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Effects of CuO nanoparticles addition on properties of PMNT ceramics

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Abstract

This research investigates the role of CuO nanoparticles addition on properties of 0.9PMN–0.1PT (PMNT) ceramics. Phase purity, density, microstructure, dielectric and ferroelectric properties of the ceramics were investigated. The density of the ceramics reaches a maximum when 0.5 wt% of CuO is added into the ceramics while grain size of the ceramics tends to increase with the increase in CuO content. ε_{max} of the ceramics tends to increase with increasing CuO concentration. The improvement of P_r of the ceramics is observed in the ceramic incorporated with over 0.1 wt% of CuO.

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Keywords: Dielectric properties; Ferroelectric properties; Perovskite

1. Introduction

$0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ (PMNT) compound has been extensively studied and popularly used in multilayer-capacitor and electrostrictive actuator applications due to its high dielectric constant and high electrostrictive strain [1–3]. During the sintering process of PMNT ceramics, the volatility of PbO is a significant problem. It does not only degrade the properties of the ceramics but also harmful to the environment [4]. Therefore, a lower sintering temperature is required for fabrication of PMNT ceramics. In order to facilitate densification at lower temperature the addition of CuO as a sintering aid was investigated [5,6].

CuO is known to have semiconductive properties and is popularly used in *p*-type semiconductors. It has a great potential for applications such as gas sensors, catalysts and superconductors [7,8]. In previous work, CuO has been selected as a sintering aid for many ceramics such as KNN-BT piezoelectric ceramics [4], $LaAlO_3$ [9] and $ZnTa_2O_6$ [10] dielectric ceramics. These works report the possibility to improve densification of materials by the addition of CuO. Thus, it is believed that the addition of CuO can improve the density of PMNT ceramics. Furthermore, it is expected that the use of CuO with nano-size can effectively increase reactive surface area which enhance the efficiency of the sintering process of the ceramics. In this study, CuO nanoparticles were added into PMNT ceramic and the effects of CuO nanoparticles addition on phase, microstructure, dielectric and ferroelectric properties of the PMNT ceramics were investigated and discussed.

2. Experimental

$0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ or 0.9PMN–0.1PT or PMNT powder was prepared by a columbite precursor method [11]. The columbite precursor ($MgNb_2O_6$) was prepared by mixing stoichiometric amounts of MgO (99.9%, Fluka, USA) and Nb_2O_5 (99.9%, Sigma-Aldrich, USA) in ethanol, followed by ball-milling for 24 h using ZrO_2 grinding medium. The slurry was dried at a temperature of 120 °C and calcined at a temperature of 1000 °C for 4 h [12]. The columbite precursor was then mixed and ball-milled with stoichiometric amounts of PbO and TiO_2 powders (99.9%, Sigma-Aldrich, USA) for 24 h and calcined at 850 °C for 2 h. The calcined powders were added with CuO nanoparticles (30–50 nm, 99%, Nanostructured & Amorphous Materials, USA) to form PMNT/xCuO powders; where $x=0$, 0.05, 0.1, 0.5 and 1 wt%, respectively. The mixed powders were uniaxially pressed

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into pellets and sintered at 950 °C for 2 h in an atmosphere of PMN powder. Bulk density of the ceramics was determined using Archimedes' method. Phase composition of the PMNT/CuO ceramics was characterized using X-ray diffraction method (XRD, Model X-pert, Panalytical B.V., the Netherlands). Microstructure of the ceramics was observed via a scanning electron microscope (SEM, JSM-6335F, JEOL, Japan). Average grain size was determined using a mean linear interception method from SEM micrographs. Dielectric constant (ε_r) and loss tangent ($\tan\delta$) were measured at various temperatures using an LCR meter (Hitester 3532-50, Hioki, Japan). Ferroelectric hysteresis (P–E) loops were characterized using a computer-controlled modified Sawyer-Tower circuit.

3. Results and discussion

Phase characteristics of PMNT/CuO ceramics are shown by XRD patterns in Fig. 1(a) which were found to be well matched with standard ICSD file No. 99710 of cubic $PbMg_{0.3}Nb_{0.6}Ti_{0.1}O_3$ in $pm\overline{3}m$ space group [13]. The result indicates that an addition of CuO does not change the crystal structure of PMNT ceramics. Fig. 1(b) showed XRD peaks at $2\theta \approx 45°$. The peak position shifted to lower angles was increased with increase in CuO added content. Lattice parameters (see Table 1) of the ceramics showed the small increase from ~4.03 Å for pure PMNT to ~4.04 Å for 1.0 wt% CuO added sample. This was caused by the substitution of larger Cu^{2+} ions into the smaller Mg^{2+} ions in B-site lattice of PMNT ($r_{Cu^{2+}} = 0.73$ Å and $r_{Mg^{2+}} = 0.72$ Å [14]).

