PZT ceramics prepared through a combined method of B-site precursor and wet mechanically activated calcinate in a planetary ball mill

H. Goudarzi, S. Baghshahi⁎

Department of Materials Science and Engineering, School of Engineering, Imam Khomeini International University, Qazvin, Iran

A R T I C L E   I N F O

Keywords:
PZT 95/5
Microstructure
Ferroelectric
Piezoelectric
Young’s modulus

A B S T R A C T

0.02 Nb-PZT 95/5 (PZTN) and 0.02 Nb-0.004La-PZT 95/5 (PLZTN) samples were prepared by a combined method of B-site precursor, whereby ZrO2, TiO2, Nb2O5 and La2O3 were pre-reacted, prior to reaction with PbO. Then the wet mechanically activated PZT calcinates prepared using a planetary ball mill were pressed into pellets and sintered at 1275 °C for 2 h in air. The microstructure, ferroelectric and piezoelectric properties of the samples were studied. PLZTN samples had microstructures with fine grains (average grain size of 2.98 μm) in comparison with the PZTN samples (average grain size of 4.53 μm). The relative densities of the PZTN and PLZTN samples were approximately 92.8% and 94.8%, respectively. The piezoelectric coefficient (d33), voltage coefficient (g33), relative dielectric constant (εr), dielectric loss (tanδ), electromechanical coupling coefficient (k33), Young’s modulus (Y11), Poisson’s ratio (ν13), mechanical quality factor (Qm) for PLZTN samples were 70 PC/N, 25.50 mVm/N, 310, 0.022, 0.163, 126.1 GPa, 0.2535 and 304, respectively, which were better than those of PZTN samples (65 PC/N, 25.46 mVm/N, 288, 0.024, 0.162, 118.0 GPa, 0.2444 and 227, respectively).

1. Introduction

Ferroelectric Nb-doped Pb(Zr0.95Ti0.05)O3 is an important material used for pulsed power devices [1–4]. Bulk density of 7.75 g cm−3, electromechanical coupling coefficient of 0.0182, and elastic compliances S11 of 7.68 and −1.97×10−12 m2/N, respectively, sound velocity of 4194 m/s, Poisson’s ratio of 0.2572, elastic modulus of 130×109 N/m2, the relative dielectric constant and loss of 300 and 0.02%, respectively, and piezoelectric coefficients g33 of 26.28 and −5.99×10−3 Vm/N, respectively were the typical properties of the niobium modified PZT 95/5 ferroelectrics [1]. Homogeneity of the PZT powder calcinate is very important for obtaining better physical properties of ceramics. It is known that PbO evaporates during sintering process at high temperatures from PZT phase, which causes degradation of ferroelectric and piezoelectric properties as a result of the formation of nonstoichiometric perovskite phase. Furthermore, PZT ceramics with higher Zr: Ti ratios have some difficulties in densification, leading to a lower performance [5]. A great deal of effort has been made during the last decades for enhancing the activity of PZT calcinate, while retaining proper ferroelectric and piezoelectric properties. Since intermediate reactions occur in the formation of the complex perovskite PZT [6], the B-site precursor method developed by Swartz and Shrout [7] was used, whereby ZrO2, TiO2 and Nb2O5 were pre-reacted, prior to adding PbO. In the first step of the process, the (Zr1−x,0.02−x,Ti)x−0.02−x,O mixture is prepared by mechanical milling of ZrO2, TiO2 and Nb2O5. Then PbO is mixed into the initial powder mixture [8]. The maximum densification temperature is significantly lowered when using this method compared to the powders made with conventional methods [9,10]. Various dopants have been examined for enhancing densification and improving performance of the samples [11–13]. Especially, donor dopants, such as Nb5+[14,15], W6+[16], Nd3+[17] and La3+[18,19] have been extensively investigated. Up to now, a special and extensive attention has been given to the PZT with x~0.53 [20,21], which corresponds to the morphotropic phase boundary (MPB) composition. However, little work has been done on the second MPB composition, namely, the PZT with x~0.95, and research on doping modification of Pb0.99(Zr0.95Ti0.03)0.98Nb0.02O3 (PZTN) ceramics adapted from Fritz [22].

