

Effect of La₂O₃ doping on the piezoelectric properties of PbZrO₃-PbTiO₃-Pb(Zn_{1/3}Nb_{2/3})O₃-Pb(Sn_{1/3}Nb_{2/3})O₃-YMnO₃ ceramics for high-power applications

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Piezoelectric materials with high vibrational velocities are desired for high-power applications. We doped La₂O₃ into 0.98 [0.4PbZrO₃-0.42PbTiO₃-0.12Pb(Zn_{1/3}Nb_{2/3})O₃-0.06Pb(Sn_{1/3}Nb_{2/3})O₃]-0.02YMnO₃ piezoelectric ceramics in order to enhance their vibrational velocities. Dissolving the La₂O₃ into the ceramics changed their crystal structures and material properties. However, when a La₂O₃ content of over 10 mol% was used, XRD data showed that some of the La₂O₃ precipitated. A 4 mol% La₂O₃-doped ceramic had a phase transition temperature of 278 °C and a vibrational velocity of 0.73 m/s (for a 20 °C temperature rise). Compared with the vibrational velocities of current hard PZT ceramics, which are in the range of 0.4 to 0.6 m/s, this large vibrational velocity will be promising for high-power piezoelectric applications.

Key words: Vibrational velocity, Doping, Piezoelectric ceramics, High power.

Introduction

Piezoelectric materials are used in various devices, such as physical sensors, actuators, tiny ultrasonic motors, and piezoelectric transformers, because they can convert electrical energy into mechanical energy or vice versa [1-9]. Piezoelectric ceramics having a large electromechanical coupling factor and mechanical quality factor at high driving electric fields are desired especially for high-power device applications, such as ultrasonic motors and transformers. However, because the piezoelectric properties change with the applied electric field, it is very difficult to obtain good piezoelectric characteristics under high electric fields. This is mainly related to the non-linear degradation of the electromechanical quality factor of piezoelectric materials, which is due to the large amount of abruptly generated heat under the high-field driving conditions and large vibration [1]. There are currently several piezoelectric compositions that are suitable for high-power applications. Most of these have a high electromechanical coupling factor and mechanical quality factor under low-field driving conditions. There have been several approaches to overcome these shortcomings for high-field driving conditions. Examples of such piezoelectric ceramics are PbZrO₃-PbTiO₃-Pb(Zn_{1/3}Nb_{2/3})O₃-Pb(Sn_{1/3}Nb_{2/3})O₃ (PZT-PZN-PSN) to which MnO₂ or YMnO₃ is added [8], PbZrO₃-PbTiO₃-Pb(Mn_{1/3}Nb_{2/3})O₃ (PZT-PMnN) [3, 10], and PbZrO₃-PbTiO₃-Pb(Sb_{1/3}Mn_{2/3})O₃ (PZT-PSM) [9]. These are known to have excellent piezoelectric

properties even under high-field driving conditions. Consequently, piezoelectric ceramics whose mechanical quality factor does not decrease significantly even under high-field driving conditions are in great demand.

A solid solution of PZT-PZN-PSN has been shown to possess excellent piezoelectric properties for low-field driving applications. In addition, it has been reported that doping with MnO₂ or YMnO₃ can improve its piezoelectric properties under high-field driving conditions [8]. In this research, we tried to modify the composition in order to achieve excellent piezoelectric properties under high-field driving conditions. In particular, we aimed to improve the mechanical quality factor and vibrational velocity of the material with doping La₂O₃ so that it may be used for high-power piezoelectric applications.

Experimental

Following a previous study [8], we chose a base composition of 0.98[0.4PbZrO₃-0.42PbTiO₃-0.12Pb(Zn_{1/3}Nb_{2/3})O₃-0.06Pb(Sn_{1/3}Nb_{2/3})O₃]-0.02YMnO₃ (PZT-PZN-PSN-YM). This base composition was doped with 4, 8, 10, and 12 mol% La₂O₃. The piezoelectric ceramics were synthesized by conventional solid-state oxide methods. Pure reagent-grade (99.9% purity, all from Alfa Aesar Co. Ltd., USA) ceramic powders were ball-milled using ethanol and 3Y-TZP balls for 24 hours. The slurry mixture was dried and calcined at 850 °C for 2 hours to induce a phase formation. After this calcination process, the new phase was confirmed by XRD (X-ray diffraction, Scintag Inc). The calcined powder was then ball-milled again for 24 hours in order to obtain finer particles. After drying the slurry, it was crushed and passed through a stainless steel screen. Pellets (φ12.7 × 3 mm³)

