

Influences of cobalt dopant on the phases, microstructures and dielectric properties of PZT ceramics

B. Cherdhirunkorn^{a,*}, B. Pidthong^a, P. Jeamwutthisak^a, D.A. Hall^b, M. Shuaib^b and T. Tunkasiri^c

^aDepartment of Physics, Thammasat University, Patum Thani 12121, Thailand

^bSchool of Materials, University of Manchester, Manchester, M1 7HS, U.K.

^cDepartment of Physics, Chiang Mai University, Chiang Mai 52020, Thailand

The effects of cobalt dopant on the properties of PZT ceramics with the formula of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})_{1-x}\text{Co}_x\text{O}_3$ (where $x = 0, 0.002, 0.005, 0.01, 0.015, 0.02, 0.025$ and 0.03) were studied. The cobalt doped PZT ceramics were produced using a conventional mixed oxides route. Phase structure and microstructure of these PZT ceramics were investigated using XRD and SEM techniques. The XRD spectra of the cobalt doped PZT ceramics showed that the higher level of cobalt incorporated into PZT ceramics could shift the MPB toward the rhombohedral phase region of the PbZrO_3 - PbTiO_3 phase diagram. The SEM images revealed that cobalt acted as a grain growth inhibitor. Furthermore, the solubility limit of cobalt in PZT ceramics seemed to be less than 3 mol%, since a second phase (cobalt-rich phase) was detected at the grain boundary. The P-E loops and dielectric properties of cobalt doped PZT ceramics were measured at high ac electric field in the range of 0.2 to 2 kVmm⁻¹. An increase of the Curie point was also observed in cobalt doped PZT ceramics.

Key words: PZT, Dielectric properties, Impurities, Perovskites.

Introduction

PZT ceramics have been used in many applications, such as ultrasonic motors, sensors and actuators due to their excellent properties. Generally, the composition of PZT ceramics lies at the Zr/Ti ratio of 53/47 where the morphotropic phase boundary (MPB) occurs [1]. In order to modify the electrical properties of PZT ceramics, small amounts of doping ions could be added to the PZT compositions. There are three types of ions typically used as dopants: (1) acceptor ions (2) donor ions and (3) isovalent ions. The effects of some heterovalent dopants such as Ce [2], Mn [3-6] and Cr [7] on the properties of PZT were reported. Liang and Wu [4] reported that minor Cr additive ≤ 0.1 wt% could improve the piezoelectric properties such as mechanical quality factor, Q_m . He and Li [3] also found that the minor Mn additive gave rise to the increase in Q_m . These heterovalent dopants seemed to give rise to a donor-like effect for the compositions with low concentration of additives. The present work deals with the physical and electrical properties of cobalt doped PZT ceramics. Co^{2+} (ionic radius ~ 88.5 pm) and Co^{3+} (ionic radius ~ 75.8 pm) are expected to substitute B-site ions (Ti^{4+} or Zr^{4+} with the ionic radius of ~ 74.5 and ~ 86 pm, respectively) due to their similar ionic sizes. The hardening behavior would be expected in this case since the cobalt ions substituted for Ti results

in oxygen vacancies as shown in equation (1) for the case of Co^{3+} .



Experimental

PZT ceramics with the composition of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})_{1-x}\text{Co}_x\text{O}_3$ (where $x = 0, 0.002, 0.005, 0.01, 0.015, 0.02, 0.025$ and 0.03) were produced using the mixed oxides route. 3 mol% excess PbO was added into all compositions in order to compensate for the evaporation of PbO at high temperature. Raw materials of PbO ($> 99.5\%$), TiO_2 ($> 99.5\%$), ZrO_2 ($> 99.5\%$) and Co_3O_4 ($> 99\%$) were ball milled in polypropylene bottles with zirconia balls and isopropanol for 50 hours. The mixtures were oven dried at 80 °C. All powders were calcined at 800 °C for 1 hour with a heating rate and a cooling rate of 5 °C/min. The single phase PZT powders were produced after the calcination process. Binder (0.5 wt% PVA) and lubricant (0.5 wt% PEG) were added to the calcined powders, which were then planetary milled (Fritsch, D 55743) in distilled water for 1 hour with a speed of 200 rpm. The milled slurry of each composition was dried using a freeze-drying method (Flexi-Dry, FD-3-85D-MP) in order to prevent the segregation of binder and to improve the compositional homogeneity of the powders. The slurry was frozen in liquid nitrogen, and was then transferred to a vacuum unit to sublimate the ice and leave behind the dry powder in a flask. The dried powders were uniaxially pressed into 10 mm

