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Effect of sintering temperature on the piezoelectric and ferroelectric characteristics of CuO doped $0.95(Na_{0.5}K_{0.5})NbO_3$–$0.05LiTaO_3$ ceramics

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ABSTRACT

In this paper, lead-free $(Na_{0.5}K_{0.5})NbO_3$ ceramics doped with 5 mol% $LiTaO_3$ and 2 mol% CuO were prepared using the conventional mixed-oxide method. The samples were characterized by X-ray diffraction analysis, scanning electron microscopy, and atomic force microscopy measurements. The effect of sintering temperature on the bulk density, piezoelectric and ferroelectric properties was investigated. The results show that an increase of CuO very effectively lowers the sintering temperature and improves the electric properties of $(Na_{0.5}K_{0.5})NbO_3$–$LiTaO_3$ ceramics. High piezoelectric properties of $k_p = 37.8\%$, $k_t = 50.7\%$, and $k_{33} = 58.9\%$ and ferroelectric properties $E_c = 34.6$ kV/cm and $P_r = 22.6$ were obtained for the specimen containing 2 mol% CuO sintered at a suitable temperature. Cu^{2+} ions acted as a hardener, which increased the E_c, P_r, and Q_m values of $(Na_{0.5}K_{0.5})NbO_3$–$LiTaO_3$ ceramics.

1. Introduction

Piezoelectric materials play an important role in actuators and sensors [1,2]. Modified ceramics have a desirable combination of properties, such as high surface phase velocity, electromechanical coupling coefficient (k^2) and a low temperature coefficient of frequency (TCF) [3,4]. The most commonly used piezoelectric materials are $PbTiO_3$–$PbZrO_3$ (PZT) based multi-component systems. They have been widely studied and used for transducers, piezoelectric actuators, surface acoustic wave device (SAW device) and sensors because of their excellent piezoelectric properties [1–3,5]. However, these materials may be restricted in the near future because of the high volatilization of PbO. Lead-free materials have received increasing attention worldwide for replacing PZT-based piezoelectric ceramics.

There are several candidates for lead-free materials, such as Bi compounds [6–8] and alkaline niobate compounds [9,10]. Sodium potassium niobate ($(Na_{0.5}K_{0.5})NbO_3$, NKN) ceramic is an attractive material that has been thoroughly investigated as a result of its high electromechanical coupling coefficient (k^2) and high phase transition temperature (Tc ∼ 420 °C), especially near the morphotropic phase boundary (MPB) [4,10–12]. However, the difficulty of sintering NKN ceramics under atmosphere is a serious drawback. The main problem is the volatilization of potassium oxide (K_2O) at 800 °C which makes it difficult to control stoichiometry [13,14]. Oxygen deficiency is another problem during preparation which results from high-temperature processing and gives rise to electronic conductivity [14]. The hot-pressing technique as well as spark plasma sintering (SPS) with high densities produce materials with excellent piezoelectric properties [15], but such processing techniques are not appropriate for industrial applications. The incorporation of $LiTaO_3$ into the perovskite structure of NKN improves piezoelectric properties [16,17]. The best piezoelectric properties of the $(1-x)K_{0.5}Na_{0.5}NbO_3$–$xLiTaO_3$ ($(1-x)$NKN–xLT) system have been achieved at the MPB region where $x = 5$–6 mol%. However, the sintering temperature of this system is too high (∼1075 °C) to inhibit the volatilization of K_2O. In order to improve the sinterability of NKN-based ceramics, CuO is often used because of its low melting point and formation of a liquid phase [18,19]. CuO is expected to improve the sinterability of NKN. It should be noted that CuO also improves the value of Q_m.

The present study is a continuation of our previous work [14,20]. $LiTaO_3$ (5 mol%) and CuO (2 mol%) [21,22] were added to NKN ceramics to improve the piezoelectric properties and to decrease the sintering temperature (900 °C), and the microstructure and piezoelectric properties were systematically investigated.

