

Effects of complex doping on microstructural and electrical properties of PZT ceramics

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Abstract The influence of complex dopants including donor and acceptor ions on microstructure and electrical properties of PZT ($Zr/Ti = 53/47$) ceramics was investigated. The prepared PZT ceramics modified with complex soft dopants, La^{+3} and Nb^{+5} , showed that the piezoelectric properties were enhanced and stable with the compositional variations, which made it possible to establish the higher reliability and reproducibility of the piezoelectric performances. For 1.0 mol% La and 1.2 mol% Nb doped composition, the maximum value, $k_p = 0.66$, was obtained. Unlike single element doping, the complex doping of both the donor and acceptor ions caused various compensation effects for the piezoelectric properties of the PZT ceramics. The improved piezoelectric properties, i.e., enhanced Q_m with remaining higher k_p , were obtained in the PZT composition complexly doped with La^{+3} and Fe^{+3} . For 1.0 mol% La and 2.0 mol% Fe doped PZT composition, relatively high Q_m and k_p values of 580 and 0.53, respectively, were obtained. It was also shown that the PZT composition had the rather lowered dielectric constant, $\epsilon_r = 800$, and considerably low loss, $\tan\delta = 0.003$. By changing the dopants compositions, the properties can also be tailored over wider range.

Keywords PZT · Complex doping · Dopants · Piezoelectric · Dielectric properties

1 Introduction

Lead zirconate titanate ($PbZr_xTi_{1-x}O_3$ or PZT) ceramics are the most widely studied and technologically important ferroelectric materials. Especially, the solid solution composi-

tion located near the rhombohedral-tetragonal morphotropic phase boundary (MPB, $x \sim 0.53$) possesses eminent piezoelectric characteristics [1, 2]. In particular, compositionally modified lead zirconate titanate (doped-PZT) ceramics with their improved electrical properties are widely utilized in the dielectric and piezoelectric applications.

The perovskite-type PZT can be expressed by a general formula ABO_3 . Both A^{+2} and B^{+4} site ions can be substituted with different dopants. Higher valence dopants like La^{+3} [3–6] and Nb^{+5} [3, 7–9] contribute electrons, being thus a donor, substitute the A and B site, respectively, and may create A vacancies [2, 6, 7], while lower valence ones like Na^+ [2, 10] and Fe^{+3} [10–12], acting as an acceptor, could enter the A and B site, respectively, and create some O vacancies [2, 12].

Pure (undoped) PZT has the intrinsic lead vacancies created due to Pb loss during the high temperature sintering [2, 13]. Donors induce the lead vacancies to maintain the charge neutrality. The increase of lead vacancies can generate electrons by ionization; most of holes from lead vacancies are compensated by electrons from the donor level to make resistivity of PZT increased with the addition of donor dopants. As a result of higher resistivity, PZT ceramics are easily poled. Dielectric constant of the doped PZT samples is improved with increasing donor contents. The induced lead vacancies in the lattice may minimize the local stresses and make the domain motions easier, which high mobility of domain walls in this doped ceramics leads to an increase in dielectric loss and a low mechanical Q_m . This also increases polarization, resulting in more charges being generated as well as increases in the dielectric constant [2, 14, 15]. The soft (PZT) for the donor doped composition is termed from these characteristics.

Unlike donor (soft) doping, acceptor doping increases of oxygen vacancies and, coagulated with the intrinsic lead

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vacancies, an internal space charge is built inside the PZT grains, which restricts the domain motion and domain walls are pinned by oxygen vacancies: thereby increased mechanical quality factor, coercive field, but caused low dielectric properties and low resistivity by space charge [2, 14]. The acceptor doping results in hard PZT ceramics.

In general, with the amount of dopant content, the compositional modification (doping) by single dopant leads the unstable electrical properties with drastic variations for the PZT ceramics. The complex doping of two or more elements is expected to combine the properties of donor doped and/or acceptor doped PZT, which could exhibit better stability or improved piezoelectric and dielectric properties [16–19] than those of the single element doped PZT.

