. In general, the reflections at $45^\circ$ can be divided into three peaks, corresponding to tetragonal (002), rhombohedral (200) and tetragonal (200). As shown in Fig. 1b, as the addition of CoCO3 increases, the reflection intensity of rhombohedral (200) decreases compared with that of tetragonal (200) and (002), revealing an increasing trend in the tetragonal phase. To quantitatively investigate the effect of CoCO3 addition on phase transformation, the tetragonal phase content ($TP$) was calculated using Eq. (1):

$$TP\% = \frac{I_{(200)T} + I_{(002)T}}{I_{(200)T} + I_{(002)T} + I_{(200)R}} \times 100\%$$  

(1)

where $I_{(200)R}$ is the integral intensity of rhombohedral (200) reflection, and $I_{(002)T}$ and $I_{(200)T}$ are the integral intensities of tetragonal (002) and (200) reflections, respectively [27]. The results of the calculation using Eq. (1) are shown in Fig. 2. For the undoped specimen, the content of the tetragonal phase is $\sim 55\%$, and very close amounts of rhombohedral and tetragonal phases imply the presence of MPB. The tetragonal phase fraction increases abruptly with the increase in CoCO3 addition. For the CoCO3 addition of 0.2 wt.%, the content of tetragonal phase is near 74%. When the addition exceeds 0.2 wt.%, the change in the content of the tetragonal phase becomes inconspicuous. Moreover, the lattice parameters and tetragonality $c/a$ of these compounds were calculated, and the results are shown in Table 1 and Fig. 2. It can be seen from Fig. 2 that both curves show similar variation trends, and the turning point appears at the same position of 0.2 wt.% CoCO3 addition. These results suggest that the solubility limit of CoCO3 in the 0.2PZN–0.8PZT system may be near 0.2 wt.%.

Phase transition is related to the evolution of the ferroelectric domain structure, which can be directly visualized by TEM. Fig. 3a and b shows the bright-field TEM images of the undoped and the 1.2 wt.% CoCO3 added 0.2PZN–0.8PZT, respectively. Based on the classic view of the domain theory, rhombohedral PZT has polarization vectors that intersect the domain walls at $71^\circ$ and $109^\circ$, giving walls lying on the $\{110\}_p$ and $\{100\}_p$ planes [28], whereas the polarization vectors in the tetragonal PZT intersect the domain wall at $90^\circ$, giving domain walls lying on the $\{110\}_p$ plane. In Fig. 3a, both the lamellar tetragonal domains and the lenticular rhombohedral domains are clearly observed. However, the rhombohedral domains are scattered in the tetragonal domain matrix, supporting the nature of the “two-phase zone” of the MPB structure in the undoped 0.2PZN–0.8PZT [29]. However, in Fig. 3b, only lamellar tetragonal domains can be observed, and the corresponding domain size greatly increases compared with that of the undoped specimen [30,31], indicating that the Co dopant induces phase transition on the tetragonal side. These results are in accordance with the previous XRD analysis.