2. Experimental procedures

The starting materials of $(1-x)K_{0.5}Na_{0.5}NbO_3$–$xLiTaO_3$–$y$CuO (NKN–$x$LT–$y$Cu, for $x = 5.0$ mol% and $y = 0.2$ mol%) samples processed using the conventional

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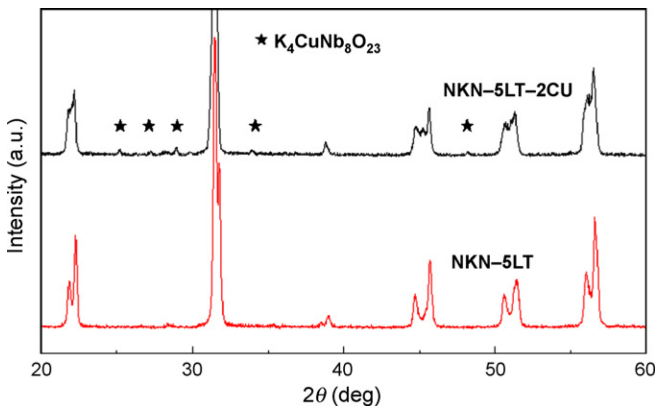

Fig. 1. XRD patterns of pure NKN–5LT and NKN–5LT–2Cu ceramics.

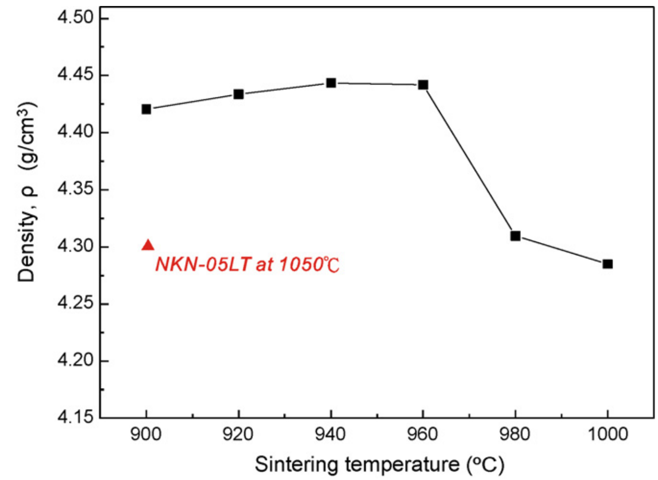

Fig. 2. Bulk densities as a function of the sintering temperature.

mixed-oxide method were pure reagent Na_2CO_3 (SHOWA, 99.5%), K_2CO_3 (SHOWA, 99.5%), Nb_2O_5 (SHOWA, 99.5%), Ta_2O_5 (STREM CHEMICALS, 99.8%), Li_2CO_3 (STREM CHEMICALS, 99.99%) and CuO (SHOWA, 99.5%) powders. The compounds were weighed according to the desired compositions. The starting materials were transferred to a 100 mm diameter cylindrical plastic jar, partially filled with 10 mm diameter ZrO_2 grinding balls. Sufficient ethanol (99.5%) was added to cover the powders. Ball milling was carried out for 24 h, followed by drying at 130 °C. The mixture was ground using an alumina mortar and pestle to break up large agglomerates that formed during drying. In order to enhance the uniformity of the composition, the mixture was calcined at 850 °C in air for 5 h. The resulting powders were ball milled for 24 h and dried again. The powders, milled with 5 wt.%