Determination of chemical composition of the ceramics was given in Table 2. It can be seen that Cu element was detected inside the ceramic grains (EDX results are not given here) which confirmed the entering of Cu^{2+} ion into PMNT. The secondary phase determined to be Mg-rich phase was observed in the ceramics incorporated with 0.5–1.0 wt% CuO. It is indicated by circles in Fig. 2(d) and (e). The secondary phase is believed to be occurred due to the substitution of Cu^{2+} ion into Mg^{2+} ion. Total charge for each composition is given in Table 2. It was found to increase from −4.14 to +0.91 with an increase in CuO content. This is likely attributed to the decrease in the volatilization of Pb content when higher amount of CuO is added.

Grain size of the ceramics was evaluated from fractured surfaces as shown in Fig. 2 and the result is listed in Table 1. An addition of CuO less than 0.1 wt% does not significantly change the average grain size of the ceramics where the size is ~1 μm. However, the grain size is sharply increased with further increase in CuO content to 0.5 and 1.0 wt%, where the grain size is ~5–6 μm. The increase in

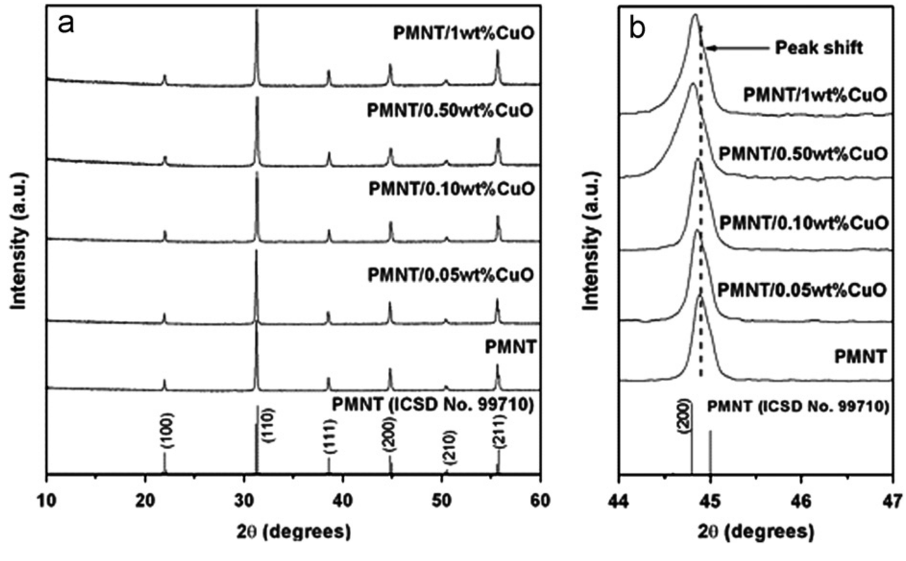

Fig. 1. (a) XRD patterns of PMNT/CuO ceramics sintered at 950 °C and (b) XRD peaks at $2\theta \approx 45°$.

Table 1
Lattice parameters and physical properties of PMNT/CuO ceramics.

CuO content (wt%)	Lattice parameter (Å)	Grain size (μm)	Relative density (%)
0	4.0336	0.89 ± 0.03	94.09 ± 0.03
0.05	4.0361	1.06 ± 0.04	94.47 ± 0.01
0.1	4.0361	1.11 ± 0.05	94.16 ± 0.01
0.5	4.0404	4.82 ± 0.36	97.74 ± 0.01
1	4.0378	5.65 ± 0.51	97.14 ± 0.03

Table 2
Chemical composition and possible phases of PMNT/CuO ceramics.

CuO content (wt%)	Chemical composition (at%)						Total charge	Possible phase
	Pb	Mg	Nb	Ti	Cu	O		
0	13.15	4.16	9.54	1.58	–	71.57	-4.14	$Pb_{0.55}(Mg_{0.17}Nb_{0.40}Ti_{0.07})O_3$
0.05	16.47	4.58	12.30	2.23	0.35	64.06	-0.90	$Pb_{0.77}(Mg_{0.21}Nb_{0.58}Ti_{0.10}Cu_{0.02})O_3$
0.1	16.44	5.06	13.64	1.83	1.54	61.49	-0.08	$Pb_{0.80}(Mg_{0.25}Nb_{0.67}Ti_{0.09}Cu_{0.08})O_3$
0.5	20.56	3.13	16.07	0.50	1.37	58.37	$+0.77$	$Pb_{1.06}(Mg_{0.16}Nb_{0.83}Ti_{0.03}Cu_{0.07})O_3$
1.0	19.02	4.35	14.62	1.47	3.18	57.37	$+0.91$	$Pb_{0.99}(Mg_{0.23}Nb_{0.76}Ti_{0.08}Cu_{0.17})O_3$
Secondary phase	10.54	24.46	7.72	1.03	5.18	51.07	–	Mg-rich

Note: Secondary phase is indicated in the circles in Fig. 2(d) and (e). Total charge was caculated from an amount and a valency of each element in the ceramic grains.

