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High-power properties of piezoelectric hard materials sintered at low temperature for multilayer ceramic actuators

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Abstract

$0.05Pb(Mn_{1/3}Sb_{2/3})O_3$–$0.05Pb(Al_{1/2}Nb_{1/2})O_3$–$0.9Pb(Zr_{0.48}Ti_{0.52})O_3$ (PMS–PAN–PZT) high power piezoelectric system with both La_2O_3 as a hardener and CuO as a low sintering agent had been synthesized at 900 °C for 2 h. When La_2O_3 doping of the main composition went over 0.5 wt%, the mixed tetragonal and rhombohedral perovskite structure changed to pure rhombohedral perovskite structure. In case of the CuO, 1.0 and 1.5 wt% CuO content significantly improved the sinterability of the PMS–PAN–PZT system processed at 900 °C for 2 h. When La_2O_3 and CuO co-doped in PMS–PAN–PZT ceramics, piezoelectric constants (d_{33}), quality factor (Q_m), electromechanical coupling factor (k_p) and dielectric constant ($\varepsilon_3^T/\varepsilon_0$) of the piezoelectric ceramics sintered at 900 °C for 2 h were optimized, such as 336 pC/N, 841, 60%, and 1358, respectively. New developed piezoelectric materials are promising for high power multilayer ceramic actuators.

Keywords: Low temperature sintering; CuO; La_2O_3; PMS–PAN–PZT; Multilayer ceramic actuators

1. Introduction

Piezoelectric ceramics are currently used in applications such as actuators, ultrasonic motors and piezoelectric transformers. Lead zirconate titanate (PZT) systems have been widely modified by doping method.[1,2] Recently, high-power piezoelectric ceramics has been a popular topic due to their increasing applications in piezoelectric actuators and transformers.[3] Particularly, multilayer piezoelectric actuators and transformers have been studied for their high-power density.[4] Co-fired multilayer piezoelectric actuators have long been demonstrated for a wide variety of electromechanical applications requiring precision positioning over short time scales.[5] In general, multilayer devices fabricated with co-firing pure Ag as an internal electrode instead of Ag–Pd alloy promise to reduce the mass production cost. So, the piezoelectric ceramics should be sintered at 900 °C or below for multilayer piezoelectric devices. In addition, when piezoelectric ceramics are sintered at 900 °C or below, the volatilization of PbO can be suppressed. In order to reduce the sintering temperature, various methods such as nano powder sintering,[6] liquid-phase sintering,[7,8] and surface modification method[9] were implemented in PZT piezoelectric systems.

Recently, some ternary or quaternary high-power piezoelectric ceramics were obtained by adding perovskite structure relaxors into the PZT system, such as PZT–PMS,[10] PZT–PMN,[11] PZT–PMS–PMN,[12] and PZT–PMS–PZN.[13] $0.05Pb(Mn_{1/3}Sb_{2/3})O_3$–$0.05Pb(Al_{1/2}Nb_{1/2})O_3$–$0.9Pb(Zr_{0.48}Ti_{0.52})O_3$ (PMS–PAN–PZT) was selected because of typical hard piezoelectric characters (d_{33} = 312 pC/N, Q_m = 1351, and k_p = 56% sintered at 1175 °C) to apply for high-power piezoelectric actuators. This composition, however, is not satisfactory for multilayer actuators with Ag electrode due to high sintering temperature (over 1150 °C) and low electromechanical coupling factor, as well.

In case of the low-sintering temperature ceramics, Zhilun et al.[14] reported $Pb_{1-x}Cd_x(Ni_{1/3}Nb_{2/3})_yZr_zTiWO_3 + g_1$ wt% $MnO_2 + g_2$ wt% SiO_2 + 1 wt% Pb_3O_4 compositions. The optimized piezoelectric properties of the ceramics sintered at 900 °C were d_{33} = 400 pC/N, Q_m = 1000, and k_p = 61%. These piezoelectric properties are the world best, but this composition includes a hazardous element

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like cadmium (Cd). Therefore, this material cannot apply to piezoelectric industry and devices. Recently, $Pb(Zr_{0.52}Ti_{0.48})O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Zn_{1/3}Nb_{2/3})O_3$ + 0.2 wt% CuO system[15] was reported. Even though this system had 1645 of Q_m value, d_{33} (280 pC/N) and k_p (53%) values were relatively low and the 920 °C of the sintering temperature was slightly higher than 900 °C. One more required property in a piezoelectric industry field is that electromechanical coupling factor (k_p) value is at least 60% to apply high power ceramic actuators.

In this study, various amounts of CuO and La_2O_3 were added in PMS–PAN–PZT ceramic to decrease the sintering temperature and to further improve piezoelectric properties such as d_{33}, Q_m, and k_p. The crystal structure, the micro-morphology and the piezoelectric properties of PMS–PAN–PZT ceramics with various dopants will be discussed.