*Corresponding author:
Tel : +66-8-4667-6500
Fax: +66-2-564-4529
E-mail: benya@tu.ac.th

diameter disks at 100 MPa. All disk samples were sintered in a closed alumina crucible at 1200 °C for 2 hours using a heating and cooling rate of 5 °C/min. The PbZrO₃ was used as an atmosphere powder in order to compensate for loss of lead oxide during the sintering process. Both undoped and cobalt-doped PZT ceramics with relative densities higher than 95% were produced. Phase structures of all sintered samples were characterized using XRD (Bruker D-8) with a scanning step of 0.02°/second from 20° to 65° of 2θ. Microstructures of the polished and chemically etched PZT ceramics were examined using SEM (Jeol JSM 5410).

Temperature dependence of relative permittivity for the undoped and various cobalt-doped PZT samples was determined. When the electroded sample was heating up at a rate of 5 °C/min, capacitance measurements were carried out using a Hewlett-packard 4192A LF Impedance Analyzer, with an applied AC voltage of 1.0 V at a frequency of 100 kHz. The Curie point was determined by plotting relative permittivity as a function of temperature. The relative dielectric permittivity (ϵ_r) was calculated using the measured capacitance value C and the geometric dimensions according to equation (2)

$$C = \frac{A \epsilon_r \epsilon_0}{t} \quad (2)$$

where A = electrode area

ϵ_r = dielectric permittivity

ϵ_0 = dielectric permittivity of vacuum (8.85×10^{-12} Fm⁻¹)

t = thickness

The dielectric properties at high electric field strengths, in the range 0.2 to 2.0 kVmm⁻¹ at a frequency of 2 Hz, were determined by means of a high voltage test set incorporating a Hewlett-Packard HP33120A function generator and a Trek 609D-6 HV amplifier. The dielectric permittivity and loss were then calculated from the measured P-E (Polarization-Electric Field) loops using the method described by Hall *et al* [8].

Results and discussion

Phase investigation and microstructures

Fig. 1 shows the XRD pattern of the PZT ceramic without cobalt addition, indicating a tetragonal phase due to the presence of (002) and (200) peaks at 2θ of 43° and 45°, respectively. In addition, the XRD patterns for the PZT ceramics with the higher amount of cobalt additive (1.5 to 3 mol% Co) show the presence of {020}_R peak between the (002) and (200) peaks which indicates the presence of the rhombohedral phase. This effect is similar to the presence of Mn in PZT ceramics which were reported by Kim and Yoon [9].

The addition of cobalt could inhibit grain growth in PZT ceramics as shown in Fig. 2. The average grain sizes of all samples were determined using the line

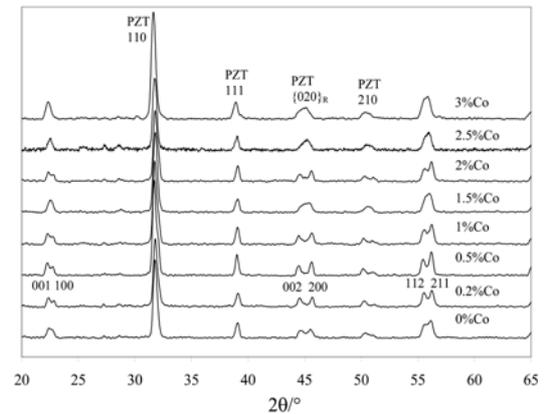


Fig. 1. XRD patterns of undoped and various cobalt-doped PZT ceramics sintered at 1200 °C.