Generally, Co ions enter the $B$-site of the perovskite lattice to replace the Ti$^{4+}$ and Zr$^{4+}$ ions, because the radius of Co$^{2+}$ (0.665 Å) or Co$^{3+}$ (0.525 Å) is close to that of Zr$^{4+}$ (0.720 Å) or Ti$^{4+}$ (0.605 Å) ions. Co ions are reported to exist mainly in the +2 or +3 valence states in oxides or hydroxides [32]. To clarify the exact valence state of Co ions in 0.2PZN–0.8PZT ceramics, the XPS spectra of Co 2p$^{3/2}$ were recorded. The Co2p$^{3/2}$ band were partitioned into two sub-bands centered at 780.4 and 781.4 eV, using the standard Gaussian fitting method. The two decoupled sub-bands are shown in Fig. 4a. To quantitatively investigate the valence transformation of Co ions in different additions, the relative content of Co$^{3+}$ was calculated according to the fitting results, as shown in Fig. 4b. As seen from the figure, the Co$^{3+}$ concentration obviously changes with CoCO3 addition. For the ceramics with 0.2 wt.% CoCO3 addition, the mole ratio of Co$^{3+}$ ion to Co$^{2+}$ ion is 92:8, which suggests that the dominant valence state in the current sample is Co$^{3+}$. However, further addition results in a significant decrease in Co$^{3+}$ concentration. When the addition of CoCO3 is 0.5 wt.% the Co$^{3+}$ concentration is near 60 mol.%, which is near unity for more addition. From these results, Co ions can be concluded to exist in the mixed valence forms of $+2$ and $+3$, and their relative ratio depends on doping content. Generally, high-temperature sintering leads to a reduced atmosphere, which is favorable to the formation of low-valence ions [33]. Compared with ions occupying the crystal lattice, dopants existing in the grain boundary are more sensitive to the outer sintering atmosphere. In the present work, the solubility limit of CoCO3 in the 0.2PZN–0.8PZT matrix is near

![Fig. 2. Content of the tetragonal phase and the lattice tetragonality $c/a$ vs. CoCO3 addition.](image-url)
Below the solubility limit, the Co ions enter the crystal lattice, and most of them exit with +3 valence. Compared with Co^{2+} (0.665 Å), Co^{3+} (0.525 Å) has a relatively large radius difference from Zr^{4+} (0.720 Å) and Ti^{4+} (0.605 Å) ions. Thus, the related substitution results in a large distortion of the unit cell, as shown in Fig. 2. Above the solubility limit, excess Co ions gather in the grain boundaries. The effect of the surroundings reducing the atmosphere causes part of the Co ions to transform into the low valence of +2, which shows little effect on lattice distortion. In summary, cation radius, which is related to Co valence state, determines the variation in tetragonality c/a.

Table 1

<table>
<thead>
<tr>
<th>Composition (wt.%)</th>
<th>Lattice parameters</th>
<th>Lattice tetragonality (c/a)</th>
<th>Tetragonal phase TP (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (Å)</td>
<td>c (Å)</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>3.9873</td>
<td>4.0156</td>
<td>1.0071</td>
</tr>
<tr>
<td>0.1</td>
<td>3.9961</td>
<td>4.0333</td>
<td>1.0093</td>
</tr>
<tr>
<td>0.2</td>
<td>3.9976</td>
<td>4.0392</td>
<td>1.0104</td>
</tr>
<tr>
<td>0.3</td>
<td>4.0015</td>
<td>4.0427</td>
<td>1.0103</td>
</tr>
<tr>
<td>0.5</td>
<td>4.0091</td>
<td>4.0512</td>
<td>1.0105</td>
</tr>
<tr>
<td>0.8</td>
<td>3.9954</td>
<td>4.0366</td>
<td>1.0103</td>
</tr>
<tr>
<td>1.0</td>
<td>3.9938</td>
<td>4.0345</td>
<td>1.0102</td>
</tr>
<tr>
<td>1.2</td>
<td>3.9978</td>
<td>4.0394</td>
<td>1.0104</td>
</tr>
<tr>
<td>1.5</td>
<td>4.0178</td>
<td>4.0471</td>
<td>1.0073</td>
</tr>
</tbody>
</table>

Fig. 3. Bright-field TEM domain image of 0.2PZN–0.8PZT ceramics with different CoCO_3 additions: (a) 0.0 wt.%; (b) 1.2 wt.%. (Rh., rhombohedral; Tet., tetragonal).

0.2 wt.%. Below the solubility limit, the Co ions enter the crystal lattice, and most of them exit with +3 valence. Compared with Co^{3+} (0.665 Å), Co^{3+} (0.525 Å) has a relatively large radius difference from Zr^{4+} (0.720 Å) and Ti^{4+} (0.605 Å) ions. Thus, the related substitution results in a large distortion of the unit cell, as shown in Fig. 2. Above the solubility limit, excess Co ions gather in the grain boundaries. The effect of the surroundings reducing the atmosphere causes part of the Co ions to transform into the low valence of +2, which shows little effect on lattice distortion. In summary, cation radius, which is related to Co valence state, determines the variation in tetragonality c/a.