In this work, the microstructure and ferroelectric and piezoelectric properties of PZT 95/5/2 and 0.004La-PZT 95/5/2 ceramics prepared from a combined method of B-site precursor and wet mechanically activated PZT calcinate in planetary ball mill is investigated.

2. Experimental

Samples with the general formula Pb0.99(Zr0.95Ti0.03)0.98Nb0.02O3...
(PZTN) and (Pb0.99La0.004)(Zr0.95Ti0.05)0.98Nb0.02O3 (PLZTN) were fabricated by a combined method of B-site precursor and wet mechanically activated PZT calcinate in planetary ball mill using the solid state method with the PbO, ZrO2, TiO2, Nb2O5, and La2O3 powders. The raw materials were all oxide powders of analytical grade. In the first step of preparation process, all the powders, except for lead oxide were mixed and milled in a planetary fast mill, with zirconia jar (V=250 cm³), balls (d=15 mm) and ball-to-powder weight ratio of 15:1. The powder quantity was 40g, the milling speed was 300 rpm and the milling time was 20 min [23]. Distilled water was used as the media. The suspensions were dried and calcined at 1400 °C for 4 h. The calcined powders were then ball-milled again for 20 min to crash the agglomerates and achieve a submicron particle size distribution. PbO was mixed in the second step into the firstly prepared powder mixture and mixed and milled again in the planetary fast mill with the same conditions, except that the milling time was 30 min. Distilled water was used as the media. The suspensions were dried and calcined at 900 °C for 2 h. The calcined powders were then ball-milled again for 20 min to crash the agglomerates and achieve a submicron particle size distribution.

After granulation using a solution of polyvinyl alcohol as the binder, the as-synthesized samples were uniaxially pressed into discs of 10 mm diameter and about 4 mm thickness at a pressure of 120 MPa. After the binder burnout, the pressed samples were subsequently sintered in sealed alumina crucibles with a PbO rich atmosphere buffer at sintering temperature of 1275 °C for two hours. The sintered samples were polished and lapped to the final dimensions of 9 mm diameter and 2 mm thickness and coated with silver paste as electrodes. The ceramic samples were polarized under a direct current field of 2 kV/mm at 120 °C in a silicone oil bath for 20 min.

The microstructure was investigated with a scanning electron microscope (SEM, Model VEGA//TESCAN). The dielectric constant was studied by measuring the capacitance at 1 kHz at the room temperature using an impedance-gain analyzer (IGA, Model HP4194A). Dielectric constant ε was computed using the specimen dimensions and the vacuum permittivity (ε0=8.854×10−12 F.m−1). The piezoelectric constant (d33) was measured using a d33 meter (Model KCF-3500) at 110 Hz. The electromechanical coupling coefficient (kp) and mechanical quality factor (Qm) were determined by the resonance/anti-resonance frequencies method according to the IRE standards using a HP4194A impedance analyzer. The parameter kp and Qm were related to the resonance/anti-resonance frequencies by the following expressions [24]:

\[
\begin{align*}
k_p &= \frac{(f_r - f_a)(0.395f_r + 0.574(f_r - f_a))^{1/2}}{2\pi Z_m C_f (f_r^2 - f_a^2)} \\
Q_m &= f_r^2/2\pi Z_m C_f (f_r^2 - f_a^2)
\end{align*}
\]

Where f_r is the resonant frequency and f_a is the anti-resonant frequency in the fundamental vibration mode. Z_m and C represent the resonant impedance and the capacitance on the mechanical branch of the equivalent circuit, respectively. The elastic compliances S_{11}^E and S_{12}^E, Poisson’s ratio (\sigma), Young’s modulus (Y_{11}^E), sound velocity (v) and the piezoelectric coefficient (d_{33}) were determined by measurements of fundamental resonance frequencies of the two radial and thickness extension modes by the following expressions [11]:

\[
\begin{align*}
S_{11}^E &= (2f_r)^2/p \\
S_{12}^E &= -\alpha D f_r/(\pi) \\
\sigma &= -S_{12}^E/S_{11}^E \\
v &= (\rho S_{11}^E)^{1/2} \\
Y_{11}^E &= 1/S_{11}^E
\end{align*}
\]

Where d_{33}, d_{31}, and v are the piezoelectric coefficients and the dielectric constant of sample, respectively and \varepsilon_0 is the vacuum permittivity.