In the present study, to combine and to improve the piezoelectric properties of PZT ceramics, a complex doping with two or more metal elements including donor (softener) and acceptor (hardener) has been adopted. Compositionally modified-PZT [doped with softeners, i.e., La^{+3} and Nb^{+5} , and both the softeners, i.e., La^{+3} and/or Nb^{+5} , and hardener, i.e., Fe^{+3}] ceramics were prepared by the conventional solid-state reaction process. The effects of dopants on the properties of sintered ceramics were investigated systematically.

2 Experimental procedure

Compositionally modified-PZT [doped with La^{+3} , Nb^{+5} and Fe^{3+} , with a nominal composition of $\text{Pb}_{1-1.5x-0.5y+0.5z}\text{La}_x(\text{Zr}_{0.53}\text{Ti}_{0.47})_{1-y-z}(\text{Nb}_y\text{Fe}_z)\text{O}_3$ ($x = 0-0.018$, $y = 0-0.022$ and $z = 0-0.02$) ceramics of near the MPB compositions were prepared by the conventional solid-state reaction of metal oxides. Polycrystalline ceramic materials were obtained using reagent-grade raw materials: PbO , ZrO_2 , TiO_2 , La_2O_3 , Nb_2O_5 and Fe_2O_3 . Raw materials in the appropriate ratios with 3 wt% excess PbO for compensation for Pb evaporation were ball-milled, and calcined at 800°C for 2 h. The calcined powder was ball-milled again and pressed into 10 mm diameter discs. Sintering was conducted at 1150°C for 2 h, in a lead-rich environment with PbZrO_3 atmosphere powder. For complex soft doping, La and Nb doped PZT samples ($x = 0.002-0.018$, $y = 0.0024-0.022$) compositions were made and, for complex both the soft and hard doping, La and Fe ($x = 0.01$, $z = 0.004-0.02$), Nb and Fe ($y = 0.012$, $z = 0.004-0.02$), and La, Nb and Fe ($x = 0.01$, $y = 0.012$, $z = 0.004-0.02$) doped PZT compositions were prepared. Table 1 summarizes the samples and compositions prepared in the present study. The 100- x , 100- y and 100- z values are equivalent to mol% of each metal dopant. Poling for the sintered and electroded specimens was conducted in silicone oil bath at 150°C , 30 min under a dc bias 3 kV/mm.

Table 1 Samples and compositions prepared

Samples	Compositions
100- $x\text{L}$ -100- $y\text{N}$	La (L) and Nb (N) doped PZT* ($x = 0.002-0.018$, $y = 0.0024-0.022$)
100- $x\text{L}$ -100- $z\text{F}$	La (L) and Fe (F) doped PZT ($x = 0.01$, $z = 0.004-0.02$)
100- $y\text{N}$ -100- $z\text{F}$	Nb (N) and Fe (F) doped PZT ($y = 0.012$, $z = 0.004-0.02$)
100- $x\text{L}$ -100- $y\text{N}$ -100- $z\text{F}$	La (L), Nb (N) and Fe (F) doped PZT ($x = 0.01$, $y = 0.012$, $z = 0.004-0.02$)

*Doped PZT: $\text{Pb}_{1-1.5x-0.5y+0.5z}\text{La}_x(\text{Zr}_{0.53}\text{Ti}_{0.47})_{1-y-z}(\text{Nb}_y\text{Fe}_z)\text{O}_3$

The phase formations of the sintered specimens were studied by an X-ray diffractometer (XRD) using $\text{Cu-K}\alpha$ radiation. For the polished and thermally etched (1100°C , 30 min) specimens, morphology studies and grain size measurements (line-intercept method) were performed by a scanning electron microscopy (SEM). The dielectric properties (at room temperature) of the poled ceramics were investigated using an inductance-capacitance-resistance (LCR) meter at 1 kHz. The piezoelectric properties of the specimens were calculated by the resonance-antiresonance method using an impedance analyzer.