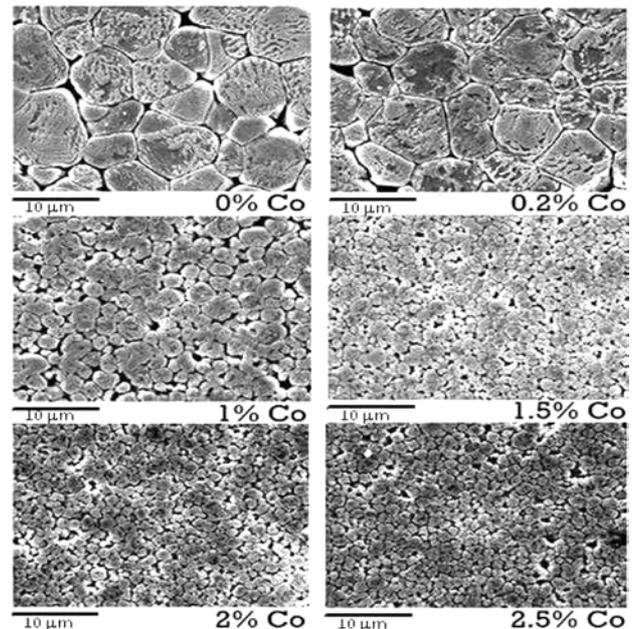


Fig. 2. SEM images of undoped PZT and cobalt-doped PZT ceramics.

Table 1. Average grain diameter obtained from SEM images using the line intercept method.

Samples	Average grain diameter (μm)
PZT 0 mol% Co	11.7
PZT 0.2 mol% Co	11.1
PZT 0.5 mol% Co	6.7
PZT 1.0 mol% Co	2.5
PZT 1.5 mol% Co	2.1
PZT 2.0 mol% Co	2.2
PZT 2.5 mol% Co	2.2
PZT 3.0 mol% Co	1.7

intercept method as shown in Table 1. The average grain size of PZT ceramics without cobalt dopant and with small amount of cobalt (0.2 mol%) were 11.7 and 11.1 μm , respectively. The smaller grain size was observed in the PZT ceramics with higher cobalt contents. The average grain sizes of the PZT ceramics with 0.5, 1, 2 and 3 mol% Cobalt were 6.7, 2.5, 2.2 and 1.7 μm , respectively.

The solubility limit of cobalt in PZT ceramic seemed to be less than 3 mol%, since the presence of a second phase (cobalt-rich phase) at the grain boundaries was detected by the EDAX analysis (Fig. 3). It is likely that the enrichment of cobalt ions in the grain boundary region provides an effective mechanism for grain growth inhibition through a ‘solute drag’ effect.

Temperature dependence of dielectric properties under low electric field strength

The relative permittivity of ferroelectrics generally increases to reach the highest Curie temperature, where the phase transition from the ferroelectric to paraelectric state occurs. The plots of relative permittivity as a function of temperature for the cobalt doped PZT ceramics are shown in Fig. 4. The Curie points of these materials are summarized in Table 2. It is evident that the Curie

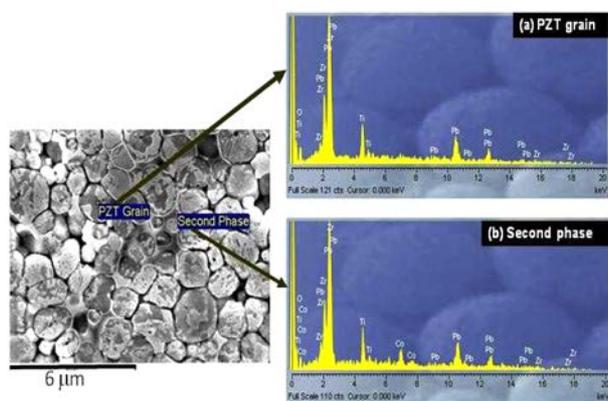


Fig. 3. EDAX results of the 3%Co doped PZT ceramics (a) grain (b) second phase.

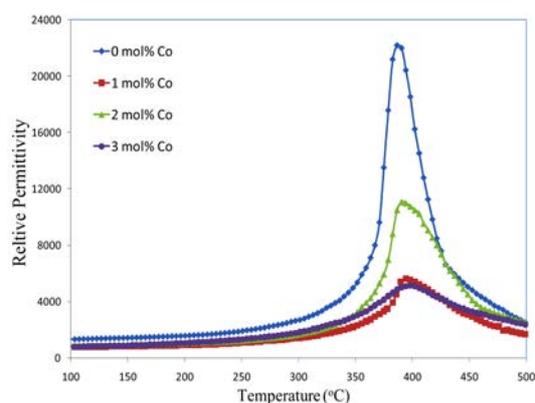


Fig. 4. Plots of relative permittivity as a function of temperature for cobalt doped PZT ceramics.