---

**Table 1**
The starting compositions and phases detected by XRD analysis after calcination at 1400 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Starting comp. (mol%)</th>
<th>Detected phases by XRD analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZTN</td>
<td>94.0 5.0 1.0 0.0</td>
<td>ZrO2 (solid solution)</td>
</tr>
<tr>
<td>LZTN</td>
<td>93.9 4.9 1.0 0.2</td>
<td>ZrO2 (solid solution)</td>
</tr>
</tbody>
</table>

**Fig. 1.** The XRD patterns of the ZrO2, 0.02 Nb-ZT 95/5(ZTN) and 0.02 Nb-0.004La-ZT 95/5(LZTN) precursor powders.

**Fig. 2.** The XRD patterns of calcined powder of Pb0.99(Zr0.95Ti0.05)0.98Nb0.02O3 (PZTN) and (Pb0.99La0.004)(Zr0.95Ti0.05)0.98Nb0.02O3(PLZTN).

\[
d_{31} = k_p[(S_{11}^E + S_{12}^E)\varepsilon_0]/2^{1/2}
\]

Where f_r and f_a are the resonant frequencies in the two radial and thickness extension modes, respectively, t, D, \rho and v are thickness, diameter, bulk density and the dielectric constant of sample.

The voltage coefficients (g_{33}) and (g_{31}) were computed by the following expressions [11]:

\[
\begin{align*}
g_{33} &= d_{33}/\varepsilon_0 \varepsilon_r \\
g_{31} &= d_{31}/\varepsilon_0 \varepsilon_r
\end{align*}
\]

Where d_{33}, d_{31}, and \varepsilon_r are the piezoelectric coefficients and the dielectric constant of sample, respectively and \varepsilon_0 is the vacuum permittivity.
Fig. 3. The SEM photographs of the fractured surfaces of the PZTN (Left) and PLZTN (Right) samples.

Fig. 4. The SEM and mapping of the PZTN ceramics.
3. Result and discussion

3.1. Sintering behavior

The sintering behavior of the PZTN and PLZTN ceramics was investigated. It was found that the PZTN and PLZTN ceramics sintered at 1275 °C shows the maximum bulk density of approximately 92.8% and 94.8% of theoretical density, respectively. The optimum bulk density of PZTN ceramics was approximately 94.6% of theoretical density when sintered at its optimum sintering temperature of 1350 °C [25]. It proves that the addition of La enhances the densification and also reduces the sintering temperature of the PZTN ceramics. It is known that the main densification mechanism is volume diffusion, which is controlled by the number of vacancies [26]. The La ions will substitute the Pb ions on the A site of the perovskite structure. Then to conserve the electron neutrality, Pb vacancies are created, which enhance the volume diffusion and consequently the final densities. The Pb-vacancy concentration in the PZTN ceramics is high enough to obtain a high densification rate [27], with the resulting final bulk density of 7.42 g cm$^{-3}$. PLZTN specimens will create a significant amount of Pb-vacancies in order to achieve the electron neutrality condition and as a consequence enhances volume diffusion and final bulk density of 7.58 g cm$^{-3}$.

3.2. Phase and microstructure analysis

The XRD patterns of the ZrO$_2$, 0.02 Nb-ZT 95/5(ZTN) and 0.02 Nb-0.004La-ZT 95/5(LZTN) precursor powders are shown in Fig. 1. As observed, the only phase detected by XRD was monoclinic zirconia phase (GCPDS Card No. 00-007-0343). The solid solubility limit of TiO$_2$, Nb$_2$O$_5$, and La$_2$O$_3$ in ZrO$_2$ was determined by Bannister [28], Mestres [29] and Rouanet [30] to be 14.9, 10 and 2 mol% at 1400 °C, respectively. Starting compositions and phases detected by XRD analysis after calcination at 1400 °C are shown in Table 1. The intensity peaks of ZTN and LZTN precursor powders indicate the formation of the zirconia solid solution phase. The XRD patterns of the PZTN and PLZTN powder are shown in Fig. 2. The patterns indicate the formation of the single perovskite phase. The XRD pattern of the PZTN sample shows the existence of the rhombohedral phase. XRD results are in agreement with the literature [31–33].

