The Effect of CuO addition on low temperature co-firing PZT ferroelectric ceramics in multilayer device application

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Abstract. Low-temperature sintering of $Pb_{0.995}Cd_{0.005}(Zr_{0.965}Ti_{0.035})O_3$ ceramics was investigated using CuO as a sintering aid. Effect of CuO addition on the sinter ability, microstructure, and electric properties of PZT ceramics were systematically studied. The addition of CuO significantly promoted the densification of PZT and reduced the sintering temperature of PZT ceramics to 1050°C. PZT ceramics with CuO addition were sintered at 1150°C and exhibit a high density of 7.6g/cm^3, which corresponds to the approximately 96% theoretical density. And the optimized value for the piezoelectric coefficient d_{33} of 66 pC/N was obtained for 0.05% CuO-added PZT ceramics, which shows a great promise for multilayer actuator applications.

Introduction

PZT95/5 ceramics is one of the most useful functional materials; it is not only used as excellent driven material, but also as sensitive transducer material. Because of excellent ferroelectric capability and large electromechanical coupling coefficient, it fits well with the designed requirements of multilayer piezoelectric device, and has been widely used in many fields such as micro-electronics, photoelectron systems and high-voltage power supply components[1,2]. For these applications, several pieces of ceramics need to be stacked in series to enhance the output electric current. Co-firing multilayer PZT95/5 ceramics is a promising way to prevent the multilayer piezoelectric devices from dielectric breakdowns under shock compression. During fabrication of multilayer piezoelectric devices, co-firing of ceramic and internal metallic electrodes is very critical [3]. Generally, silver and even silver-palladium alloy which are the most commonly used for internal electrode for their high conductivity and low cost have a problem of migration when the sintering temperature is above 960˚C[4]. However, the sintering temperatures of conventional lead-based piezoelectric ceramics are exceedingly higher than 1200˚C[5,6]. Therefore, it is very important to decrease the sintering temperature of PZT95/5 ceramics for multilayer device application. The addition of low-melting-point materials is a promising way to lower the sintering temperature.

The effects of different additions such as WO_3, MnO_2, $LiBiO_2$ et al. with different contents on the properties of low temperature sintering of PZT based ceramics have been investigated[7,8]. The results showed that the addition of WO_3 and MnO_2 can improve the sintering density and electric properties, but samples still are sintered at 1100˚C. The addition of $LiBiO_2$ could make samples sintered at 1000˚C, but the electric properties had bad decline [9, 10]. So it is critical to seek a method to lower the sintering temperature while maintaining the ferroelectric properties. In our present work, low temperature sintering of $Pb_{0.995}Cd_{0.005}(Zr_{0.965}Ti_{0.035})O_3$ ceramics with CuO additives were systematically investigated. It was found that CuO significantly reduced the sintering temperature to 1050°C while the density was 7.65g/cm^3, and electric properties could be maintained.

Experimential procedure

Materials

The ceramics of $Pb_{0.995}Cd_{0.005}(Zr_{0.965}Ti_{0.035})O_3$+1%wt$Nb_2O_5$+ xwt% CuO (x = 0, 0.05, 0.1, 0.15, 0.2) were prepared with traditional solid-state method. Reagent-grade raw materials of Pb_3O_4, ZrO_2, TiO_2, CdO, CuO were weighed by mole ratio and mixed together by ball milling for 8h, subsequently dried and filtered through a net of 40 meshes. The mixture was calcined at 850˚C for 2h. Pellets with the diameter of 15mm were pressed and sintered in a sealed alumina crucible at various temperatures for 4h. And for the electrical property measurement, sintered samples were machined into φ15mm×1mm disks and coated with silver paste to form electrodes.

