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Effect of CuO addition on sintering temperature and piezoelectric properties of $0.05Pb(Al_{0.5}Nb_{0.5})O_3$–$0.95Pb(Zr_{0.52}Ti_{0.48})O_3$+0.7 wt.% Nb_2O_5 + 0.5 wt.% MnO_2 ceramics

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Abstract Effect of CuO addition on piezoelectric properties of $0.05Pb(Al_{0.5}Nb_{0.5})O_3$–$0.95Pb(Zr_{0.52}Ti_{0.48})O_3$+0.7 wt.% Nb_2O_5 + 0.5 wt.% MnO_2 (PAN-PZT) ceramics was studied to decrease the sintering temperature below 900°C for LTCC. The PAN-PZT ceramics sintered at 1200°C had piezoelectric properties of d_{33} = 340 pC/N, k_p = 61.6%, Q_m = 1,725, and density of 7.5 g/cm^3. The addition of CuO significantly decreased the sintering temperature due to the formation of liquid phase containing a binary combination of PbO and CuO in grain boundary. Piezoelectric properties of d_{33} = 361 pC/N, k_p = 57%, Q_m = 145, and density of 7.8 g/cm^3 were achieved at sintering temperature of 900°C. The CuO doped PAN-PZT ceramics show high density and d_{33} at low sintering temperature though its electromechanical quality factor abruptly decreases due to the CuO additive effect.

Keywords $0.05Pb(Al_{0.5}Nb_{0.5})O_3$–$0.95Pb(Zr_{0.52}Ti_{0.48})O_3$+0.7 wt.% Nb_2O_5 + 0.5 wt.% MnO_2 ceramics · Piezoelectric properties · Low temperature sintering · CuO

1 Introduction

Multilayer actuators have been intensively investigated for the miniaturization and hybridization of the devices. Multilayer actuator is composed of alternating ceramics and internal metallic electrode layers. The multilayer piezoelectric devices inevitably require an internal metallic electrode, which is co-fired with piezoelectric ceramics [1]. In general, the sintering temperature of conventional lead-based piezoelectric ceramics is high as approximately 1200°C. Consequently, a reduction in the sintering temperature of the piezoelectric ceramics is required to fabricate the multilayer piezoelectric devices. Moreover, the microstructure and properties of the piezoelectric ceramics are difficult to control because of the evaporation of PbO during sintering at high temperature. Therefore, it is important to develop piezoelectric ceramics with low sintering temperature [2–5].

CuO have been used as additive to decrease the sintering temperature of ceramics. Ahn et al. have observed that the addition of CuO and ZnO at APC 841(PZT-PZN) decreased the sintering temperature form 950 to 900°C and in particular, the low-fired APC 841 with 0.2 wt.% CuO and 1.1wt.% ZnO addition showed good piezoelectric properties (d_{33} = 351 pC/N, k_p = 53%, Q_m = 750) [6].

In this paper, the low temperature sintering of PAN-PZT ceramics using CuO addition is investigated. We have found that the addition of CuO significantly decreases the sintering temperature from 1200°C to 900°C. The structure, dielectric and piezoelectric properties of PAN-PZT with CuO additive also have been investigated.

2 Experimental procedures

The general formula studied was $0.05Pb(Al_{0.5}Nb_{0.5})O_3$–$0.95Pb(Zr_{0.52}Ti_{0.48})O_3$+0.7 wt.% Nb_2O_5 + 0.5 wt.% MnO_2. All the specimens were prepared with a conventional solid state reaction method.

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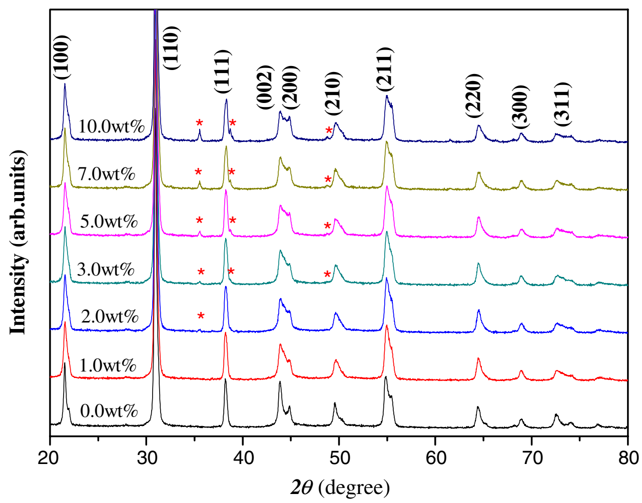

Fig. 1 X-ray diffraction patterns of the $0.05Pb(Al_{0.5}Nb_{0.5})O_3$–$0.95Pb(Zr_{0.52}Ti_{0.48})O_3$ + 0.7 wt.% Nb_2O_5 + 0.7 wt.% Nb_2O_5+0.5 wt.% MnO + x wt.% CuO ceramics with $0.0<x\leq10.0$ wt.% sintered at 900 °C for 1 h and x=0 sintered at 1200 °C for 1 h