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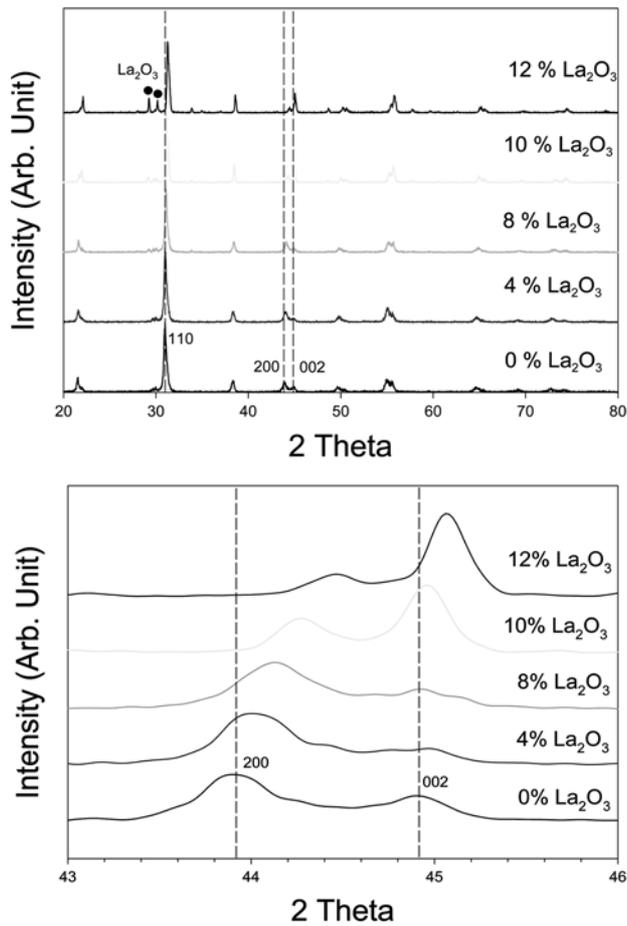


Fig. 1. XRD patterns of the piezoelectric ceramics having various La_2O_3 contents. All of the samples had been sintered at 1200°C for 2 hours.

and rectangular bars ($50 \times 10 \times 3 \text{ mm}^3$) were made in hardened-steel dies using a hydraulic press under a pressure of about 30 MPa. The samples were then isostatically pressed under a pressure of 272 MPa in rubber bags using a wet cold isostatic press. The piezoelectric ceramics were sintered in a box furnace at 1200°C for 2 hours. The sintered density was measured by the Archimedes liquid immersion method using xylene ($\rho = 0.861 \text{ g/cm}^3$ at 20°C). For all of the measurements, 6 or more samples of each composition were tested. The crystalline phases of the sintered ceramics were analyzed by XRD.

For the dielectric measurements, gold was sputtered onto the polished surfaces. The samples were poled in silicone oil at $120\text{-}150^\circ\text{C}$ by applying a DC field of 3 kV/mm for 10 minutes. The piezoelectric coefficient d_{33} was measured from one-day-old samples using a Berlincourt d_{33} meter (IAAS ZJ-2, Beijing, China). For each sample, the dielectric constant and loss for the temperature change were measured using an LCR meter (HP model 4284) and an automated temperature-controlled furnace. The electromechanical coupling factor (k_{31}) and mechanical quality factor (Q_m) were measured according to the IEEE standards [12], using an impedance analyzer (Model