It is known from the literature that in the case of Zr-rich PLZT materials, La mainly replaces Pb, creating vacancies in the sublattice. The La sites are considered as donors, whereas Pb vacancies behave as acceptors. The La-Pb pairs can also be considered as dipoles giving rise to dipolar polarization. In the vicinity of the AFE-FE phase transition, they can play the role of nucleation centers of FE domains similar to the Nb$^{5+}$-Pb dipoles in the Nb-doped PbZrO$_3$, and PZT ceramics. The diffraction peak positions of the PLZTN sample gradually shift toward smaller angles. The relationship between the shifted angle and the composition is consistent with substitution of La$^{3+}$(radius=1.32 Å) for Pb$^{2+}$(radius=1.49 Å). Due to the smaller electronegativity of the La$^{3+}$ ions (1.10) in comparison to the Pb$^{2+}$ ions (2.33) [34], the oxygen atoms are less displaced and the contribution of the LaO dipoles on the

Fig. 5. The SEM and mapping of the PLZTN ceramics.
polarizability is smaller. However, a small change in the lattice parameters can also be inferred by the small shift in peak intensity positions.

The lanthanum substitution in the PZTN samples affected the microstructure of the specimens. The SEM photographs of the fractured surfaces of the PZTN and PLZTN samples are presented in Fig. 3. Moreover, the PLZTN samples had finer microstructures. It is known that the addition of dopants substituting A- or B-site atoms can cause a strong reduction of the grain size. This “grain growth inhibition effect” has been attributed to the pinning effect of the segregated additives at the grain boundary, without any corroborating evidence as pointed out by Hammer and Hoffmann [26].

The SEM and mapping of the PZTN and PLZTN ceramics are presented in Figures 4 and 5. A more homogeneous and denser microstructure can be clearly observed in the PLZTN than in the PZTN ceramics, which is in accordance with the density measurements mentioned before.

Furthermore, the grain size distributions of the two kinds of ceramics are quantitatively characterized by Clemex Vision software, as shown in Fig. 6a, b, respectively. The distribution parameters of the grain diameter for the different ceramics are listed in Table 2. The average grain size and the standard deviation for PLZTN samples are 2.98 µm and 1.51, respectively, less than that of PZTN ceramics (4.53 µm and 1.70, respectively). Evidently, the grain size of PZTN ceramics tends to be smaller by the addition of La.

Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>Minimum(µm)</th>
<th>Maximum(µm)</th>
<th>Average(µm)</th>
<th>Standarddeviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZTN</td>
<td>2.0</td>
<td>10.2</td>
<td>4.53</td>
<td>1.70</td>
</tr>
<tr>
<td>PLZTN</td>
<td>0.5</td>
<td>8.1</td>
<td>2.98</td>
<td>1.51</td>
</tr>
</tbody>
</table>

3.3. The ferroelectric and piezoelectric properties

The relative dielectric constant and dielectric loss of the PZTN and PLZTN ceramics are listed in Table 3.

It is observed that the addition of 0.4 mol% La enhanced the relative dielectric constant and reduces the loss factor (tanδ). It is known that increasing densification causes an increase in the relative dielectric constant and a decrease in the dielectric loss as a result of the reduction in pore content. Therefore, when 0.4 mol% lanthanum was doped, the maximum value of dielectric constant and the minimum dielectric loss were obtained due to the maximum density. Of course, the higher εr, for the PLZTN samples compared to the PZTN has also been attributed to a higher domain wall motion due to a higher Pb-vacancy concentration [26].

The piezoelectric coefficients (d33 and d31), the voltage coefficients (g33 and g31), the planar electromechanical coupling coefficient (k33) and mechanical quality factor (Qm) of the PZTN and PLZTN ceramics are listed in Table 4.