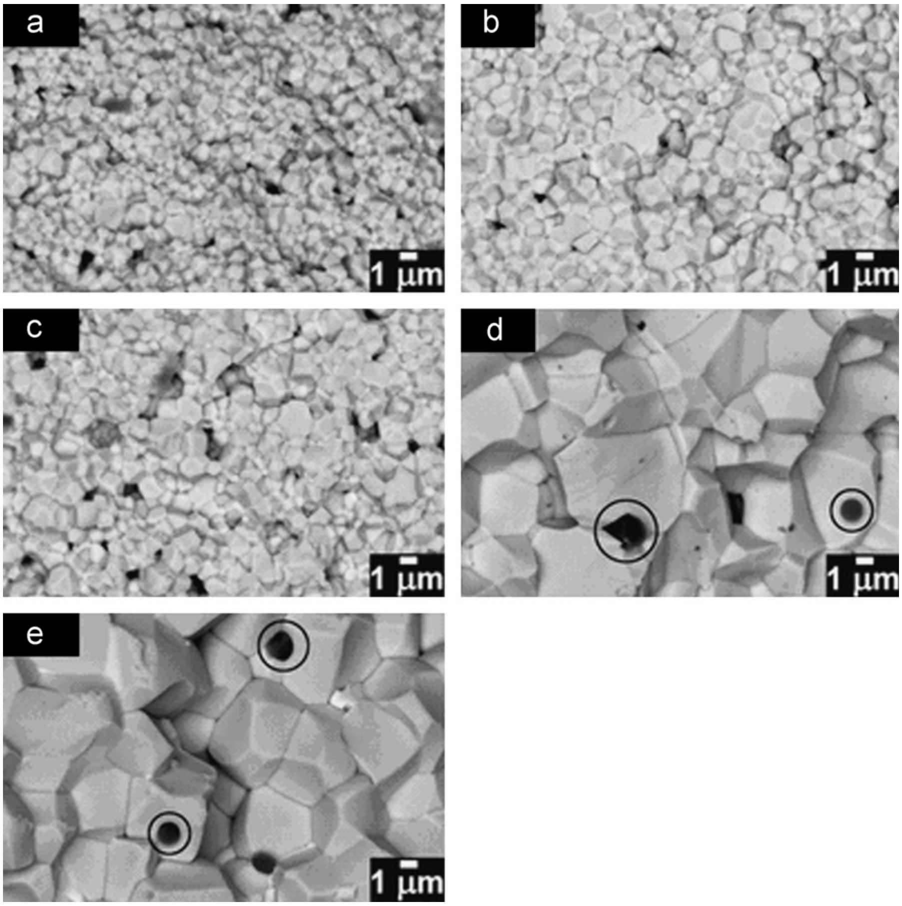

Fig. 2. Backscattered electron images of fractured surface of (a) pure PMNT and the ceramics incorporated with (b) 0.05, (c) 0.1, (d) 0.5 and (e) 1.0 wt% of CuO nanoparticles.

Pb content is believed to be contributed to the increase in grain size of the PMNT ceramics. The grain growth behavior was similarly observed in a previous result of PMN–PT ceramics with an excess of PbO [15]. Likewise, it is believed that the increase in Pb content also results to densification enhancement. Density values of the ceramics are not significantly changed with an addition of 0.05–0.1 wt% of CuO (see in Table 1). However, the density of the ceramics is increased from ∼94 to ∼97 % when an amount of CuO was over 0.1 wt%.