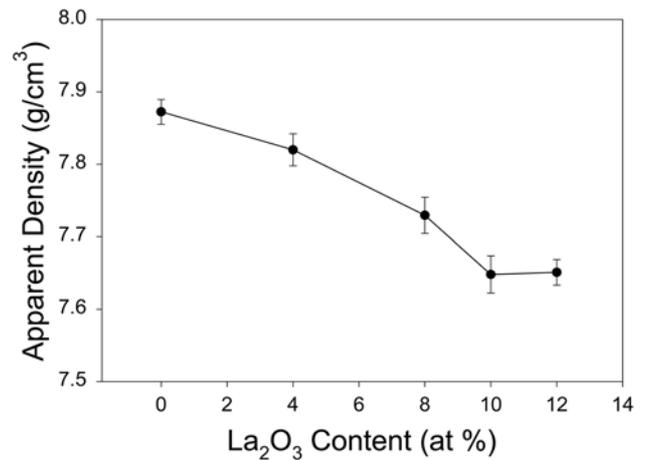


Fig. 2. Apparent densities of the piezoelectric ceramics as a function of La_2O_3 content.

HP 4194). The vibration velocity (v_0) of rectangular bars was measured using laser doppler vibrometers (LDVs) (models OFV-3001 and OFV-511, Polytec PI). It should be noted that the vibration level was the rms value of the vibration velocity, which is independent of the sample size at the mechanical resonance frequency [9]. The vibration velocity was calculated using the following equation:

$$v_0 = \left(\frac{1}{\sqrt{2}} \omega_0 \xi_m \right) \quad (1)$$

where ω_0 and ξ_m are the angular resonance frequency and the maximum vibration amplitude, respectively [9]. By putting a thermocouple on the nodal point of the vibrating rectangular bar, the temperature change was determined.

Results and Discussion

Fig. 1 shows the XRD patterns of the PZT-PZN-PSN-YM ceramics doped with the various amounts of La_2O_3 . The crystalline structure of La_2O_3 -doped PZT-PZN-PSN-YM was found to be affected by the La_2O_3 content. When the La_2O_3 content was low, the PZT-PZN-PSN-YM crystal had a tetragonal perovskite structure. This was evident from the (200) and (002) peaks near a 2θ of 45° of. However, doping of the PZT-PZN-PSN-YM ceramics with La_2O_3 resulted in a decrease in the lattice constants of (200) and (002). In addition, at higher La_2O_3 contents, the tetragonality decreased. These results are in good agreement with other reports on La-doped PZT-based systems [4-7]. The ceramics having less than 8% La_2O_3 appeared to have a tetragonal phase without a secondary phase. However, as the La_2O_3 content was increased to over 8%, some of the La_2O_3 precipitated out. It is known that in some complex perovskite structures (e.g. $\text{Pb}(\text{ScTa})\text{O}_3\text{-PbTiO}_3$ and $\text{PZN-BaTiO}_3\text{-PbTiO}_3$ systems) many of the La ions do not enter the lattice after the perovskite crystal formation, but instead assemble at the grain boundaries [4-7].

Fig. 2 shows the apparent densities of the various La_2O_3 -doped piezoelectric ceramics sintered at 1200°C for 2 hours.