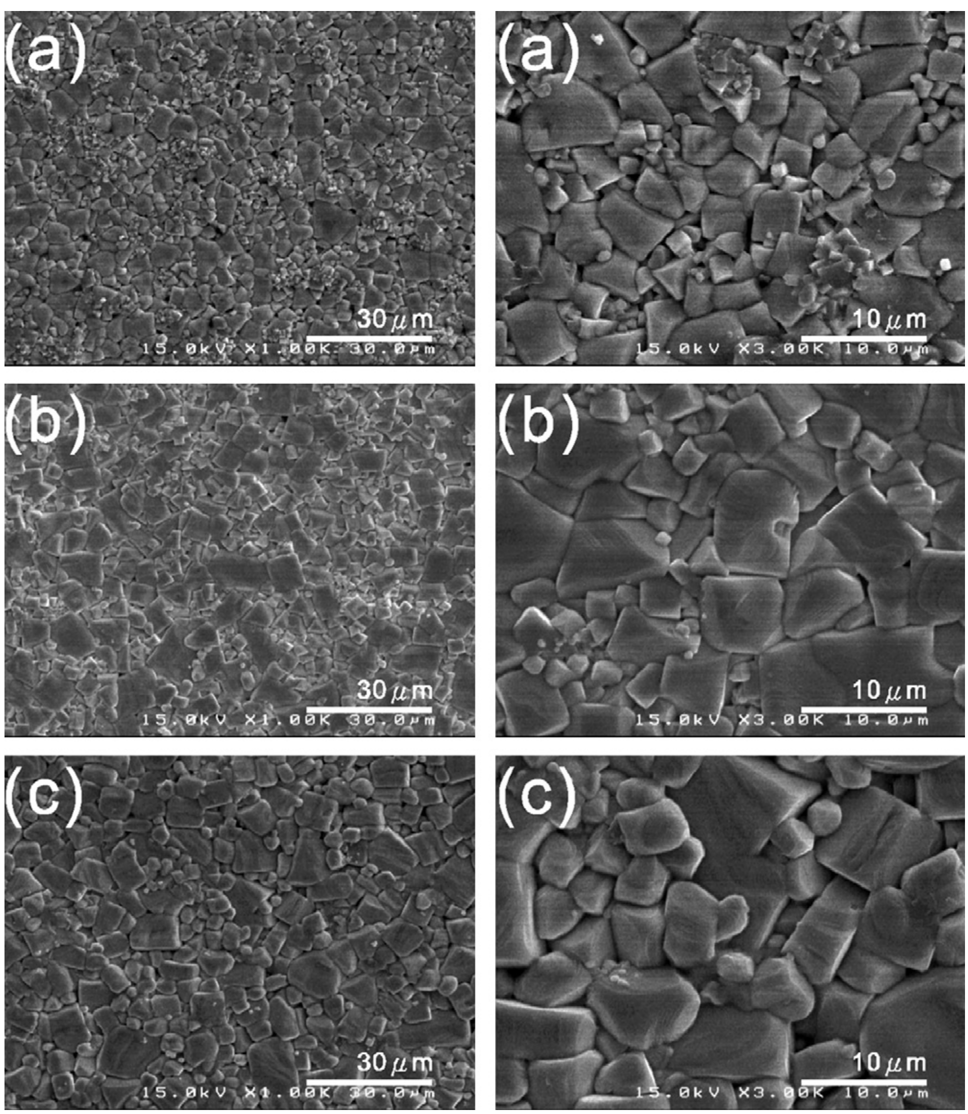

Fig. 3. SEM images of NKN–5LT–2Cu ceramics sintered at temperatures of (a) 900 °C, (b) 940 °C, and (c) 1000 °C.

PVA aqueous solution, were then uni-axially pressed into a disk with a 12 mm diameter at a pressure of 25 kg/cm^2, and subsequently sintered in air at 900–1050 °C for 3 h.

Bulk densities were measured using the Archimedes method with distilled water as the medium. The microstructure was observed using a field emission scanning electron microscope (FESEM) with a Hitachi S-4100 microscope. The crystallographic study was confirmed by X-ray diffraction (XRD) using Cu Kα (λ = 0.154 nm) radiation with a Seimens D-5000 diffractometer operated at 40 kV and 40 mA. The dielectric and piezoelectric properties were measured with a HP 4294A precision impedance analyzer. To measure the electrical properties, silver paste was painted on both sides of the samples to form electrodes. The samples were then subsequently fired at 150 °C for 20 min and poled under a 40 kV/cm DC field at 150 °C in silicone oil for 30 min. The electromechanical coupling factor of the thickness (k_t) and planar (k_p) modes was calculated using the resonance–anti-resonance method. Ferroelectric hysteresis loops (*P*–*E*) were obtained under a 50 kV/cm AC field at 60 Hz in a modified Sawyer–Tower circuit [23]. In order to prevent arcing, the samples were submerged in 150 °C silicon oil.

3. Results and discussion

Fig. 1 shows the XRD profiles of pure NKN–5LT ceramics sintered at 1050 °C for 3 h and NKN–5LT–2Cu ceramics sintered at 960 °C for 3 h. A homogeneous NKN–5LT phase was well developed without second phase. However, when CuO was added 2 mol%, the $K_4CuNb_8O_{23}$ (KCN) second phase (JCPDS card No. 21-1250), indicated by the asterisk, formed in the NKN–5LT–2Cu ceramics.