3 Results and discussion

3.1 Effect of complex La and Nb dopants

Figure 1 shows the XRD result of the un-doped and both La and Nb doped PZT compositions. It is found that all the compositions have only perovskite phase with coexisting both the tetragonal and rhombohedral phases. The addition of both La and Nb ($x = 0.002-0.018$, $y = 0.0024-0.022$) did not

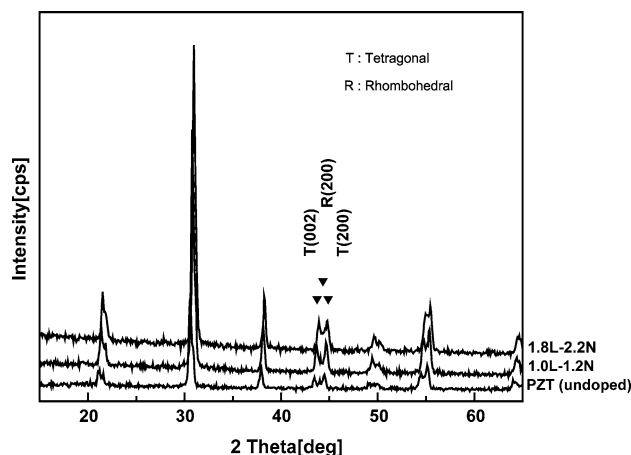


Fig. 1 XRD patterns of the prepared PZT ceramics undoped and doped with La and Nb