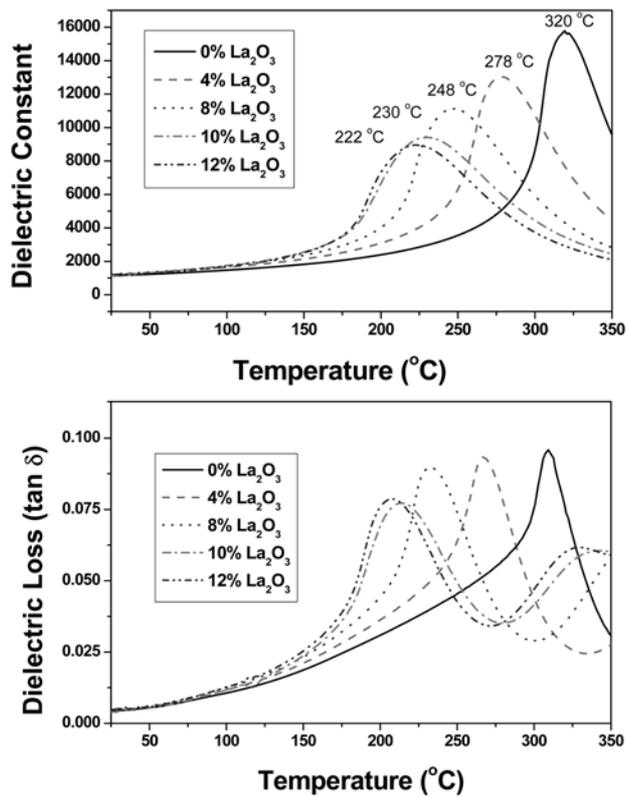


Fig. 3. Dielectric constants and losses as a function of temperature for the various different ceramic compositions. All of the samples had been sintered at 1200 °C for 2 hours.

As the La₂O₃ content was increased from 0 to 10%, the apparent density also decreased. Since it is quite difficult to calculate the theoretical densities of La₂O₃-doped ceramics, we could not calculate the relative densities of the La₂O₃-doped ceramics. From the XRD data, La₂O₃ doping might have changed the lattice constant and theoretical density also. However, when over 10% La₂O₃ was used, the apparent density did not change (considering the experimental error range). In this case, some of the La₂O₃ could not dissolve into the piezoelectric ceramic; instead, it precipitated out.

The dielectric constants of the samples as a function of temperature are shown in Fig. 3. As the content of La₂O₃ was increased between 0, 4, 8 and 10%, the phase transition temperature (T_c), which is known as the Curie temperature, decreased from 320, 278, 248 to 230 °C, respectively. When over 10% La₂O₃ was used, the T_c did not change much; for instance, the ceramic doped with 12% La₂O₃ exhibited a T_c of 222 °C. This result also indicates that up to 10% La₂O₃ can easily be dissolved into PZT-PZN-PSN-YM ceramics, resulting in both structural and property changes. However, when the La₂O₃ content was increased further, some of the La₂O₃ was concentrated at the grain boundaries.

Fig. 4 shows the piezoelectric properties measured under low-field driving conditions (1 V_{p-p}). With increasing La₂O₃ content, while the piezoelectric constant (d_{ij}), coupling factor (k_{31}), and elastic compliance (S_{11}^E) decreased, the