Reagent-grade oxide powders, PbO, ZrO_2, TiO_2, MnO_2, Al_2O_3, Nb_2O_5 (99.9%, Aldrich) and ZrO_2 (99%, Aldrich) were used as the starting materials. The mixture was calcined at 850°C for 2h in air, The calcined powders, added CuO where x = 0.5, 0, 1, 2, 3, 5, 7 and 10 wt.%, respectively, which had been mixed by second ball milling, pressed into discs of 18.0 mm in diameter at around 2 tons, and then sintered at 900–1100°C for 1 h in a sealed alumina crucible with a calcined powder. The sintered discs were polished into the thickness of 1 mm, and then electrodeposited by screen-printing with Ag paste. The specimens for the piezoelectric property measurements were poled in a silicone oil bath at 120°C by applying a DC electric field of 3.5 kV/mm for 30 min. The specimens were aged for 24 hrs prior to testing.

The crystal structure of the samples was analyzed using an X-ray diffractometry (XRD; Model PANalytical, Netherlands) with a 2 θ range from 20 ° to 80 °. The bulk density was measured using the Archimedean method. Microstructure and chemical composition of the sintered bodies were observed using a scanning electron microscopy (SEM; Model FEI XL-30 FEG). The piezoelectric constant (d_{33}) was measured using a piezoelectric d_{33} meter (Model ZJ-3D, Sinica) and the piezoelectric properties were measured using an impedance analyzer (Model Agilent 4294A).

3 Results and discussion

Figure 1 shows the X-ray diffraction patterns of the $Pb(Al_{0.5},Nb_{0.5})O_3$–$Pb(Zr_{0.52},Ti_{0.48})O_3$ +0.7 wt.% Nb_2O_5 + 0.5 wt.% MnO_2 (PAN-PZT) + x wt.% CuO ceramics with $0<x\leq10.0$ wt.% sintered at 900°C for 1h. When CuO is added up to 1 wt.%, specimens show a single phase without any secondary phase. As increasing CuO over 1 wt.%, however, secondary phases start to appear at 35.5°, 38. °, and 58.3°, which are thought to be CuO related peaks. Figure 2 shows