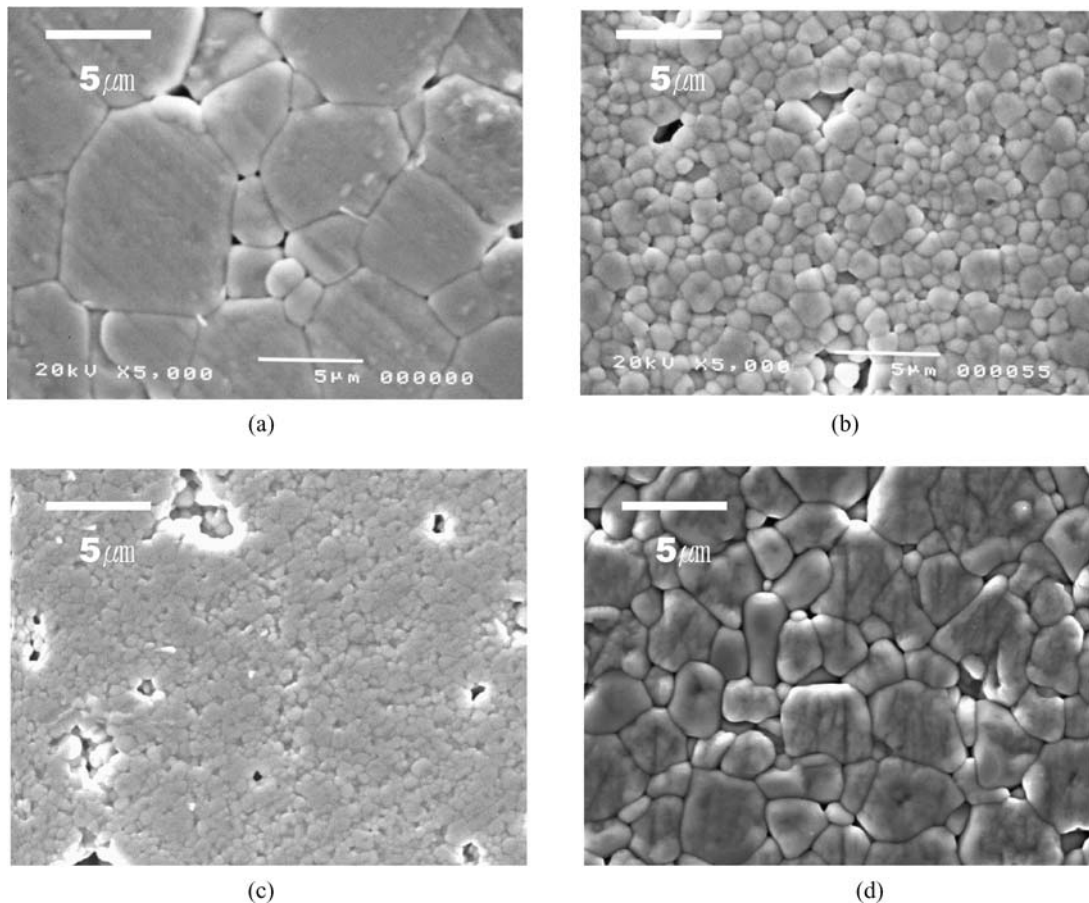


Fig. 2 SEM micrographs of surface morphology of prepared PZT ceramics undoped and doped with La, Nb and Fe: (a) Undoped PZT, (b) 1.0L-1.2N, (c) 1.4L-1.7N, and (d) 1.0L-1.2N-2.0F

significantly modify coexisting ferroelectric phases at MPB, but led to the lowered tetragonality (i.e., c/a ratio) from 1.23 of un-doped PZT to 1.017 of 1.8L-2.2N composition. The values of lattice parameter, a and c , of the tetragonal structure are also reduced with the dopants addition as shifted diffraction peaks to higher 2θ with the addition of dopants, hence this leads to a shrinkage of the PZT unit cell volume from 69.18 \AA^3 of undoped PZT to the lowest value of 67.52 \AA^3 of 1.8L-2.2 N composition. It is presumed that both the lowered tetragonality and unit cell volume are resulting from the increased cation vacancies with the addition of donor dopants, which relieve the tetragonal lattice distortion and lead to the reduced lattice parameter values. It is also known that the structural characteristics are attributed to the reduced grain size, because the hydrostatic compression due to the higher surface tension of finer grains (Fig. 2) of doped PZT ceramics leads to the lowered tetragonality and unit cell volume [20, 21].

The microstructures of pure PZT without dopants and both La and Nb doped are shown in Fig. 2(a)–(c). It is obvious that the grain size is strongly influenced by the additive content. The un-doped PZT has an average grain size of

$\sim 5 \mu\text{m}$. However, it is noted that the impurity addition of both La^{+3} and Nb^{+5} ions results in a significantly reduced grain size. The average grain sizes for the samples of 1.0La-1.2Nb and 1.4La-1.7Nb are observed to ~ 0.9 and $\sim 0.6 \mu\text{m}$, respectively, and no further reduction in grain size was found for the composition of 1.8La-2.2Nb. In general, it is well known that an addition of dopants caused an inhibition of grain growth [8, 9, 14, 22]. In the case of undoped PZT, the sintering kinetics can be described by lattice diffusion of vacancies from pores to grain boundaries, and the Nb doping reduces the diffusion coefficient: the vacancies as created by this doping are supposed to be bound to the impurity ion (e.g., Nb^{+5}), so that they inhibit the mass transport [9, 22]. For the both the donor (La and Nb) and acceptor (Fe) doped composition 1.0La-1.2Nb-2.0F, the effect of grain growth inhibition was lowered as shown in Fig. 2(d), because of the lowered vacancy density resulting from charge compensation, i.e., partially leveled-off charge, by substitution of lower valency cation Fe^{+3} on B site.