Fig. 4. (a) XPS spectra of Co 2p^3/2 of 0.2PZN–0.8PZT ceramics with different CoCO_3 additions and (b) dependence of Co^{3+} concentration on CoCO_3 addition.

Fig. 5 shows the dependence of the apparent density and the relative density of 0.2PZN–0.8PZT on CoCO_3 addition. Clearly, a maximum in the density curve appears. When the doping is <0.2 wt.%, density sharply increases as doping increases. However, further addition of CoCO_3 causes a decrease in ceramic density. The variation trend in the curve indicates that the suitable CoCO_3 addition benefits the densification of ceramics during the sintering process. Fig. 6 shows the SEM micrographs of the thermally etched surface of 0.2PZN–0.8PZT ceramics with different CoCO_3 additions. Grain size remarkably increases with CoCO_3 addition. As stated earlier, below the solubility limit of 0.2 wt.%, Co ions, mostly with +3 valence, enter the perovskite lattice to replace the Ti^{4+} or Zr^{4+} site.
Therefore, the imbalance in ion valence leads to the creation of oxygen vacancies, which enhance the transfer of mass and energy between reactants, thus improving the sintering behavior and inducing an increase in grain size.

Interestingly, grain size still shows an increasing trend, with further increase in CoCO₃ addition above the solubility limit. This phenomenon is different from previous observation in other transitional metal ion (i.e., Cr³⁺ [12], Mn²⁺ [14]) doped 0.2PZN–0.8PZT systems. In these doped systems, grain growth is inhibited, as the addition of dopants exceeds the solubility limit. The so-called solid solution impurity drag mechanism has been proposed to explain the inhibitor role of excess doping ions aggregated at the grain boundary. Thus, in this case, what is the exact mechanism responsible for grain growth when CoCO₃ addition is above the solubility limit? To obtain direct evidence at the nanoscale, the 0.2PZN–0.8PZT sample doped with 1.2 wt.% CoCO₃ was studied using TEM. Fig. 7a shows the bright-field TEM image of triple pockets and grain boundary regions. The triple pockets reveal a slightly concave shape, indicating that grain-boundary wetting occurred. Fig. 7b gives the HRTEM imaging of the interface region between PZN–PZT grains. The distinct lattice fringe confirms the good crystallinity of the PZN–PZT grains. The interplanar spacing is ~0.401 nm, correspond-
ing well to the spacing of (100). Moreover, the presence of an amorphous phase with thickness ~2–3 nm can be clearly observed, which is direct evidence of liquid-phase sintering. Fig. 7c and d shows the EDX analysis of the triple pockets and grains, respectively. The Co ions are difficult to detect in the matrix grains. The concentration is assumed below the detection limit of the EDX system because of the low doping level in the sample. Comparatively, a relatively high level of Co concentration was detected in the triple pocket regions, combined with excess lead content. Some PbO from the packing PbZrO3 powder possibly transfer to the PZN–PZT compacts during the sintering treatment [34], and the excess Co ions accelerate the formation of the PbO-rich liquid phase. A model for describing the grain boundary movement in liquid-phase sintering is illustrated in Fig. 8. The energy of a grain boundary between two grains is known to depend on their dihedral angle [22]. In the present case, the PbO-rich liquid phase wets and covers the surface of the grains. Grain boundaries with a liquid layer have abundant dihedral angles at the junctions, which can be easier to move compared with grain boundaries without a liquid layer. Therefore, the small particles dissolve gradually in the liquid and then reprecipitate on the larger grains, resulting in large grain growth based on the liquid-phase sintering mechanism [35]. In the final stage of sintering, an amorphous residue enriched with cobalt and lead segregates at the grain boundaries and is deposited at the triple grain junctions.

