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Dielectric and piezoelectric characteristics of the non-stoichiometric (Na,K)NbO_3 ceramics doped with CuO

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ABSTRACT

In this study, the non-stoichiometric composition $[(Na_{0.5}K_{0.5})_{0.97}(Nb_{0.96}Sb_{0.04})]O_3$ + x mol% CuO + 0.2 wt% Ag_2O (where x = 0, 0.2, 0.4, 0.6, 0.8, 1.0, respectively) ceramics were fabricated as a function of the amount of CuO addition. Then, their dielectric and piezoelectric properties were investigated. With a 0.8 mol% CuO content, these ceramics (abbreviated as NKNS) showed excellent values of density = 4.459 g/cm^3, electromechanical coupling coefficient (k_p) = 0.469, mechanical quality factor (Q_m) = 540, dielectric constant (ε_r) = 410 and piezoelectric constant (d_{33}) = 70 pC/N at the sintering temperature of 1080 °C, respectively.

1. Introduction

Pb(Zr,Ti)O_3 (abbreviated as PZT) system piezoelectric ceramics have been widely used in various applications such as ceramic resonators and filters, piezoelectric actuators, and transformers because of their excellent piezoelectric properties [1–3]. However, their high content of lead can cause environmental pollution and human health problem during the processing. Recently, the Restriction of Hazardous Substances (RoHS) in Electrical and Electronic Equipment has been enforced as the directive of the European Union [4,5] and some countries have demanded new electronic products for the environmental protection and human health. Therefore, it is necessary to develop lead-free piezoelectric ceramics with excellent piezoelectric properties and high Curie temperature for replacing the PZT system ceramics in various applications [6–9]. Recently, much research has focused on the $(Na_{0.5}K_{0.5})NbO_3$ (abbreviated as NKN) system ceramics as one of the promising candidate lead-free materials because these ceramics have large piezoelectric response and strong ferroelectricity [10]. However, pure NKN-based ceramics are very difficult to obtain dense and well-sintered ceramics using normal sintering processes because of the volatility of alkaline elements at the high sintering temperature. In order to improve the densification and piezoelectric properties of NKN-based ceramics, the sintering aids such as CuO and MnO_2 have been added. Especially, Yang et al. [11] and Nahm et al. [12] found that the introduction of CuO could decrease sintering temperature and improve the densification and piezoelectric properties of $(Na_{0.5}K_{0.5})NbO_3$ system ceramics. However, piezoelectric properties of above compositions are still weak for application in high-power devices such as piezoelectric transformers, ultrasonic motors or actuators. Because these devices should be electrically driven with high mechanical vibration at near resonance frequency, high mechanical quality factor (Q_m) with high electromechanical coupling factor (k_p) are simultaneously required [13]. Moreover, in order to enhance the thermal stability of piezoelectric properties, the tetragonal–orthorhombic phase transition (To-t), which can cause the domain instability between the two ferroelectric phases, should be shifted to above 150 °C and below room temperature.

Other methods for fabricating the NKN-based ceramics are hot pressing and spark plasma sintering ones. Dense Pb-free piezoelectric ceramics with excellent piezoelectric properties can be manufactured using the above methods. However, the hot pressing and the spark plasma sintering methods are not easily used in industrial fields because of their high cost.

Compound escaped from stoichiometric composition is called as the non-stoichiometric one. Amongst the solid ceramic compounds, it was found that these non-stoichiometric compositions have an influence on physical properties such as grain shape, defect of crystallographic structure and electrical conductivity. Therefore,

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researches concerning non-stoichiometric composition ceramics are necessary to facilitate the development of lead-free piezoelectric material with favorable piezoelectric characteristics because non-stoichiometric compositions can cause variations in the sinterability and microstructure of the ceramic. Furthermore, the $(K_xNa_{1-x})(Nb_ySb_{1-y})O_3$ ceramics which have an ABO_3 perovskite structure, if an A site mol component of (K_xNa_{1-x}) is smaller than a B site one of (Nb_ySb_{1-y}), can be made as a non-stoichiometric composition. The addition of CuO is performed with raw materials such as K_2CO_3, Na_2CO_3, Nb_2O_5, and Sb_2O_5 in the mixing process. Then, after calcination, excess B site components can be reacted with CuO. As the results, secondary products such as $K_aCu_bNb_cO_d$ and $K_aCu_bSb_cO_d$ are formed. These secondary products, that are capable of acting as sintering aids, can be sintered in lower sintering temperature and improve both dielectric and piezoelectric properties. Also, it is well known that the CuO is good sintering aid for low temperature sintering of PZT-based ceramics as well as shifting the tetragonal–orthorhombic phase transition toward higher temperature and proved to be an effective acceptor dopant to induce hardening features in NKN compositions [12]. Furthermore, from the previous result, because Ag_2O addition might enhance piezoelectric and dielectric properties and achieve the low sintering temperature with minimized property degradation, Ag_2O addition to $(K_{0.5}Na_{0.5})NbO_3$ system was performed [14].