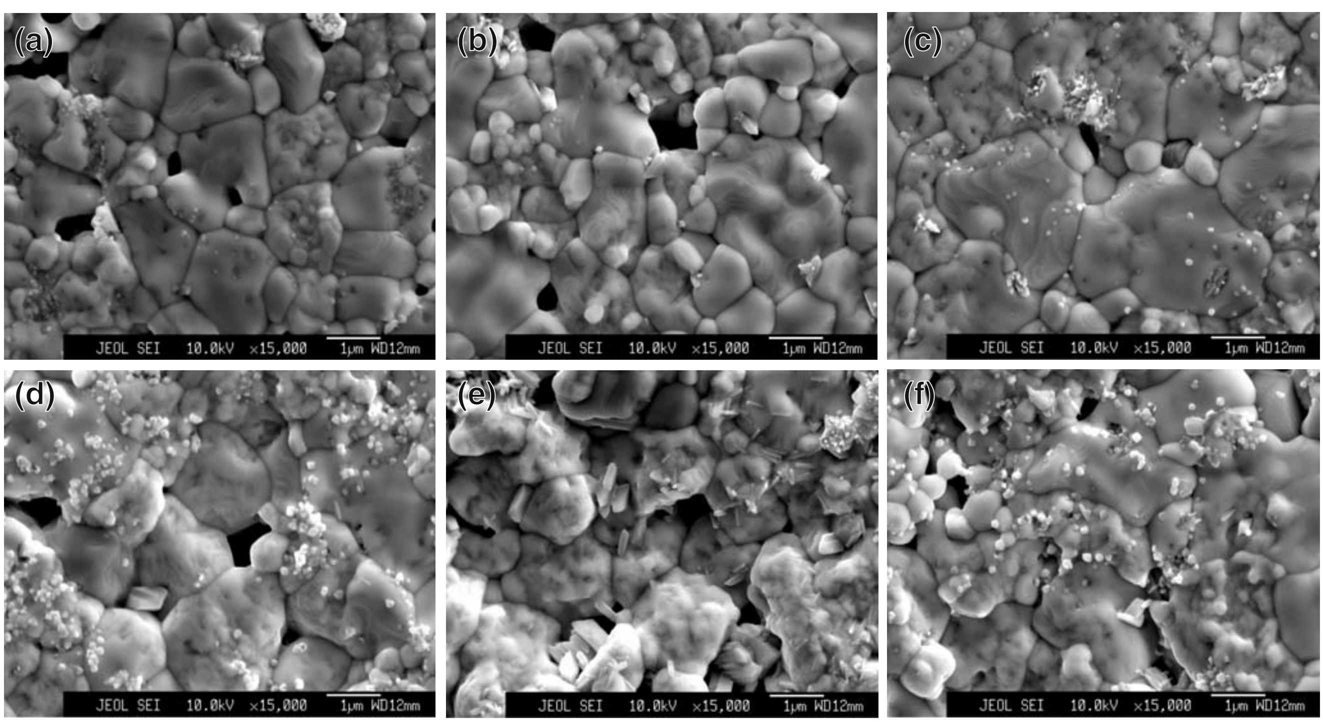

Fig. 2 SEM images of PAN-PZT ceramics with various CuO contents sintered at 900 °C for 1 h. (a) 1 wt.%, (b) 2 wt.%, (c) 3 wt.%, (d) 5 wt.%, (e) 7 wt.%, (f) 10 wt.%

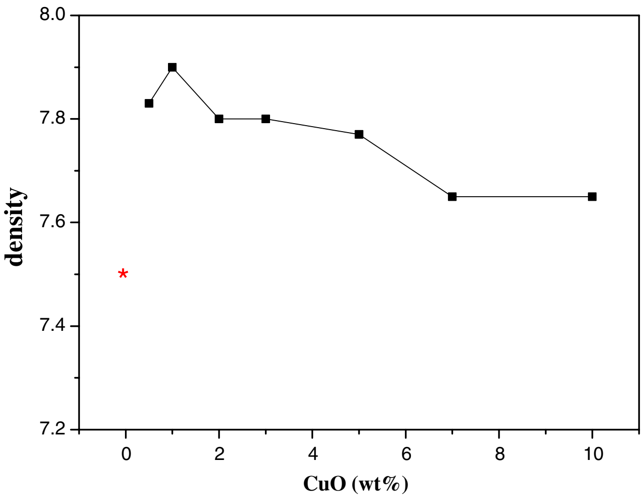

Fig. 3 Density of PAN-PZT according to $0.0<x\leq10.0$ wt.% sintered at 900 °C for 1 h and $x=0$ sintered at 1200 °C for 1 h amount of CuO

the SEM images of PAN-PZT ceramics with various CuO contents sintered at 900°C for 1h. The addition of CuO in PAN-PZT decreased the sintering temperature due to the formation of liquid phase containing a binary combination of PbO and CuO in grain boundary.[6–10] When CuO is added up to 1 wt.%, specimens show well sintered and homogeneous morphologies. However, as increasing CuO over 1 wt.% abnormal grain growth appears due to too much liquid phase.

Figure 3 shows the density of PAN-PZT according to the amount of CuO sintered at 900°C for 1 h and without CuO addition sintered at 1200°C for 1 h. The density of specimens sintered at 900°C shows the maximum value of 7.9 g/cm^3 at 1 wt.% CuO addition of which value is much higher than one of PAN-PZT specimen sintered at 1200°C for 1 h. As an increase of CuO over 1 wt.%, however, density decreases due to abnormal grain growth and secondary

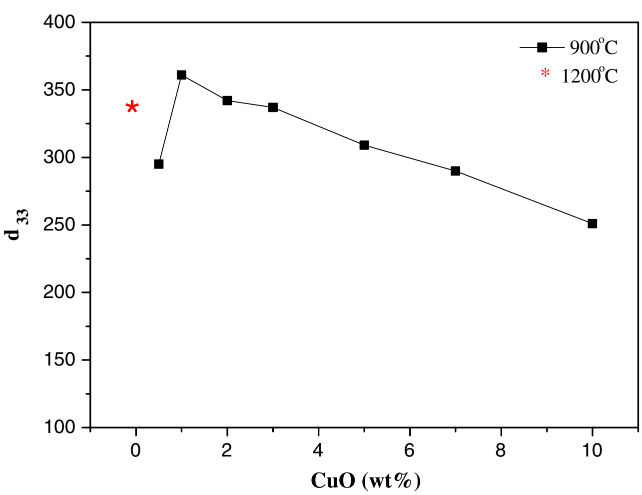

Fig. 4 Piezoelectric constants (d_{33}) of PAN-PZT according to $0.0<x\leq10.0$ wt.% sintered at 900 °C for 1 h and $x=0$ sintered at 1200 °C for 1 h amount of CuO