The piezoelectric properties were measured in a whole composition range from 0.20L-0.24N (corresponding to 0.1 wt% La_2O_3 and 0.1 wt% Nb_2O_5) to 1.8L-2.2N (0.9 wt%

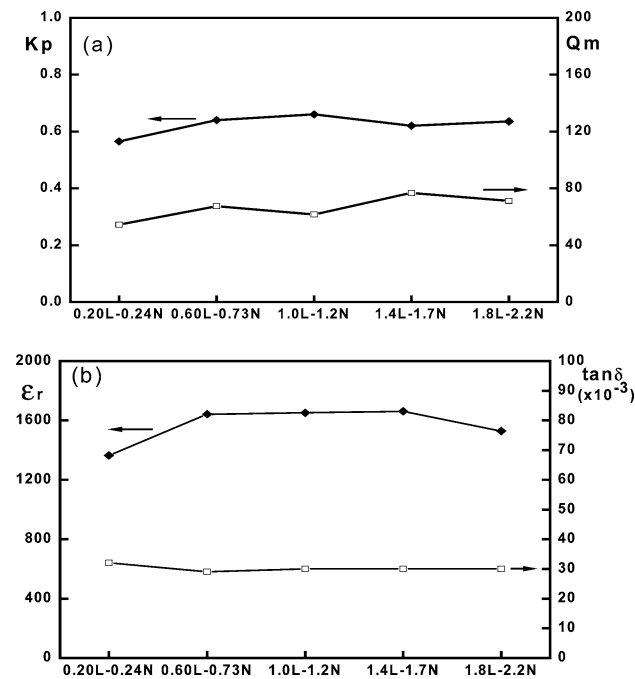


Fig. 3 Variation of piezoelectric and dielectric behaviors with various 100-xL-100-yN compositions: (a) k_p and Q_m , and (b) ϵ_r and $\tan\delta$

La_2O_3 -0.9 wt% Nb_2O_5). The values of planar coupling factors (k_p) and mechanical quality factor (Q_m) as a function of both the La and Nb dopants are shown in Fig. 3(a). As expected in donor doped PZT, the values of Q_m are as low as < 80 . The k_p values of all complex La and Nb doped samples are larger than 0.58; the maximum k_p value was as high as 0.66 for 1.0L-1.2N (0.5 wt% La_2O_3 -0.5 wt% Nb_2O_5) composition. For comparison, the k_p and Q_m were measured for the pure PZT and the values were 0.36 and 125, respectively. The values are lower than those ($k_p \sim 0.5$, $Q_m \sim 400$) of pure PZT ceramics reported elsewhere [1, 2, 12], which could be due to the poorly densified specimen sintered at relatively lower temperature (1150°C) for the undoped PZT. Dielectric constant (ϵ_r) at room temperature and loss factor ($\tan\delta$) at 1 kHz for the doped samples are presented in Fig. 3(b). The dielectric constant shows considerably higher values over 1300 than that of pure PZT of ~ 500 and the value increases at first and reaches its maximum values of 1650 for 1.4L-1.7N, then decreases to 1560 for 1.8L-2.2N composition. The values of $\tan\delta$ are around 0.03 through all composition range and the values are higher than those of pure PZT ceramics ($\tan\delta \sim 0.004$ [1, 2, 12] or 0.015 in the present study) as expected in donor doped PZT.

From the results, the complex donor dopants acts properly as softeners as widely reported [2–9] and the properties are saturated at the composition of 1.4L-1.7N (0.7 wt% La_2O_3 -0.7 wt% Nb_2O_5) leading to no further enhanced electrical properties with additional dopants content.