Accordingly, in this study, in order to develop the lead-free piezoelectric ceramics with high mechanical quality factor (Q_m) as well as high electromechanical coupling factor (k_p) and to increase the tetragonal–orthorhombic phase transition, non-stoichiometric $[(Na_{0.5}K_{0.5})_{0.97}(Nb_{0.96}Sb_{0.04})]O_3$ + 0.2 wt% Ag_2O composition ceramics as a function of the amount of CuO(x = 0–1.0 mol%) addition were fabricated using a conventional sintering process and their piezoelectric and dielectric characteristics were investigated.

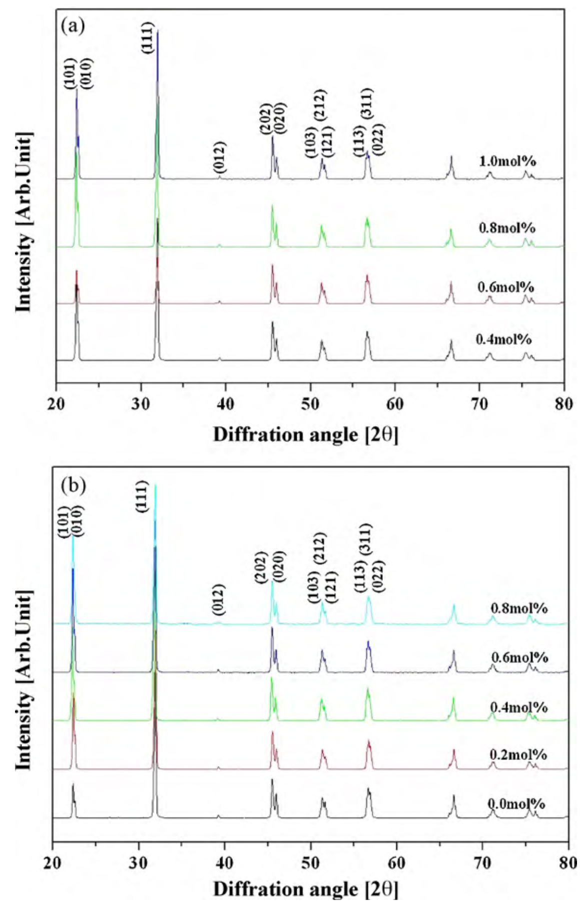

Fig. 1. The X-ray diffraction pattern of specimens as a function of the amount of CuO addition. (a:1080 °C, b:1100 °C).

2. Experimental details

The specimens were manufactured using a conventional mixed oxide process. The compositions used in this study were as follows:

$[(Na_{0.5}K_{0.5})_{0.97}(Nb_{0.96}Sb_{0.04})]O_3$ + x mol%CuO + 0.2 wt%Ag_2O (where x = 0, 0.2, 0.4, 0.6, 0.8, 1.0, respectively)

K_2CO_3 (99.5%), Na_2CO_3 (99%), Nb_2O_5 (99.9%), Sb_2O_5 (99.9%), CuO(99.9%)were used as starting raw materials. They were ball milled for 24 h with zirconia ball media and acetone. After calcinations at 900 °C for 6 h, the calcined powders were milled again with Ag_2O, and pressed into disks of 21 mm Ø in diameter and 1 mm in thickness under a pressure of 1000 kg/cm^2 using PVA as a binder. After burning out the PVA, the specimens were sintered at 1080 °C and 1100 °C for 5 h. Poling was carried out in a 120 °C silicon oil bath at the electric field of 35 kV/cm for 20 min. Then, the electromechanical coupling factor and mechanical quality factor were measured using resonance–anti-resonance method with an Agilent 4294 impedance analyzer. The k_p and Q_m were calculated using the following equation:

$$\frac{1}{k_p{}^2} = 0.395 \times \frac{f_r}{f_a - f_r} + 0.574 \quad (1)$$

$$\frac{1}{Q_m} = 2\pi f_r RC\left(\frac{f_a^2 - f_r^2}{f_a^2}\right) \quad (2)$$