The bulk densities and their relative densities as a function of the sintering temperature are shown in Fig. 2. As the sintering temperature increased, the bulk density increased, reaching maximum value of 4.44 g/cm^3 at a sintering temperature of 940 °C. In the experiment, the density rapidly dropped when the temperature was increase to over 960 °C. The density of NKN–5LT–2Cu ceramics sintered at a low temperature is much higher than that of NKN–5LT ceramics (4.30 g/cm^3). As shown in Fig. 2, a small amount of CuO effectively increases the density and improves the sintering performance of the NKN–5LT ceramics.

Fig. 3 shows the microstructure of NKN–5LT–2Cu ceramics sintered at temperatures of (a) 900 °C, (b) 940 °C, and (c) 1000 °C. The grain size is larger at sintering temperatures from 900 °C to 940 °C. The structure of the ceramic gradually becomes dense. When the sintering temperature was increased from 960 °C to 1000 °C, the cavities significantly increased which is possibly due to the evaporation of potassium oxide at high temperature; this may be the reason for the deterioration of the bulk density at over 940 °C (Fig. 2).

The piezoelectric planar and thickness coupling factors, k_p and k_t, were calculated using the following equation [24]:

$$\frac{1}{k^2} = a \times \frac{f_r}{f_a - f_r} + b \quad (1)$$

where f_r is the resonance frequency, f_a is the anti-resonance frequency, a = 0.395 and b = 0.574 for planar (k_p) mode, and a = 0.405 and b = 0.810 for thickness (k_t) mode. Longitudinal coupling, k_{33}, was estimated from the piezoelectric planar and thickness coupling factors [3]:

$$k_{33}^2 = k_p^2 + k_t^2 - k_p^2 k_t^2 \quad (2)$$

The dependence of k_p, k_t, and k_{33} on the sintering temperature is shown in Fig. 4. The values of k_p increase with sintering temperature and then decrease, giving a maximum value of 37.8% at 960 °C, which is a little lower than that of NKN–5LT ceramics (38.4%). Both k_t and k_{33} increased when the sintering temperature was increased from 900 °C to 940 °C, reaching 50.7% and 58.9%, respectively, and decreased over 940 °C. The increase may be attributed to increased density, which lowers the leakage current and enhances the poling process [25,26]. Moreover, the k_t value of well-sintered NKN–5LT–2Cu ceramics is much higher than that of NKN–5LT ceramics. The thickness frequency constant (N_t) and

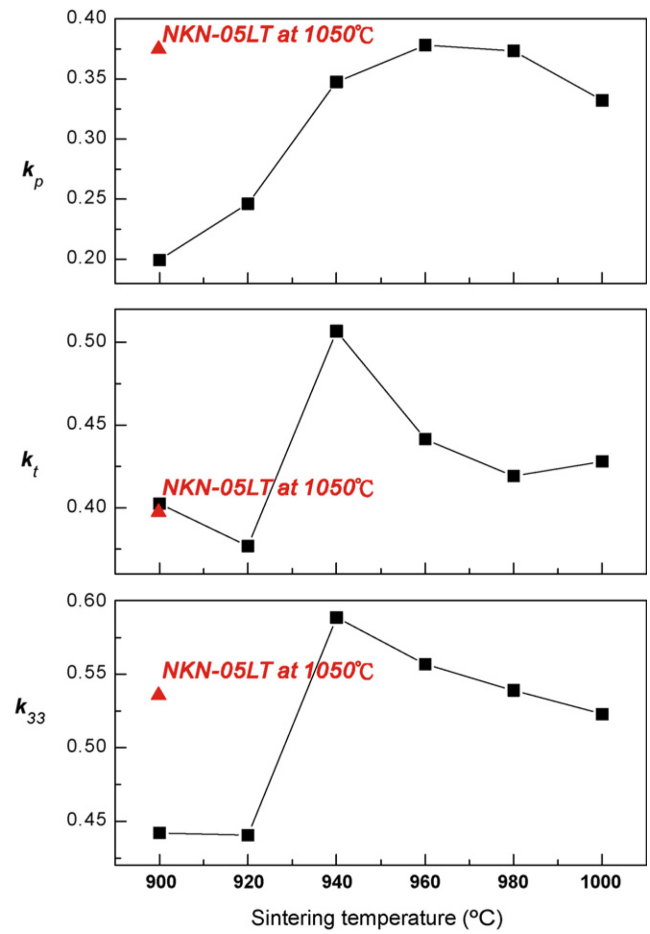

Fig. 4. Dependence of k_p, k_t, and k_{33} values on sintering temperature.