3.2. Dielectric, ferroelectric and piezoelectric properties

Fig. 9 shows the temperature dependence of the dielectric constant of 0.2PZN–0.8PZT ceramics with different amounts of CoCO3 addition. All patterns show weak frequency dispersions, but the shapes of the curves near the Curie peak present a narrow trend with the addition of CoCO3, revealing that the system changes from relaxor to normal ferroelectrics.

For a classical ferroelectric, the dielectric constant above the Curie temperature follows the Curie–Weiss law:

\[ \varepsilon = C/(T - T_c)(T > T_c) \]  

(2)
where \( C \) is the Curie–Weiss constant, and \( T_c \) is the Curie–Weiss temperature.

Fig. 10 shows the plots of the inverse dielectric constant vs. temperature at 1 kHz. The fitting results obtained by Eq. (2) are listed in Table 2. The deviation from the Curie–Weiss law can be defined by \( \Delta T_{cm} \):

\[
\Delta T_{cm} = T_{cw} - T_m
\]

where \( T_{cw} \) denotes the temperature from which the dielectric constant starts to deviate from the Curie–Weiss law, and \( T_m \) represents the temperature at which the dielectric constant reaches a maximum.

The dielectric constants of undoped ceramics obey the Curie–Weiss law at temperatures much higher than \( T_m \), and the calculated \( \Delta T_{cm} \) value is 70 °C. However, with the increase in CoCO_3 addition, the \( \Delta T_{cm} \) of the specimens distinctly shows a descending trend. At 0.8 wt.% CoCO_3 addition, the \( \Delta T_{cm} \) value is 50 °C, implying that the diffuse phase transition (DPT) behavior has weakened with the addition of CoCO_3.

For the relaxor ferroelectrics, the reciprocal of the dielectric constant and the temperature obey the Uchino and Nomura function, a modified Curie–Weiss law [36]:

\[
1/\varepsilon - 1/\varepsilon_{max} = (T - T_{max})^\gamma / C
\]

where \( \varepsilon_{max} \) is the maximum value of the dielectric constant, \( \varepsilon \) is the dielectric constant at temperature \( T \), \( T_{max} \) is the temperature at the peak of the dielectric constant, \( C \) is the Curie constant, and \( \gamma \) is the indicator of the degree of diffuseness, taking the values between 1 (normal ferroelectric) and 2 (complete DPT).

To further confirm the effects of CoCO_3 doping on the relaxor feature of 0.2PZN–0.8PZT ceramics, the plots of \( \ln(1/\varepsilon - 1/\varepsilon_{max}) \) as a function of \( \ln(T - T_{max}) \) were drawn for the 0.2PZN–0.8PZT specimens with different amounts of CoCO_3 additive, as shown in Fig. 11. A linear relationship is observed in all specimens. The slope of the fitting curves is used to determine the \( \gamma \) value. With the increase in CoCO_3 addition, the \( \gamma \) value decreases from 1.94 to 1.72, further confirming that the CoCO_3 additive can lower the DPT behavior of 0.2PZN–0.8PZT.

For a lead-based relaxor, such as Pb(Zn_{1/3}Nb_{2/3})O_3 (PZN), Pb(Mg_{1/3}Nb_{2/3})O_3 (PMN) and Pb(Ni_{1/3}Nb_{2/3})O_3 (PNN), the relaxor feature appears when at least two cations with different valences occupy similar crystallographic B sites of the oxygenic octahedral center, giving rise to random fields that impede the development of long-range polar ordering. For a Co-doped 0.2PZN–0.8PZT system, the doping of Co ions can enhance the positional disorder in the B-site ions of \( ABO_3 \) perovskite, which is speculated to enhance DPT behavior. However, this prediction is inconsistent with the observation that the degree of DPT decreases with the addition of CoCO_3. A relaxor feature is directly related to domain configuration in ferroelectrics. Based on the previous XRD and TEM results, Co dopant induces a gradual phase transition process from MPB to the tetragonal side, and the corresponding tetragonal domain size shows an increasing trend. For the MPB com-