(f_r: resonance frequency, f_a: anti-resonance frequency, R: resonance impedance, C: capacitance at 1 kHz)

The bulk densities were measured by the Archimedes' method. The microstructures were observed using a scanning electron microscopy (SEM). Grain size measurements were carried out using the mean intercept length method. The capacitance was determined with an LCR meter (ANDO 4304).

3. Results and discussion

Fig. 1(a and b) shows the X-ray diffraction pattern of specimens as a function of the amount of CuO addition at sintering temperatures of 1080 °C and 1100 °C, respectively. Most of the specimens displayed the perovskite structure according to the diffraction patterns. Also, as can be seen from the (2 0 2) and (0 2 0) peaks of the patterns, it was obvious that the crystal structure of the specimens showed only an orthorhombic phase.

Fig. 2 shows the scanning electron microscopy photographs of the grain structure of the specimens and in which the variation of grain morphology on the amount of CuO addition can be seen at 1080 °C and 1100 °C, respectively. The average grain size of the specimens slightly increases with the increasing CuO. The average grain size showed maximum values of 2.61 μm and 3.58 μm, respectively, when the CuO content reached 1 mol% and 0.8 mol% at sintering temperatures of 1080 °C and 1100 °C, respectively. These observations can be explained by the fact that the Cu $^{2+}$ ion acts as an acceptor dopant and can be substituted at the Nb^{5+} ion site. Therefore, the Cu $^{2+}$ ion makes oxygen vacancies and can easily promote grain growth because of the feasibility of particle diffusion [15]. Also, a liquid phase was formed in the grain boundary of the specimens with the increasing CuO content, results in the increase of grain size and more uniform of the specimens.

Fig. 3 shows the density of the specimens as a function of the amount of CuO addition at 1080 °C and 1100 °C, respectively. With increasing CuO content, the density indicated a tendency to increase. CuO doping was sufficiently effective in promoting the densification of the ceramics. Probably, it is considered that the increase in the density with CuO content is associated with the formation of a liquid phase between the grain boundaries. Also, if the A site mol component of (K_xNa_{1-x}) is smaller than the B site component of (Nb_ySb_{1-y}) in the ABO_3 perovskite compound structure, non-stoichiometric compositions could be made. Raw materials such as K_2CO_3, Na_2CO_3, Nb_2O_5, and Sb_2O_5 are mixed with CuO and then calcined, Excess B site components then react with CuO. As the result, secondary products such as $K_4CuNb_8O_{23}$