Plots of the temperature dependence of dielectric constant and dielectric loss of the ceramics measured at a frequency of 1 kHz are shown in Fig. 3 and the values are presented in Table 3. The result shows that an addition of 0.05–0.1 wt% CuO does not significantly change the maximum dielectric constant (ε_{max}) of the ceramics compared to the pure PMNT, where ε_{max} value is ~12,000. The effect of the isovalent substitution of Cu^{2+} into Mg^{2+} site [16] is believed to be responsible for the observed ε_{max} values. However, the value tends to increase to ~24,000 for PMNT /1 wt% CuO sample. The approximate effective charge of Cu-doped PMNT ceramics is obtained from EDX compositional analysis as listed in Table 3. It is shown that charged defects involved in each Cu-doped sample cause the total effective charge to be less negative (acceptor-like system) for 0–0.1 wt% CuO and became positive (donor-like system) for 0.5–1.0 wt% CuO. The increase in dielectric constant of 0.5–1.0 wt% CuO sample therefore suggests a similar behavior observed for donor-doped ceramics [16]. Moreover, diffuseness parameter (δ) is found to decrease with the increasing CuO content. This is again affected by the increase in grain size. This result is similar to a previous work where the less broadening of dielectric constant peak of $BaTiO_3$ ceramics (lower diffuseness parameter) was observed in the ceramics with larger grain [17]. A decreasing tendency of T_{max} with an increase in CuO content is also observed. This could be partly the effect of unit cell expansion due to cationic substitution [18,19] which may bring the structure to be closer to cubic and hence lower the transition temperature.

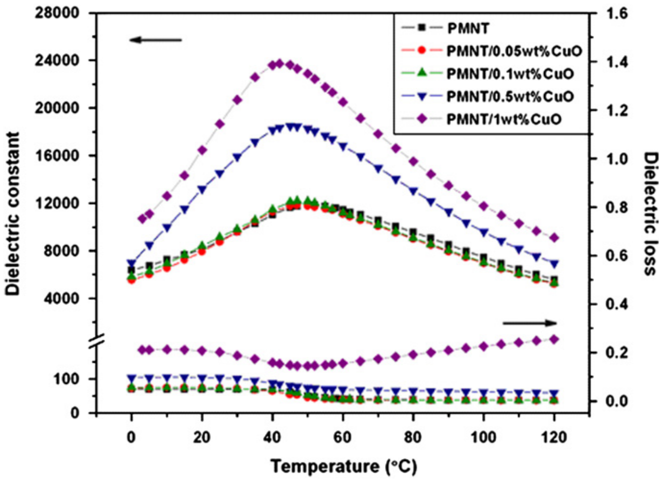

Fig. 3. Plots of dielectric constant and dielectric loss as a function of measurement temperature of PMNT/CuO ceramics.

Ferroelectric properties of PMNT/CuO ceramics were tabulated in Table 3 and the related values, i.e., remanent polarization (P_r) and coercive field (E_c) were evaluated. Because of ferroelectric properties depended strongly on temperature and measuring field [20], the ferroelectric parameters were thus normalized in the forms of P_r/P_{max} and E_c/E_{max} values, where P_{max} is the polarization value at the maximum applied field (E_{max}). Moreover, loop squareness (R_{sq}) of the ceramics is also presented. P_r/P_{max} and R_{sq} values of the ceramics are increased with an amount of CuO content added over 0.1 wt%. E_c/E_{max} is not significantly changed with CuO addition. The improvement of ferroelectric properties (e.g., higher P_r and lower E_c) is believed to be an effect of the increase in grain size and donor-like behavior of the ceramics particularly for the sample with highest CuO content.

4. Conclusions

PMNT/CuO ceramics were successfully prepared by a conventional mixed-oxide method. An addition of CuO slightly increased lattice parameter of pure PMNT ceramic. Grain size of the ceramics tended to increase with increasing CuO content while density is increased when an amount of CuO content was over 0.1 wt%. Dielectric and ferroelectric properties are found to be improved with an addition of CuO over 0.1 wt%. This research suggests that the optimum composition of CuO addition into PMNT ceramic would be 1.0 wt%, where superior dielectric and ferroelectric behaviors over the other compositions were obtained.

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Table 3
Dielectric and ferroelectric properties of PMNT/CuO ceramics.

CuO content (wt%)	Dielectric properties		T_{max} (°C)	δ (°C)	Ferroelectric properties		Loop squareness (R_{sq})
	ε_{max}	Tanδ			P_r/P_{max}	E_c/E_{max}	
0	11,870	0.0189	51	45	0.20	0.14	0.38
0.05	11,806	0.0239	47	44	0.24	0.16	0.39
0.1	12,182	0.0302	48	42	0.24	0.15	0.41
0.5	18,484	0.0631	45	41	0.25	0.14	0.41
1	23,729	0.1518	42	38	0.40	0.16	0.55

Note: ε_{max} and Tanδ represent dielectric constant and dielectric loss evaluated from a temperature which a maximum dielectric constant value (T_{max}) was shown. The measurement was done at a frequency of 1 kHz. δ represents diffuseness parameter. Ferroelectric properties were measured at room temperature with a frequency of 50 Hz.

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