Procedure

The phase structures of specimens were examined by X-ray diffraction (XRD) using CuKa radiation (D/MAX-2550; Rigaku, Tokyo, Japan). Microstructure of ceramics were observed by scanning electron microscopy (SEM, TM3000; Hitachi, Tokyo, Japan). The density was determined by Archimedes method. The temperature-dependent dielectric properties at 1 kHz were obtained using a LCR meter (Hp4284A; Hewlett-packard, Japan). The polarization-electric field (P-E) behavior loops were measured by a ferroelectric tester (TF Analyzer 2000; aix-ACCT, Aachen, Germany). The piezoelectric coefficient d_{33} was measured using a quasi-static d_{33}-meter(Model Zj-3; Institute of Acoustics, Beijing, China) after samples were polarized in silicon oil bath for 30 minutes.

Result and discussion

Microstructure

The XRD patterns of $Pb_{0.995}Cd_{0.005}(Zr_{0.965}Ti_{0.035})O_3$+1%wt$Nb_2O_5$+ xwt% CuO ceramics with $0.05 \leq x \leq 0.2$ sintered at 1050˚C for 4h shows presence of only a main pure perovskite phase and no secondary phase(Fig. 1) .

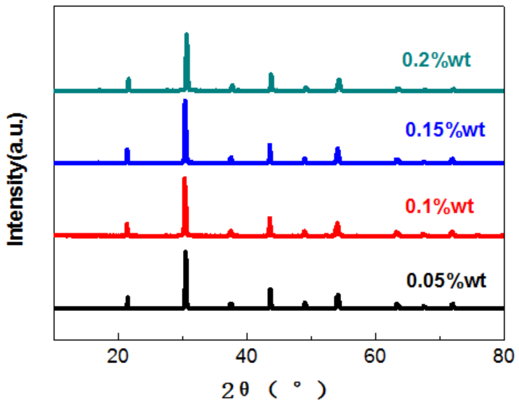

Fig. 1. X-ray diffraction patterns of $Pb_{0.995}Cd_{0.005}(Zr_{0.965}Ti_{0.035})O_3$ with different amounts of CuO additive sintered at 1050°C for 4 h: (a)x = 0.05, (b) x = 0.1, (c) x = 0.15, (d) x = 0.2

The SEM images of $Pb_{0.995}Cd_{0.005}(Zr_{0.965}Ti_{0.035})O_3$+1%wt$Nb_2O_5$+ xwt% CuO ceramics with $0.05 \leq x \leq 0.2$ sintered at 1050˚C are given in Fig. 2. Fig.2a presents the sample with 0% CuO with small and uniformly distributed pores. Microstructures of samples with 0.05%, 0.1%, 0.15% and 0.2 wt % CuO are shown in Fig.2(b, c, d and e). Uniform sized grains with a clear grain boundary are visible in these samples. And microstructure becomes denser and the grains grow bigger as the CuO content increased. It was obvious that introduction of CuO content promoted the densification during sintering of 1050°C, which was attributed to the liquid phase sintering.