Table 2. Curie Point of cobalt-doped PZT ceramics.

Samples	Curie Point (± 5 °C)
PZT 0 mol% Co	387
PZT 0.2 mol% Co	392
PZT 0.5 mol% Co	402
PZT 1.0 mol% Co	391
PZT 1.5 mol% Co	411
PZT 2.0 mol% Co	392
PZT 2.5 mol% Co	398
PZT 3.0 mol% Co	398

point of undoped PZT sample was about 386 °C, whereas those of the PZT samples prepared with the higher amounts of cobalt dopant are approximately 10 °C higher. The uncertainty in the temperature measurements during the present study was relatively high (± 5 °C) and therefore further measurements are necessary to validate the apparent shift of Curie point with Cobalt substitution.

Another aspect of interest from these results is that the peak in dielectric permittivity at the Curie point was increasingly suppressed as the cobalt doping level increased. This effect is probably associated with the change in microstructure i.e. it is primarily caused by the reduction in grain size and the associated changes in the ferroelectric domain structure of the materials. Similar observations were made previously for the influence of grain size on the dielectric properties of donor-doped PZT ceramics [10].

Dielectric nonlinearity under high electric field strength

Fig. 5 shows the P-E loops of PZT samples without cobalt and with 0.2 to 2.5 mol% cobalt measured using the field amplitudes of 0.2 to 2.0 kV mm^{-1} at a frequency of 2 Hz. For the PZT samples without cobalt dopant and with cobalt dopant up to 1 mol%, ‘propeller’-shaped loops that are typically observed in ‘hard’ PZT ceramics after ageing in an unpoled condition was obtained. However, for the samples with higher amount of cobalt additive, rounded P-E loops were obtained, which indicates an increasing contribution from electrical conduction in addition to the dielectric and ferroelectric response.

The plots of relative permittivity (ϵ_r) and $\tan\delta$ as a function of applied electric field, derived from these P-E loops, are shown in Fig. 6. The addition of cobalt up to 1 mol% in the PZT ceramic causes a slight decrease in ϵ_r and $\tan\delta$. The higher cobalt contents (1.5, 2 and 2.5 mol% Co) in PZT samples induced high loss at low field levels, which is another indication of the relatively high conductivity of the samples. However, the 1.5 mol% Co doped PZT ceramic exhibited an anomalous ‘softening’ effect in terms of unusually high ϵ_r and $\tan\delta$ values, particularly at high field levels. The higher amounts of