planar frequency constant (N_p) were obtained from the following equation:

$$N = f_r \times l \quad (3)$$

where l is the dimension relative to the vibration mode. The values of N_t and N_p are shown in Fig. 5. The experimental results show that the N_t and N_p values of NKN–5LT–2Cu ceramics increase with sintering temperature, with maximum values of N_t = 3133 Hz-cm

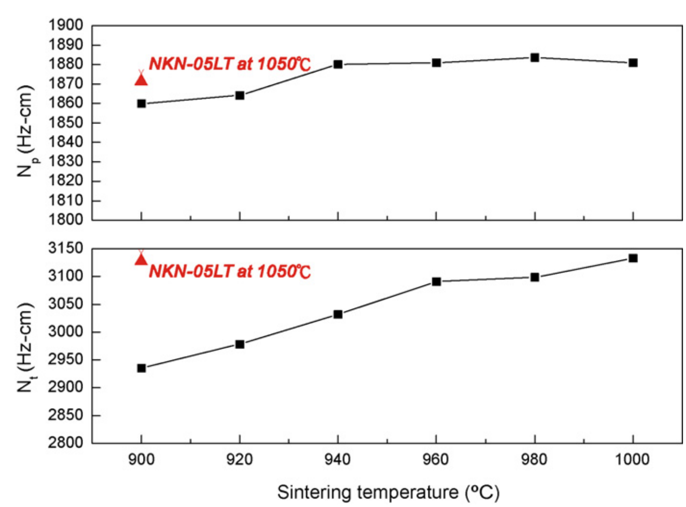

Fig. 5. N_t and N_p values of NKN–5LT–2Cu ceramics.

Table 1
Comparison of properties of $(Na_{0.5}K_{0.5})NbO_3$–$LiTaO_3$ ceramics based on reports from various groups.

Ceramic composition	ρ (g/cm^3)	K_t (%)	K_P (%)	Q_m	E_c (kV/cm)	P_r (μC/cm^2)	Reference
NKN (hot pressed)	4.46	–	45	240	–	33	[12,13]
NKN	4.3	45	39	130	20	20	[12]
NKN–$LiTaO_3$	–	–	36	–	12.5	9	[17]
NKN–05LT	4.3	40	38.4	40	27.3	10.5	Our sample
NKN–05LT–02Cu	4.44	51	37.8	293	34.6	22.6	Our sample

and N_p = 1883 Hz-cm. Ceramics with a higher frequency constant can be used in higher frequency applications without increasing bulk volume.

The values of Q_m are shown in Fig. 6. The values of Q_m were determined using the relationship [24]:

$$\frac{1}{Q_m} = 2\pi f_r RC \left(\frac{f_a^2 - f_r^2}{f_a^2}\right) \quad (4)$$

where R is the resonance impedance and C is the capacitance at 1 kHz. The experimental results show that the Q_m value of NKN–5LT–2Cu ceramics is 40 for a sintering temperature of 900 °C and increases to 293 for a sintering temperature of 960 °C. The resonance impedances of NKN–5LT–2Cu sintered at 900 °C and 960 °C were 180 Ω and 41 Ω, respectively. From Eq. (4), the Q_m value is inversely proportional to the resonance impedance. Therefore, when resonance impedance decrease from 180 Ω to 41 Ω, Q_m increased from 40 to 293. The improvement of the Q_m value from 105 for NKN–5LT to 293 for NKN–5LT–2Cu may be due to the hardening effect of the Cu ions. Cu-substitution hardens NKN. For PZT, the addition of acceptor ions, such as Mg^{2+}, Sc^{3+} and Fe^{3+}, increases the density of oxygen vacancy. This increases the value of Q_m. Cu^{2+} which also behaves as an acceptor is considered as a substitute for Nb^{5+}.