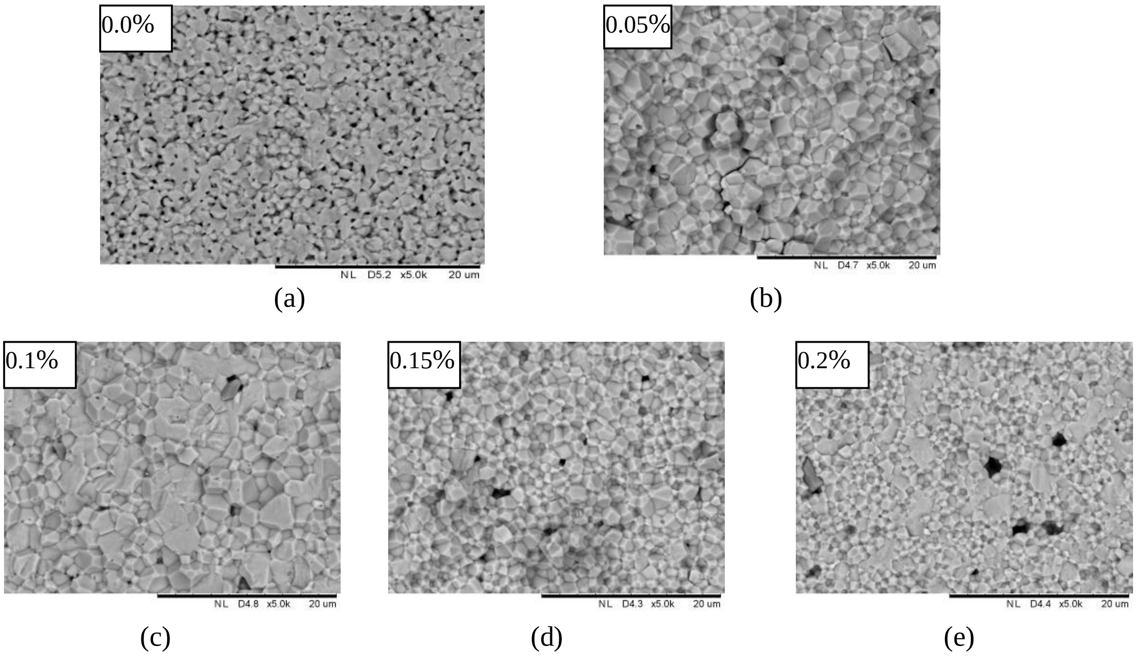

Fig. 2 SEM images of PZT ceramics with different contents of CuO additive sintered at 1050°C :
(a) x = 0.0, (b) x = 0.05, (c) x = 0.1, (d) x = 0.15, and (e) x = 0.2

Bulk Density

The density of $Pb_{0.995}Cd_{0.005}(Zr_{0.965}Ti_{0.035})O_3$ ceramics with varying addition of CuO in the range of 0.05%-0.2% is shown in Fig. 3. The PZT95/5 ceramic could be fully densified with the 0.1wt% addition of CuO at sintering temperatures 1050°C, which exhibited a high density of 7.65g/cm^3 corresponding to 96% theoretical density. The results confirm that CuO addition significantly enhances the densification and reduces the sintering temperature of PZT ceramics.

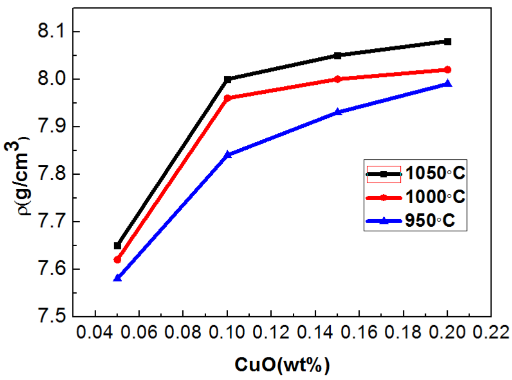

Fig.3 the bulk density of PZT ceramics with different contents of CuO additive sintered at 950°C,1000°C and 1050°C

Ferroelectric and Piezoelectric Properties

The changes in piezoelectric coefficient d_{33} with varying addition of CuO in the range of 0.05%-0.2% are shown in Fig. 4. It is observed that the piezoelectric coefficient d_{33} decreases linearly with an increase of CuO content from 0.05% to 0.15 wt%. Furthermore, increasing the amount of CuO from 0.15 wt% to 0.2wt%, then the piezoelectric coefficient d_{33} began to increase slightly. This demonstrates that the addition of CuO may produce the positive and negative influence on PZT ceramics, on the one hand, it will help to reduce the sintering temperature, on the other hand, the electric properties had bad decline with the increased addition of CuO. The optimized value for d_{33} of 66pC/N was obtained for 0.05% CuO-added PZT ceramics.