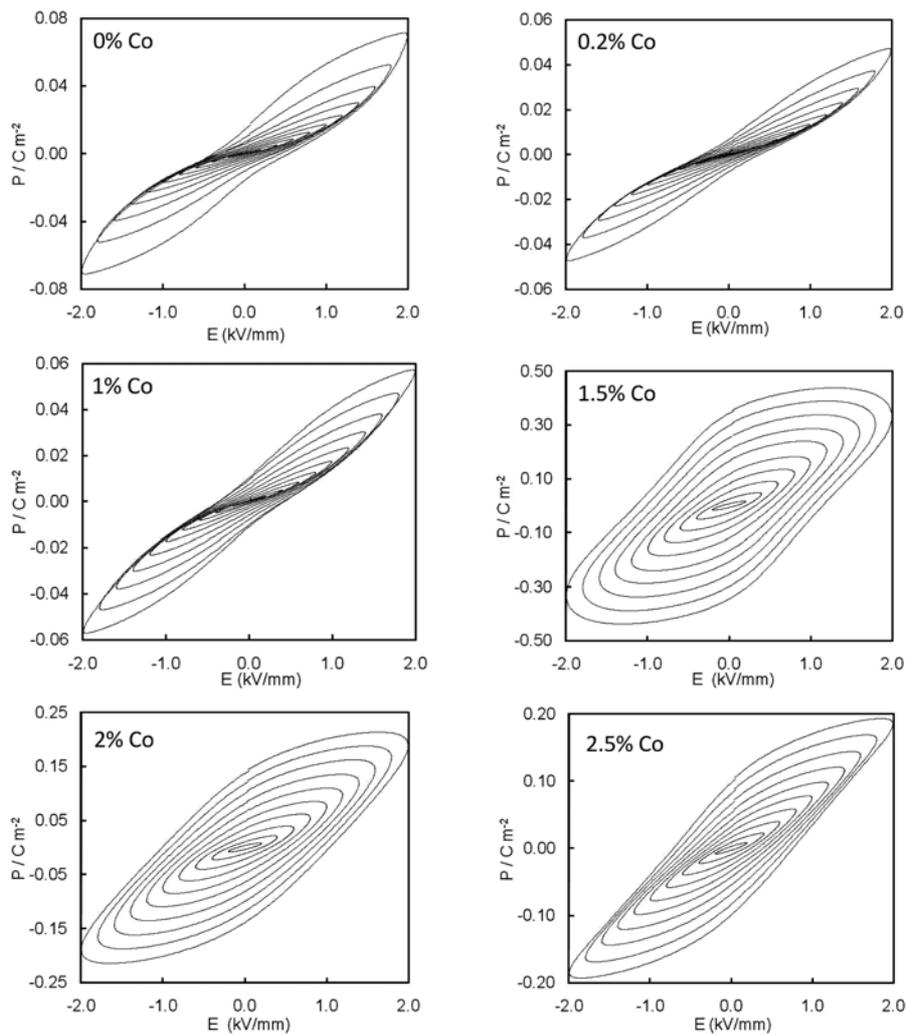


Fig. 5. Polarisation-Electric field (P-E) loops for undoped and various cobalt doped PZT samples.

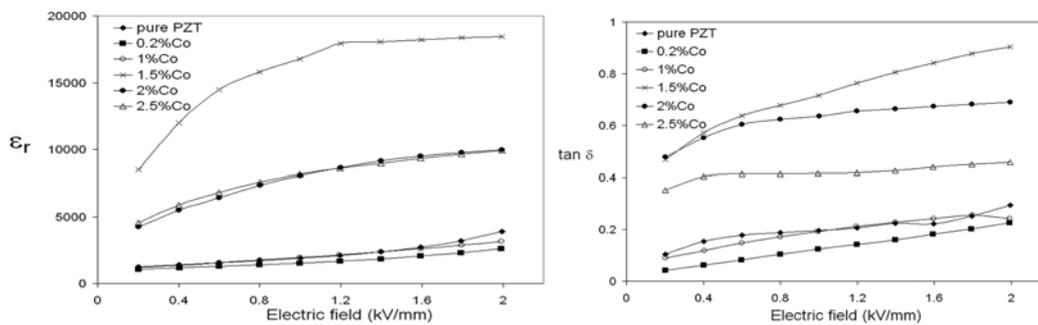


Fig. 6. Plots of ϵ_r and $\tan\delta$ as a function of applied electric field for undoped and various cobalt doped PZT samples.

cobalt ions (2 and 2.5 mol%) show a hardening effect as the reduction of ϵ_r and $\tan\delta$ are observed. The influence of cobalt ions on the dielectric properties of PZT ceramic obtained in this study is similar to the effects of other heterovalent dopants, such as Mn and Ce, as reported by several authors [2-6]. In addition, the high value of

relative permittivity observed in the PZT samples with more than 1.5 mol% Co might be associated with the presence of rhombohedral phase in these samples. The rhombohedral phase of PZT was reported to soften the effect by enhancing the piezoelectric constant d_{33} of PZT ceramic [11].

Conclusions

The XRD spectra of cobalt-doped PZT ceramics showed that the higher level of cobalt incorporated into PZT ceramics appears to shift the MPB toward the rhombohedral phase region of the PbZrO_3 - PbTiO_3 phase diagram. Cobalt acted as a grain size inhibitor and the solubility limit of cobalt incorporated into the PZT structure seems to be less than 3 mol%. The Curie point of cobalt-doped PZT ceramics increased by approximately 10 °C compared with that of the undoped PZT ceramic. Low amounts of cobalt dopant up to 1 mol% slightly lowered both ϵ_r and $\tan\delta$ at high electric field. However, the higher amount of cobalt increased both ϵ_r and $\tan\delta$ and seemed to increase the conductivity of the PZT ceramics.

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