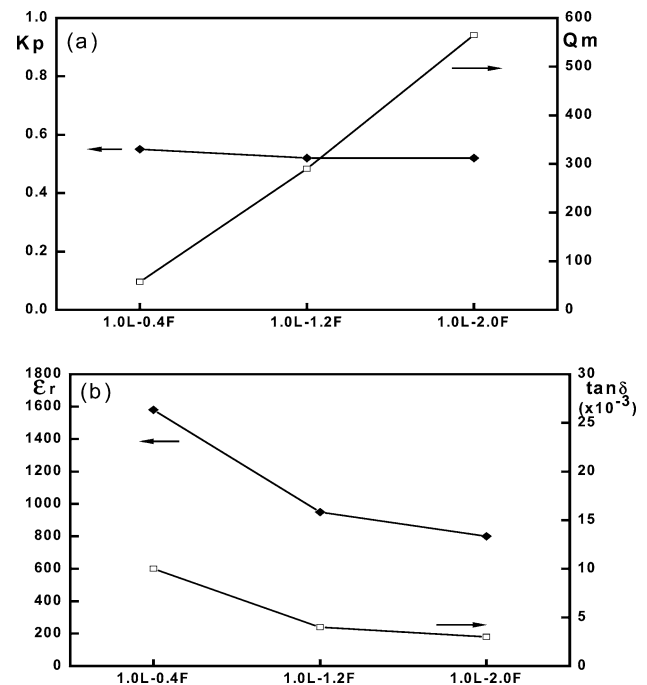


Fig. 4 Dependence of piezoelectric and dielectric behaviors for 1.0L-100-zF compositions on the amount of Fe content: (a) k_p and Q_m , and (b) ϵ_r and $\tan\delta$

3.2 Effect of Fe dopant on the La and/or Nb doped PZT

Fe^{3+} is systematically substituted for $\text{Ti}^{4+}/\text{Zr}^{4+}$ on the 1.0 mol% of La and/or 1.2 mol% Nb doped PZT (1.0L-100-zF, 1.2N-100-zF and 1.0L-1.2N-100-zF: $z = 0.004$ –0.02) compositions. The electrical properties of dielectric and piezoelectric performances for the complex doped compositions are presented in Fig. 4–6. When the Fe ion content is increased in the La and/or Nb doped PZT, all the electrical properties have a same tendency: k_p and dielectric constant are decreased; Q_m is increased. No significant differences in the dielectric and piezoelectric properties was observed between the samples with $z = 0$ and $z = 0.004$.

With increase of Fe content from 0.4 to 2.0 mol% in La and Fe doped PZT (1.0L-100-zF) composition, k_p is slightly reduced from 0.55 to 0.53 and Q_m value abruptly increases from 75 to 580 (Fig. 4(a)), while the dielectric constant is steeply reduced from 1600 to 800 and loss factor ($\tan\delta$) is down to around 0.003 (Fig. 4(b)). This is presumably attributed to the effect of Fe-doping, in that the Fe^{3+} ions substituted at the B sites for Zr^{4+} or Ti^{4+} ions compensates for the excessive charge of La^{3+} to the A site (Pb^{2+} ions). Complex doping with La^{3+} and Fe^{3+} produces semi-hard materials with the advantages of both soft and hard materials. The improved piezoelectric properties, i.e., enhanced Q_m with remaining relatively higher k_p , are obtained in the PZT composition.

As shown in Fig. 5, in 1.2N-100-zF compositions, k_p value decreases considerably with increasing Fe content and the

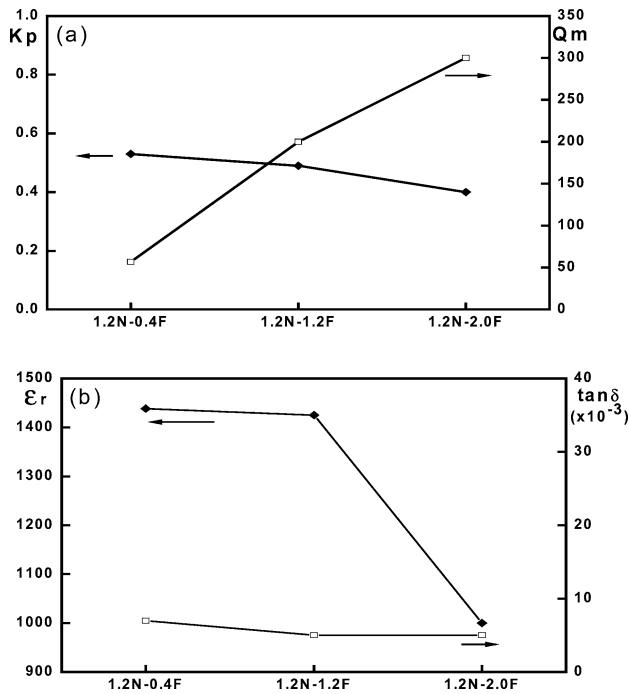


Fig. 5 Dependence of piezoelectric and dielectric behaviors for 1.2N-100-zF compositions on the amount of Fe content: (a) k_p and Q_m , and (b) ϵ_r and $\tan\delta$

values of dielectric constant and Q_m are changed less than those of 1.0L-100-zF compositions, which makes that the 1.2N-100-zF compositions are less preferable than the 1.0L-100-zF in piezoelectric applications.