2. Experimental procedure

The composition of the ceramics used in this study is $0.05Pb(Mn_{1/3}Sb_{2/3})O_3$–$0.05Pb(Al_{1/2}Nb_{1/2})O_3$–$0.9Pb(Zr_{0.48}Ti_{0.52})O_3$ (PMS–PAN–PZT) + La_2O_3 + CuO. All samples were prepared by conventional solid state reaction method. The raw materials are PbO (99.9% Kosudo, Japan), MnO (99% Aldrich, USA), Sb_2O_5 (99.9% Aldrich, USA), Al_2O_3 (99.9% Aldrich, USA), Nb_2O_5 (99.9% Aldrich, USA), ZrO_2 (99% Aldrich, USA), TiO_2 (99.8% Aldrich, USA), La_2O_3 (99.99% Aldrich, USA) and CuO (99% Aldrich, USA). The starting materials were mixed in deionized (DI) water for 24 h by ball milling process. The mixed powder was dried and calcined at 850 °C for 2 h in air. The calcined powder was milled again with the additives, La_2O_3 (0–1 wt%) and CuO (0.5–6 wt%). The powders were dried and pressed into discs of 18 mm in diameter and 2 mm thickness under uni-axial pressure of 1000 kg/cm^2. The specimens were sintered at various temperatures (875–1200 °C) for 2 h with a 5 °C/min rate of heating and cooling in an alumina crucible. For the electrical measurements, the specimens were lapped into 1 mm thickness and then metallized with silver paste at 600 °C for 10 min. The piezoelectric ceramics were poled under a dc field of 5 kV/mm in silicon oil at 120 °C for 30 min. The piezoelectric properties of all ceramics were measured after 24 h of the poling process.

Bulk densities of the sintered ceramics were measured by the Archimedes method. Piezoelectric properties such as mechanical quality factor (Q_m) and electromechanical coupling factor (k_p) were measured by an impedance analyzer (HP 4294A, USA) and calculated by a resonance and anti-resonance method and dielectric constant ($\varepsilon_3^T/\varepsilon_0$) of the piezoelectric ceramics measured by a network analyzer (HP3577A, USA) at 1 kHz. Piezoelectric constants (d_{33}) of the specimens were obtained by a piezo-d_{33} meter (ZJ-3A, Institute of Acoustics Academic Sinica). The crystal structures of the piezoelectric ceramics were examined by a powder X-ray diffractometer (XRD, Model X'Pert PRO Panalytical, Holland) with Cu Kα radiation. The microstructure of the piezoelectric ceramics was observed using a scanning electron microscope (SEM, Model FEI XL30, Philips, Holland).

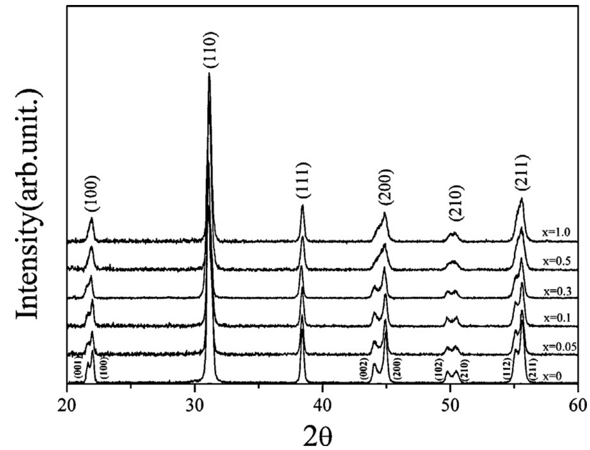

Fig. 1. XRD patterns of PZT–PAN–PMS + x wt% La_2O_3 sintered at 1175k °C for 2 h.

3. Results and discussion

3.1. The effect of La_2O_3 dopant

Fig. 1 shows the effect of La_2O_3 dopants (0–1.0 wt%) on phase formation of the PMS–PAN–PZT ceramics sintered at 1175 °C. When La_2O_3 was added up to 0.3 wt%, both tetragonal and rhombohedral perovskite phases coexisted in the PMS–PAN–PZT crystal. However, when La_2O_3 dopants were increased over 0.5 wt%, the coexisted phases changed to pure rhombohedral perovskite structure. Secondary phase peaks were not detected through all specimens. This result was observed from the combination of the (2 0 0) and (0 0 2) peaks with the increase of La_2O_3 contents. The transformation from tetragonal to rhombohedral structure can be attributed to the fact that La_2O_3 in the A-site induces lattice distortion that reduce the cell volume with shortened a-axis and c-axis in the perovskite structure.[16] In terms of ionic radius, the average size of the La^{3+} ion (1.36 Å, coordinate number/CN: 12) is similar to that of the Pb^{2+} ion (1.49 Å, CN: 12) therefore La^{3+} ions can be a solid

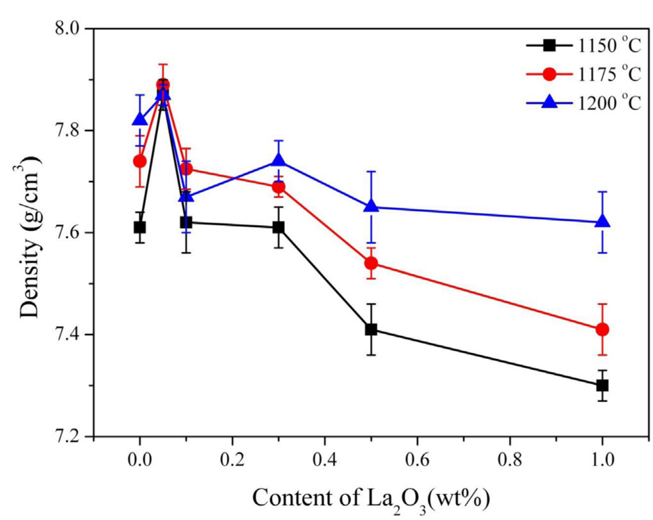

Fig. 2. Bulk density of sintered specimen of PZT–PAN–PMS with various amount of La_2O_3 contents with sintered from 1150 to 1200 °C for 2 h.