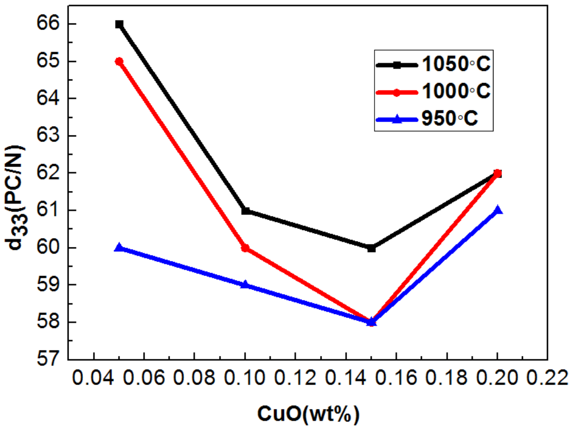

Fig.4 the piezoelectric coefficient d_{33} of PZT ceramics sintered at different temperatures

The P-E hysteresis loops of PZT ceramics with CuO addition sintered at temperature 1050°C for 4h are shown in Fig.5. It is obvious that the addition of CuO is evidently helpful for the ferroelectric properties of PZT ceramics sintered at 1050°C. It can be seen that the remnant polarization Pr increased but the coercive field Ec doesn't change when increasing the amount of CuO. The maximum Pr is about 42μC/cm^2 is achieved in 0.05wt% CuO-added sample, which should be attributed to the highly dense microstructure of pure perovskite phase.

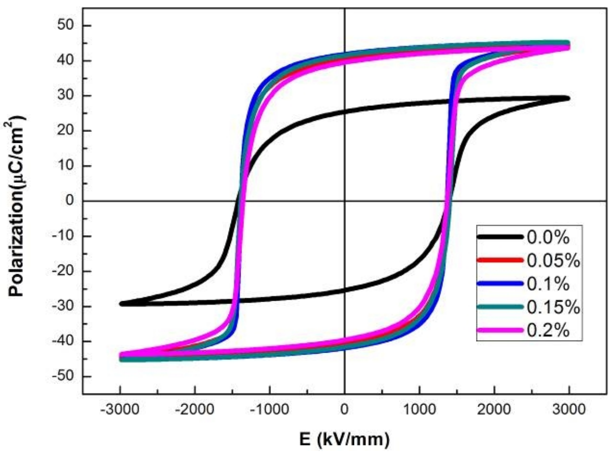

Fig. 5 Polarization-electric field (P-E) hysteresis loops of PZT with different amounts of CuO additive sintered at1050°C

Table 1 presents data on the electric properties of $Pb_{0.995}Cd_{0.005}(Zr_{0.965}Ti_{0.035})O_3$ ceramics sintered samples at 1050°C with varying addition of CuO. The results showed that the PZT ceramics has the optimum properties, that dielectric constant(ε^T), piezoelectric coefficient(d_{33}), and loss tangent(tanδ) achieve 279, 66 pC/N and 1.9 respectively, under the sintering temperature of 1050˚C with the 0.05wt% of CuO-added.

Table 1. Electric properties of $Pb_{0.995}Cd_{0.005}(Zr_{0.965}Ti_{0.035})O_3$ with different amounts of CuO sintered at 1050°C

X(wt%)	Sintering temperature(˚C)	ε^T	tgδ	d_{33} (pC/N)
0	1050	268	2.1	65
0.05	1050	279	1.9	66
0.1	1050	284	1.7	61
0.15	1050	296	2.8	60
0.2	1050	339	2.2	62

Conclusion

The $Pb_{0.995}Cd_{0.005}(Zr_{0.965}Ti_{0.035})O_3$ ceramics were fabricated by conventional solid-state sintering method. And CuO was used as a sintering aid which significantly reduced the sintering temperature to 1050°C, and meanwhile, the electric properties were improved. Sample with CuO-added PZT ceramics sintered at 1050°C exhibited a high density of 7.65g/cm^3, which corresponds to the relative density of approximately 96%. The results showed that the PZT ceramics has achieved the optimized properties, that dielectric constant(ε^T) , piezoelectric coefficient(d_{33}), and loss tangent(tanδ) achieve 279 , 66 pC/N and 1.9, respectively under the sintering temperature of 1050˚C with the 0.05wt% of CuO-added.

Acknowledgments

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