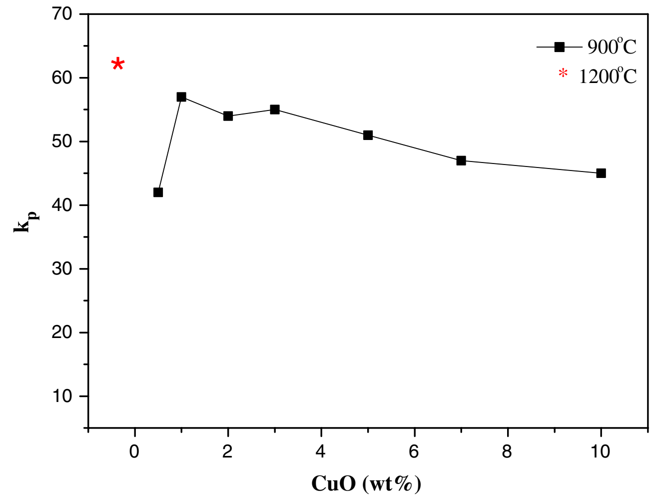

Fig. 5 Electromechanical coupling coefficient (k_p) of PAN-PZT according to $0.0<x\leq10.0$ wt.% sintered at 900 °C for 1 h and $x=0$ sintered at 1200 °C for 1 h amount of CuO

phases shown in Figs. 1 and 2. Figure 4 shows the piezoelectric constants (d_{33}) of CuO doped PAN-PZT sintered at 900°C for 1 h and without CuO addition sintered at 1200°C for 1 h. When CuO is added to 1 wt.%, the piezoelectric constant increases up to 361 pC/N due to the increase of the density and the homogeneous microstructure, which is a little higher than that of PAN-PZT sintered at 1200°C for 1 h. As increasing CuO, however, the d_{33} continuously decreases due to the increase of the abnormal grain growth and secondary phases. Figure 5 shows Electromechanical coupling coefficient (k_p) according to the amount of CuO addition sintered at 900°C for 1 h and without CuO addition sintered at 1200°C for 1 h. When CuO is added to 1 wt.%, the k_p increases up to 57%. As increasing CuO, however, the k_p gradually decreases. The k_p value of 1 wt.% CuO doped PAN-PZT ceramics sintered

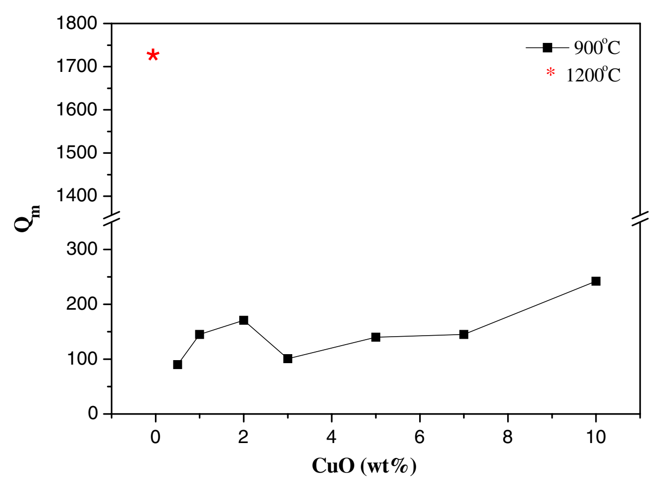

Fig. 6 Mechanical quality factor (Q_m) of PAN-PZT according to $0.0<x\leq10.0$ wt.% sintered at 900 °C for 1 h and $x=0$ sintered at 1200 °C for 1 h amount of CuO

at 900°C is lower than that of PAN-PZT sintered at 1200°C but the value is applicable to piezoelectric devices. Figure 6 shows mechanical quality factor (Q_m) as a function of CuO sintered at 900 °C for 1 h. When CuO is added to 2 wt.%, the Q_m increases up to 145. As increasing CuO to 3 wt.%, however, the Q_m abruptly decreases and gradually increases as an increase of CuO. From these results, when CuO is added to 1 wt.%, the d_{33pm}, and density of CuO doped PAN-PZT increase though the Q_m is much lower than one of PAN-PZT without CuO sintered at 1200 °C. The reason why piezoelectric properties enhance at low sintering temperature is due to liquid phase sintering without secondary phases and abnormal grain growth [11].

4 Conclusions

The structural and piezoelectric properties of $0.05Pb(Al_{0.5}Nb_{0.5})O_3-0.95Pb(Zr_{0.52}Ti_{0.48})O_3$ + 0.7 wt.% Nb_2O_5+ 0.5 wt.% MnO_2 + x wt.% CuO ceramics were investigated. The piezoelectric constants (d_{33}) of specimens sintered at 900 °C showed the maximum value of 361 pC/N at 1 wt.% CuO addition. The electromechanical coupling factor (k_p) and mechanical quality factor (Q_m) of 1 wt.% CuO doped PAN-PZT ceramics showed the maximum value of 57% and 145, respectively, at sintering temperature of 900 °C. Doping of CuO in PAN-PZT ceramics can lower the sintering temperature of piezoelectric ceramics due to liquid phase sintering and enhance the piezoelectric properties at low temperature.

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