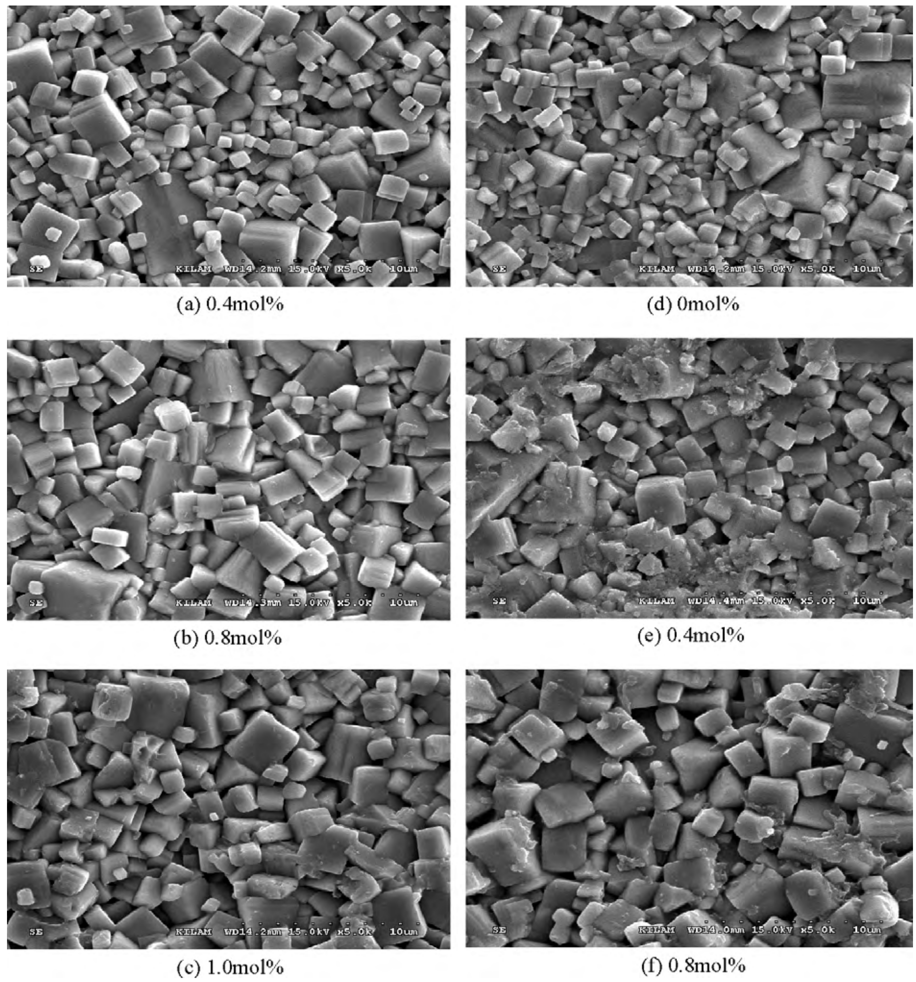

Fig. 2. The scanning electron microscopy (SEM) of specimens as a function of the amount of added CuO. (a–c:1080 °C, d–f:1100 °C).

and $K_{5.4}Cu_{1.3}Sb_{10}O_{29}$ can be formed. These secondary products that are capable of acting as sintering aids can lower the sintering temperature and restrain the strange second phases and improve the dielectric and piezoelectric properties.

Furthermore, the evaporation of K and Na and the melting of $KNbO_3$ (melting point = 1058 °C) can be prohibited by these secondary products.

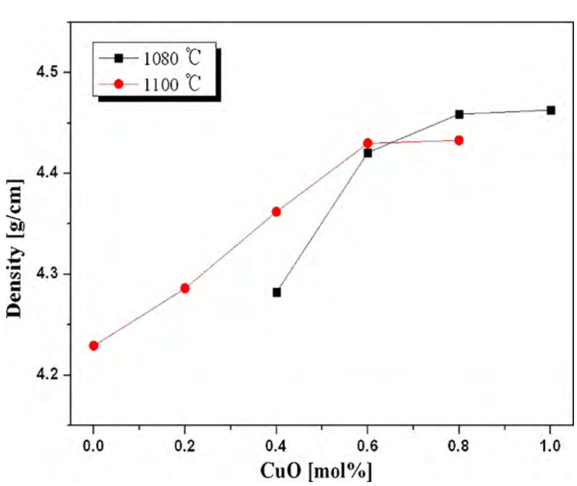

Fig. 3. Density of specimen as a function of the amount of CuO.

Fig. 4 shows the dielectric and piezoelectric properties (piezoelectric constant d_{33}, planar electromechanical coefficient k_p, mechanical quality factor Q_m and dielectric constant ε_r) of the ceramics as a function of the CuO content. At the two sintering temperatures of 1080 °C and 1100 °C, the entire physical property values showed a similar tendency. The piezoelectric constant (d_{33}), the dielectric constant decreased and the mechanical quality factor increased with increasing amount of CuO. These results are regarded as a hardening of the doping effect that the Cu^{2+} ion, which radius is 0.73 å, may substitute the B-site ion Nb^{5+} (of radius 0.68 å). In conclusion, the doping of CuO may cause "hardening" effects in this ceramics. The piezoelectric constant (d_{33}) showed the maximum values of 87 pC/N and 122 pC/N when the amount of the CuO was 0.4 mol%, 0 mol% at 1080 °C, 1100 °C, respectively. At the same sintering temperature and CuO content, the dielectric constant showed the maximum values of 503 and 822. The mechanical quality factor reached a maximum values of 540 and 468, when the amount of the CuO was 0.8 mol%, 0.6 mol% at 1080 °C, 1100 °C, respectively. The Q_m of the ceramics sintered at 1100 °C was lower than that of ceramics sintered at 1080 °C approximately about 100, because of the slightly higher sintering temperature. On the other hand, planar electromechanical coefficient showed a different tendency. The increase of it may be attributed to the increase of density and grain uniformity, which lowers the leakage current and enhances the poling efficiency [16,17]. k_p showed the maximum values of 0.469 and 0.458 when the amount of the CuO was 0.8 mol% and 0.6 mol% at 1080 °C, 1100 °C, respectively.