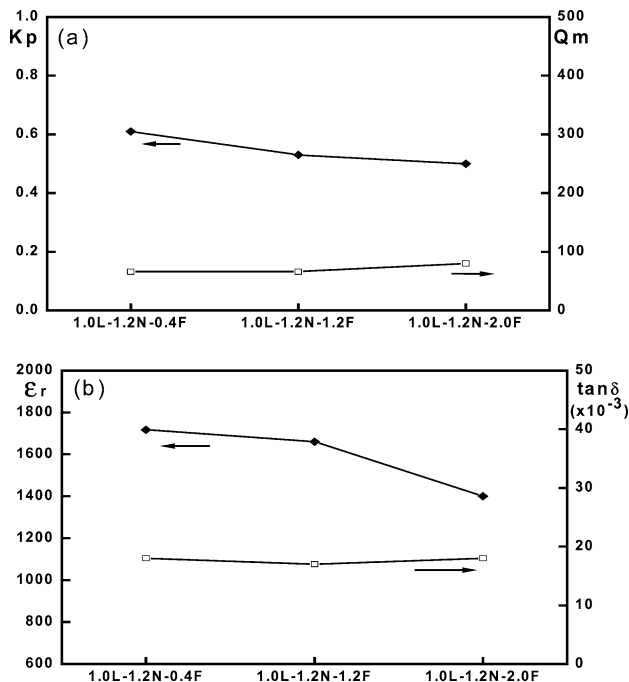


Fig. 6 Dependence of piezoelectric and dielectric behaviors for 1.0L-1.2N-100-zF compositions on the amount of Fe content: (a) k_p and Q_m , and (b) ϵ_r and $\tan\delta$

For the compositions of 1.0L-1.2N-100-zF, with increase of Fe content the piezoelectric k_p and Q_m values keep almost unchanged as shown in Fig. 6, except for the slightly reduced ϵ_r from 1700 to 1400. The results indicated that, for the prepared PZT ceramics modified with both the soft doping ions of La^{+3} and Nb^{+5} (e.g., 1.0L-1.2N), the piezoelectric properties are stable with the compositional variations, such as the unwanted additional elements from the raw materials having a considerable amount of impurities, which makes it possible to establish the higher reliability and reproducibility of the piezoelectric performances as soft PZT.

The introduction of complex dopants well modified the properties of the PZT ceramics and hence, with property selected additives and compositions, enhanced piezoelectric properties for doped PZT for various applications could be achieved.

4 Conclusions

PZT ($\text{Zr}/\text{Ti} = 53/47$) ceramics, modified with complex donor and acceptor dopants, have been synthesized by a solid-state reaction process. It was shown that, for the prepared PZT ceramics modified with complex donor doping ions of La^{+3} and Nb^{+5} , the piezoelectric properties were enhanced and stable with the compositional variations and impurity element addition, e.g., the additional acceptor (or impurity) contents, which made it possible to establish the higher reliability and reproducibility of the piezoelectric performances.

When the Fe ion content is increased in the La and/or Nb doped PZT, all the electrical properties have same tendency showing the increased Q_m and decreased k_p and ϵ_r values. The improved piezoelectric properties, i.e., enhanced Q_m with remaining higher k_p were obtained in the PZT compositions doped with La^{+3} and Fe^{+3} .

From the results obtained in this study, the properties of the compositionally modified PZT ceramics can also be tailored over wider range by changing the dopants compositions to meet the specific requirements for different applications.

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