Fig. 9. Temperature dependence of the dielectric constant at 1, 10, 100 and 1000 kHz for 0.2PZN–0.8PZT ceramics with different CoCO_3 additions: (a) 0.0 wt.%; (b) 0.4 wt.%; (c) 0.6 wt.%; (d) 0.8 wt.%.

Table 2

<table>
<thead>
<tr>
<th>Samples (wt.%)</th>
<th>0.0</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_m ) (°C)</td>
<td>321</td>
<td>320</td>
<td>317</td>
<td>313</td>
</tr>
<tr>
<td>( T_{cw} ) (°C)</td>
<td>391</td>
<td>383</td>
<td>371</td>
<td>363</td>
</tr>
<tr>
<td>( \Delta T_{cm} ) (°C)</td>
<td>70</td>
<td>63</td>
<td>54</td>
<td>50</td>
</tr>
</tbody>
</table>

Fig. 10. Plots of the inverse dielectric constant as a function of temperature at 1 kHz for 0.2PZN–0.8PZT ceramics with different CoCO_3 additions: (a) 0.0 wt.%; (b) 0.4 wt.%; (c) 0.6 wt.%; (d) 0.8 wt.% (solid line, fitting to the Curie–Weiss law).
position of the undoped specimen, the domain structure consists of the rhombohedral and tetragonal phases, which are superimposed on each other and exhibit large dispersion in phase transition temperatures $T_c$ in different areas. Thus, the spatial fluctuations in the local Curie temperature lead to the increase in degree of diffuseness [37]. With the addition of CoCO$_3$, the tetragonal domain size increases, and the induced merging of micropolar regions into macropolar regions is responsible for the transition from relaxor to normal ferroelectric behaviors.

Moreover, as shown in Fig. 9, the dielectric constant $\varepsilon_r$ shows an enhancing trend with the addition of CoCO$_3$, especially in the region near the Curie temperature [15]. For the undoped specimen, the $\varepsilon_{\text{max}}$ is merely 6000 at the Curie peak. With increasing CoCO$_3$ content, $\varepsilon_{\text{max}}$ rapidly increases. At 0.8 wt.% CoCO$_3$, $\varepsilon_{\text{max}}$ is 14,600, ~2.5 times higher than that of the undoped specimen. As a “hard” dopant, Co doping in 0.2PZN–0.8PZT can lead to the creation of oxygen vacancies, owing to the valence difference from the $B$ site ion, which tend to form defective dipoles $D_i$, producing an inner bias field $E_i$. In turn, the build-up of $E_i$ reduces polarization rotations and dielectric properties, especially by prohibiting domain wall motion [14,38]. However, this assumption is inconsistent with the experimental results. To thoroughly clarify the doping mechanism, the ferroelectric hysteresis loops of Co-doped 0.2PZN–0.8PZT were measured, the results of which are shown in Fig. 12a. As the figure shows, all $P$–$E$ hysteresis loops are saturated, and the dissymmetrical shape is the typical feature of the existence of the internal-bias field ($E_i$). Fig. 12b shows the remanent polarization $P_r$ and coercive field $E_c$ as a function of CoCO$_3$ addition at room temperature. Interestingly, $P_r$ increases, whereas $E_c$ decreases with the increase in CoCO$_3$ addition. Moreover, in the $P$–$E$ hysteresis loops measured at elevating temperatures, the variation trend of the loops shows features similar to those measured at room temperature (see Fig. S1 in Supporting information). This phenomenon is a departure from the hard doping nature of Co ions. It is known that large grain size favors the improvement in dielectric and ferroelectric properties because, as the grain size decreases, the grain boundary phases, which are directly related to the volume of the space charge regions, are enlarged. Accordingly, a strong coupling between the grain boundaries and the domain walls hinders domain switching. This mechanism related to grain size is called the size effect. In this case, the addition of CoCO$_3$ leads to the remarkable growth of the grains (Fig. 6). Thus, the development of domains becomes more consummate, neutralizing the hard doping effect and reforming the $\varepsilon_r$ of the ceramic sample.