As observed, the piezoelectric coefficient (d33), the planar electromechanical coupling (k33) and mechanical quality factor (Qm) for PZTN ceramics are less than that of PLZTN ceramics and the piezoelectric coefficient (d31) and the voltage coefficient (g33) for PZTN ceramics are near that of PLZTN ceramics. It is well known that La addition may control the piezoelectric, dielectric, and ferroelectric properties [11]. It was revealed that La2O3 as a donor type dopant, enters the A lattice site near that of PLZTN ceramics. The elastic constants and sound velocity of the PZTN and PLZTN ceramics are listed in Table 5.

As observed, the piezoelectric coefficient (d33), the planar electromechanical coupling (k33) and mechanical quality factor (Qm) for PZTN ceramics are less than that of PLZTN ceramics and the piezoelectric coefficient (d31) and the voltage coefficient (g33) for PZTN ceramics are near that of PLZTN ceramics. It is well known that La addition may control the piezoelectric, dielectric, and ferroelectric properties [11]. It was revealed that La2O3 as a donor type dopant, enters the A lattice site and thus causes Pb2+ vacancies in the PZT system due to the valence discrepancy. Due to the increase of Pb2+ vacancies, the movement of the ferroelectric domain walls can be promoted, which will consequently cause the drop of lattice stresses, leading to the improvement of d33, k33 and Qm [26].

The elastic constants and sound velocity of the PZTN and PLZTN ceramics are given in Table 5. It is observed that the addition of 0.4 mol % La enhanced Young’s modulus, Poisson’s ratio and sound velocity. It is known that increasing densification causes an increase in the elastic modulus and Poisson’s ratio as a result of the reduction in pore content. This result shows that the incorporation of the lanthanum to the perovskite structure promotes the Pb vacancies (A site) and may likely...
have an intense effect on the domain motions, because of the expansion in the unit cell in the direction of the polarization [20]. The La addition increases the A-site vacancies concentration and a higher ferroelectric domain motion [11,27]. Therefore a higher fraction of the electrical energy is converted into mechanical energy when the material is used for transducer application.

4. Conclusions

La-PZTN 95/5/2 ceramics with high density and fine grains were prepared through a combined method of B-site precursor and wet mechanically activation of PZT calcinates in a planetary ball mill. The 0.4 mol% La-added PZTN95/5/2 sample sintered at 1275 °C exhibited a bulk density of approximately 94.8% of theoretical density and an average grain size of 2.98 µm, superior to that of the PZTN 95/5/2 sample sintered at 1275 °C, 92.8% and 4.53 µm. The piezoelectric average grain size of 2.98 µm, superior to that of the PZTN 95/5/2 sample sintered at 1275 °C, 92.8% and 4.53 µm. The piezoelectric coefficient (d33), relative dielectric constant (εr), dielectric loss (tanδ), Young’s modulus (Y11), Poisson’s ratio (σ) and mechanical quality factor (Qm) and electromechanical coupling coefficient (k33) for PLZT samples are 70PC/N, 310, 0.022, 126.1 GPa, 0.2535, 304 and 0.163, respectively, better than that of PZTN samples (65PC/N, 288, 0.024, 118.0 GPa, 0.2444, 227 and 0.162, respectively), which are promising for shock-wave power supplies.

References


[25] V.J. Wang, X. Chen, J. Wang, G. Wang, H. Nie, F. Cao, X. Dong, Improved dielectric breakdown strength of Pb0.95(Zr0.95Ti0.05)0.98Nb0.02O3 ferroelectric ceramics with the addition of CuO, J. Mater. Sci.: Mater. Electron. 26 (2015) 8207–8211.


[31] J. Wang, G. Wang, H. Nie, X. Chen, F. Cao, X. Dong, Y. Gu, H. He, Low temperature sintering and electric properties of Pb0.95(Zr0.9Ti0.1)O3 doped with Nb2O5 ferroelectric ceramics with CuO additive, J. Am. Ceram. Soc. (2013) 1–4.