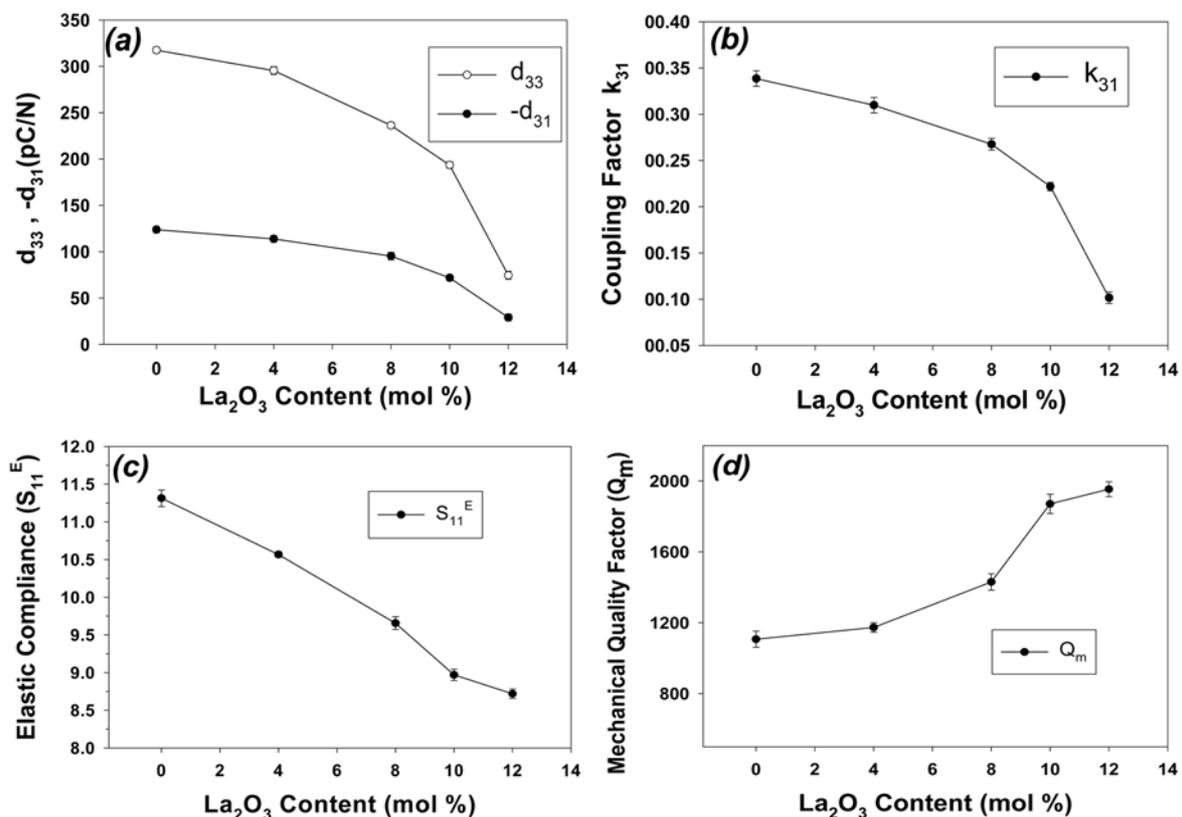


Fig. 4. (a) Piezoelectric constants, (b) electromechanical coupling factors, (c) elastic compliances, and (d) quality factors of the piezoelectric ceramics having various amounts of La₂O₃. All of the samples were tested at room temperature.

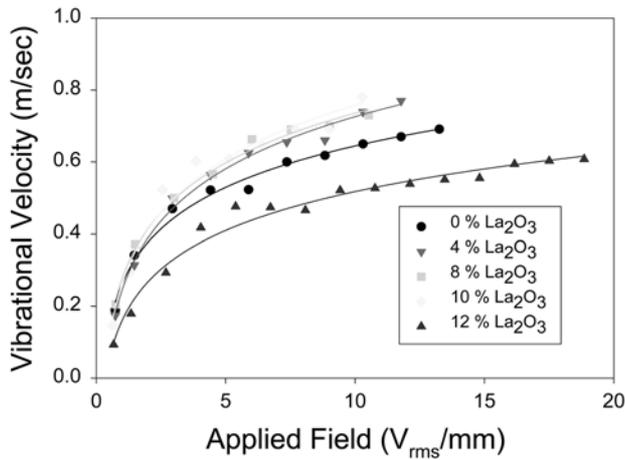


Fig. 5. Vibration velocities (v_0) as a function of the applied electric field (E_{ac}).

mechanical quality factor (Q_m) increased. Considering “hard” piezoelectric ceramics are featured as having higher mechanical quality factors, lower piezoelectric constants and electromechanical coupling factors, La_2O_3 might act as a hardener in our experiments. Similar hardening effects of La on complex perovskites have been reported elsewhere [6, 7].

Because the maximum possible power density from a particular piezoelectric material depends on the maximum achievable v_0 , the vibrational velocity characteristics (v_0 , rms value) of the piezoelectric body should be investigated for high-power applications. Since the power density increases with the square of the v_0 , a small increase in this parameter can significantly improve the power density [1, 9]. Merely increasing the electric field applied can increase v_0 . However, because of heat generation in the material, there are limitations to the maximum electric field that can be applied. In general, the maximum v_0 that a piezoelectric material of a given size can withstand is defined as the velocity that produces an increase of 20 °C in the temperature of the material. Current hard PZT materials have a v_0 in the range of 0.4 to 0.6 m/s and improvements of their vibration velocities are required to increase their power capabilities [3]. However, as the v_0 cannot simply be represented by an electromechanical coupling factor and a mechanical quality factor, which were measured at low electric field, we directly measured the v_0 under high electric field conditions. Fig. 5 shows the v_0 values, which were measured as a function of the applied electric field (E_{ac} , rms value). As the content of La_2O_3 was increased from 0 to 10%, v_0 also increased (for the same electric fields). For instance, at $E_{\text{ac}} = 10 V_{\text{rms}}/\text{mm}$, 0, 4, 8, and 10%, La_2O_3 -doped samples showed v_0 values of 0.64, 0.73, 0.74, and 0.75 m/s, respectively. However, when the La_2O_3 content was increased to 12%, the v_0 decreased abruptly to a value of 0.52 m/s (at 10 V_{rms}/mm).