Fig. 13 shows the variation in piezoelectric constant $d_{33}$ and electromechanical coupling factor $k_p$ as a function of CoCO$_3$ addition. Both $k_p$ and $d_{33}$ show a similar variation with increasing CoCO$_3$ content. The optimized values of $k_p$ (0.66) and $d_{33}$ (310 pC N$^{-1}$) were obtained for 0.8 wt.% CoCO$_3$ content, and they are superior to the reported values ($k_p = 0.50$ and $d_{33} = 278$ pC N$^{-1}$) in a Li$_2$CO$_3$-doped...
PZN–PZT system [13]. The evolution of piezoelectric responses can be explained by the conventional Landau–Devonshire relation:

\[ d_{33} = 2\varepsilon_0 Q_{11} P_r \]  

(5)

where \( \varepsilon_0 \) is the vacuum permittivity, \( Q_{11} \) is the electrostrictive coefficient, and \( P_r \) is the remanent polarization. Evidently, the steep rise in \( P_r \) and \( \varepsilon_r \) contributes to the increase in \( d_{33} \). Notably, the best piezoelectric properties are obtained for 0.8 wt.% CoCO\(_3\) content, which deviates from the composition near the solubility limit of 0.2 wt.%. This behavior is different from that in previous reports in which super piezoelectric properties are obtained at the solubility limit in a transitional metal ion-doped PZN–PZT system [11,12,14,39]. In this work, the combined effects of hard doping and microstructure evolution induced by CoCO\(_3\) addition determine the variation in piezoelectric properties. Further addition above 0.8 wt.% causes a decrease in piezoelectric properties, which may be attributed mainly to the formation of abnormal grain boundaries, as affirmed by TEM observations.

4. Conclusion

CoCO\(_3\)-added PZN–PZT ceramics were prepared through the conventional solid oxide process. The valence state and the incorporation site of Co cations significantly affect the microstructure and the electrical properties of the ceramics. XPS results demonstrate that both Co\(^{3+}\) and Co\(^{2+}\) cations coexist in the system. Below the solubility limit of 0.2 wt.% CoCO\(_3\), most Co ions exist in the +3 valence, which prefer the entry to \( B \) sites of the perovskite lattice and the phase transition from MPB to the tetragonal side, resulting in the weakness of the DPT behavior. Above the solubility limit, excess Co ions segregate at the grain boundaries, which favor the formation of the Co–Pb-rich phase and accelerate grain growth for the liquid sintering mechanism. Despite the presence of an internal-bias field and a high concentration of tetragonal phase, CoCO\(_3\)-doped ceramics exhibit superior piezoelectric properties compared with the undoped samples. This result suggests that the size effect is stronger than the reverse hardening effect of the acceptor dopant. Optimum piezoelectric properties were obtained for the 0.8 wt.%-doped 0.2PZN–0.8PZT ceramic system: \( d_{33} = 310 \, \text{pC N}^{-1} \) and \( k_p = 0.66 \).

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 51072008 and 51172006), the Natural Science Foundation of Beijing (No. 2102006), the Project of New Star of Science and Technology of Beijing (Grant No. 2007A014) and the Funding Project of IHLB (Grant Nos. PHR201008012 and PHR201007101).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.actamat.2012.11.026.

References


Fig. 13. Piezoelectric constant \( d_{33} \) and electromechanical coupling factor \( k_p \) for 0.2PZN–0.8PZT ceramics with different CoCO\(_3\) additions.