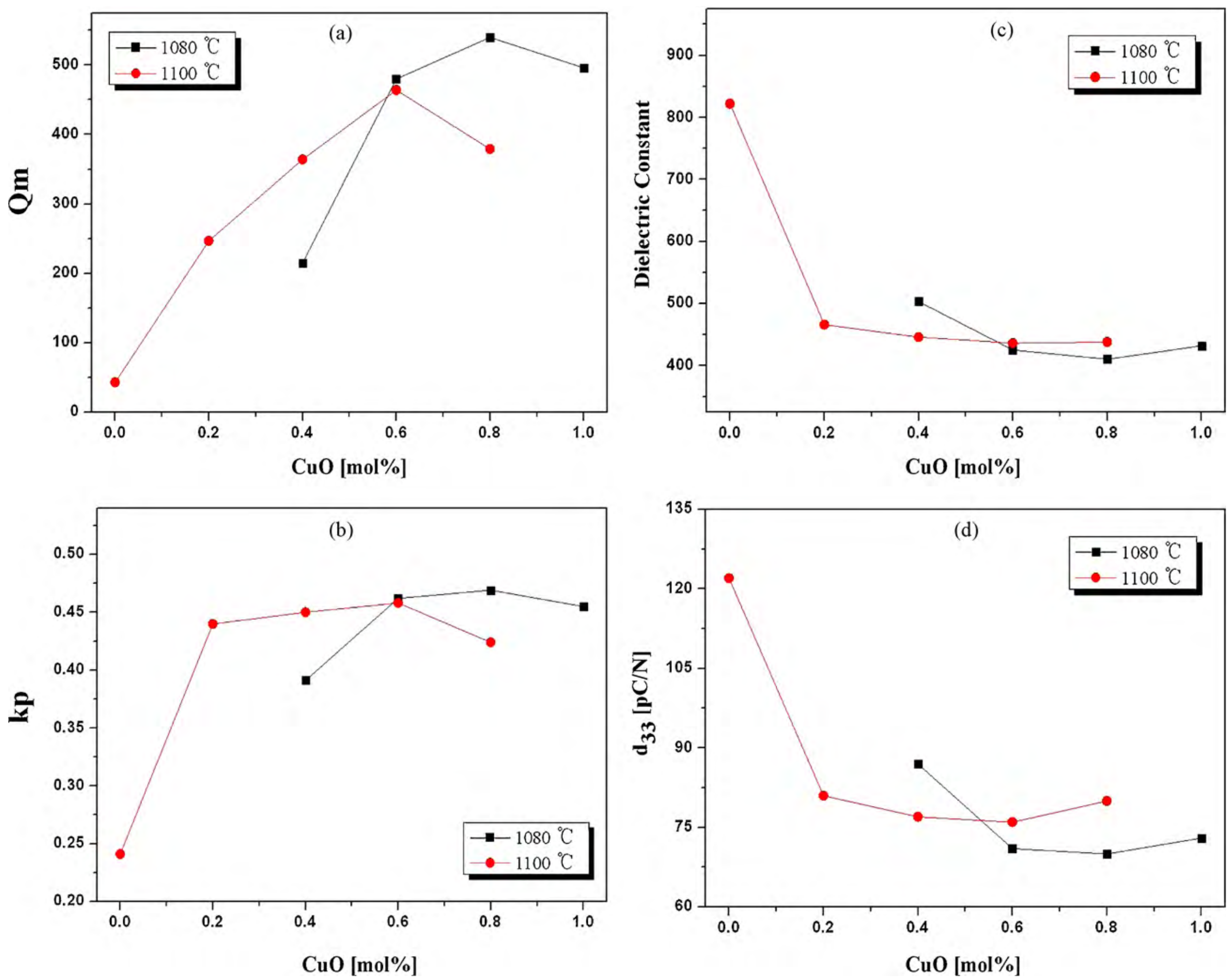

Fig. 4. Dielectric and piezoelectric properties of the ceramics as a function of the amount of CuO. ((a) Q_m, (b) k_p, (c) dielectric constant, (d) d_{33}).