In order to obtain a certain v_0 , a high electric field is usually applied and then the temperature rise (ΔT) becomes

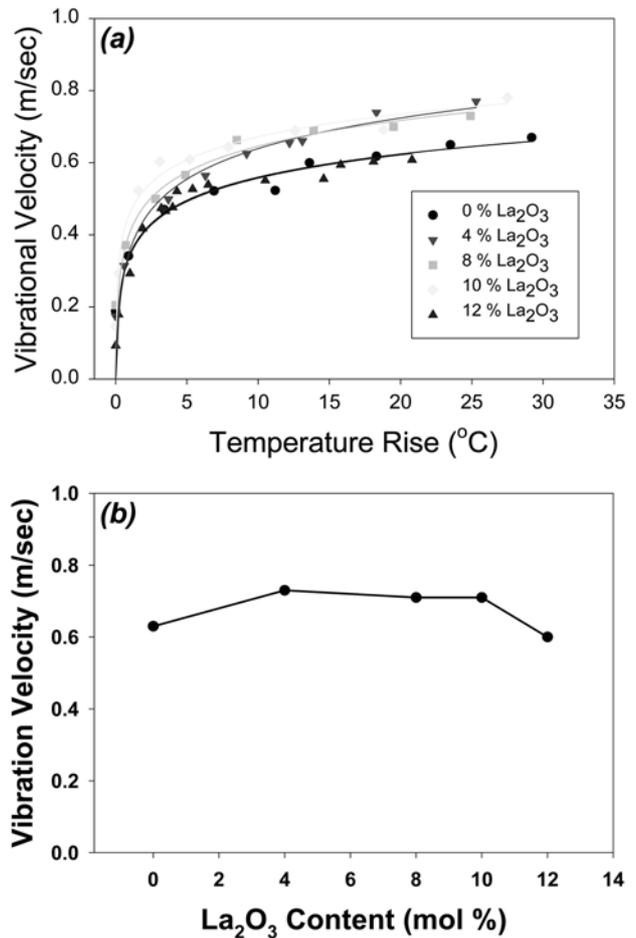


Fig. 6. (a) Vibrational velocities as a function of temperature rise, and (b) maximum vibrational velocities for the various La_2O_3 contents at a 20 °C rise.

significant due to the domain movements in ceramics. This temperature rise restricts the practical upper limit for v_0 . As can be seen in Fig. 6, compared with the undoped ceramics, La_2O_3 -doped ceramics had a larger v_0 for dopant concentrations of up to 10%, and a smaller v_0 for a dopant concentration of 12%. In our experiments, the 4% La_2O_3 -doped ceramic showed the maximum v_0 of 0.73 m/s at $\Delta T = 20$ °C. This is larger than the 0.40 m/s (rms value) of conventional hard PZT ceramics measured under higher E_{ac} drive levels.

Conclusions

A piezoelectric ceramic with the formula $0.98[0.4\text{PbZrO}_3 - 0.42\text{PbTiO}_3 - 0.12\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3 - 0.06\text{Pb}(\text{Sn}_{1/3}\text{Nb}_{2/3})\text{O}_3] - 0.02\text{YMnO}_3$ was doped with various amounts of La_2O_3 . The piezoelectric properties of these materials were investigated for high-power applications. Below a La_2O_3 content of 10%, the dissolved La_2O_3 reduced both the tetragonality of the crystal and the phase transition temperature. However, as the La_2O_3 content was increased above 10%, the La_2O_3 precipitated and the material

properties did not change significantly. In particular, the vibrational velocity, which is crucial for high-power applications, was enhanced with La_2O_3 dopant concentrations below 10%. When 4 mol% La_2O_3 was used, the phase transition temperature and the vibrational velocity (for a 20 °C temperature rise) were 278 °C and 0.73 m/s, respectively. This large vibrational velocity will be promising for high-power piezoelectric applications.

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