Fig. 5 shows the temperature dependence of the dielectric constant as a function of the amount of CuO addition in the ceramics sintered at 1080 °C and 1100 °C, respectively. The temperature dependence of the dielectric constant was measured at a frequency of 10 kHz in the temperature range of 0–450 °C. A high Curie temperature (T_c) of 382 °C was obtained for the ceramic compositions $[(Na_{0.5}K_{0.5})_{0.97}(Nb_{0.96}Sb_{0.04})]O_3$ + CuO sintered at 1080 °C for 5 h and the dielectric constant peaked at T_c and had the highest value for 0.8 mol% CuO doped ceramics. The orthorhombic–tetragonal phase transition temperature was shifted a little toward higher temperatures and corresponded to the increase in CuO content. It is considered that the reasons why the values of To-t and T_c change with the content of CuO are also attributed to harder doping effect.

Table 1 shows the physical characteristics of the specimens according to amount of CuO.

Table 1
Physical characteristics of the specimens as a function of the amount of CuO addition.

Sintering temperature [°C]	CuO [mol%]	Density [g/cm^3]	k_p	Q_m	Dielectric constant	d_{33} [pC/N]
1080	0.4	4.282	0.391	215	503	87
	0.6	4.421	0.462	480	425	71
	0.8[a]	4.459[a]	0.469[a]	540[a]	410[a]	70[a]
	1.0	4.463	0.455	496	432	73
1100	0	4.229	0.241	43	822	122
	0.2	4.286	0.44	247	466	81
	0.4	4.362	0.45	364	446	77
	0.6	4.430	0.458	464	436	76
	0.8	4.433	0.424	379	438	80

[a] The optimum value.

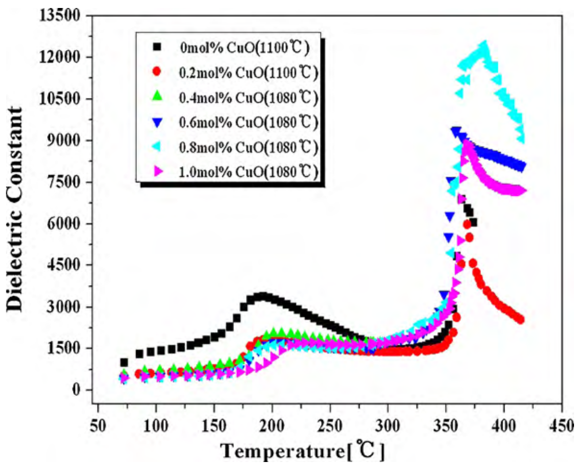

Fig. 5. Temperature dependence of dielectric constant as a function of the amount of CuO.

4. Conclusions

In this study, in order to develop the non-stoichiometric composition $[(Na_{0.5}K_{0.5})_{0.97}(Nb_{0.96}Sb_{0.04})]O_3 + x$ CuO mol% + 0.2 wt%Ag_2O (where x = 0 mol%, 0.2 mol%, 0.4 mol%, 0.6 mol%, 0.8 mol%, 1.0 mol%, respectively) ceramics were fabricated as a function of the amount of added CuO. The results obtained from the experiments were as follows:

1. Most of the specimens displayed the perovskite structure with an orthorhombic phase though increase of the amount of CuO.
2. At a sintering temperature of 1080 °C, the density increased up to 4.463 g/cm^3 when the amount of CuO reached 1.0 mol%.
3. At a sintering temperature of 1080 °C, Q_m rapidly increased up to maximum 540 when the amount of CuO reached 0.8 mol%. The Q_m of the ceramics sintered at 1100 °C was as low as approximately about 100 when compared with that of ceramics sintered at 1080 °C.
4. At a sintering temperature of 1080 °C, the density, electromechanical coupling factor, mechanical quality, dielectric constant and piezoelectric constant (d_{33}) of NKNS ceramics doped with 0.8 mol%CuO showed the optimum values of 4.459 g/cm^3, 0.469, 540, 410 and 70 pC/N, respectively.

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