The polarization versus electric field (P–E) hysteresis curves of NKN–5LT–2Cu ceramics sintered at 960 °C for 3 h, measured at 60 Hz and 150 °C, are shown in Fig. 7. The coercive electric field (E_c) and the remnant polarization (P_r) of NKN–5LT–2Cu ceramics are 34.6 kV/cm and 22.6 μC/cm^2 shown in Table 1, respectively. The values of E_c and P_r for various sintering temperatures are shown in Fig. 8. The highest E_c and P_r values were obtained at a sintering temperature of 960 °C. When the temperature was increases from 900 °C to 960 °C, E_c and P_r increased from 27.3 kV/cm and 10.5 μC/cm^2 to 34.6 kV/cm and 22.6 μC/cm^2, respectively. This change is similar to that for the Q_m value in Fig. 6. E_c and P_r increased with Cu content. NKN–5LT ceramic might have transformed into a hard piezoelectric material with CuO addition. Positively charged oxygen vacancies were produced by the addition of CuO, which thereby enabled the Cu^{2+} ions and oxygen vacancies to form defect dipoles that caused the pinning effect and transformed NKN–5LT ceramics into hard ceramics [27].

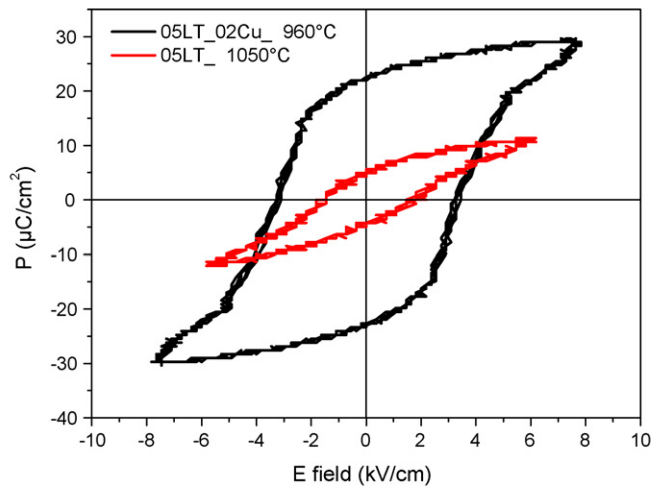

Fig. 7. P–E hysteresis loops of NKN–5LT–2Cu and NKN–5LT ceramics measured at 60 Hz and 150 °C.

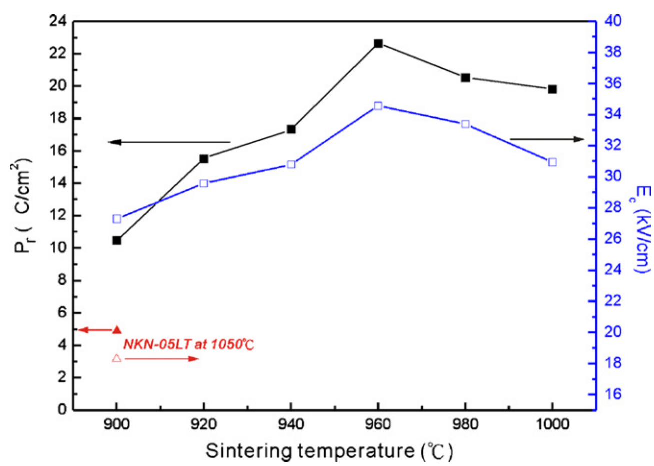

Fig. 8. P_r and E_c variations of NKN–5LT–2Cu and NKN–5LT ceramics measured at 60 Hz and 150 °C.

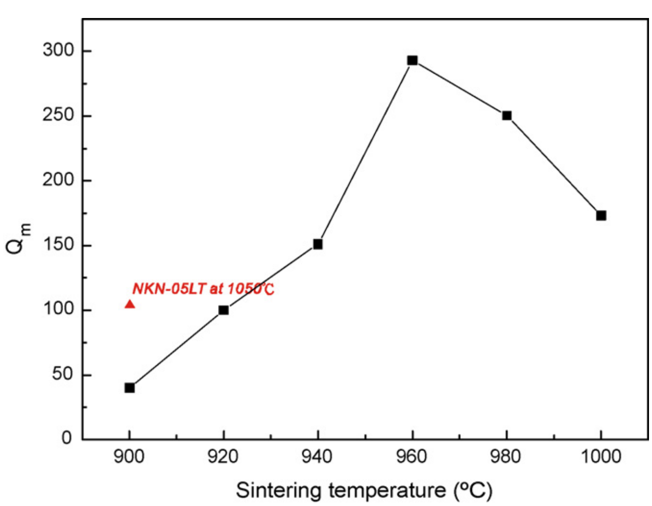

Fig. 6. Dependence of Q_m on sintering temperature.

4. Conclusions

In this study, CuO was added to NKN–5LT ceramics to decrease sintering temperature and improve the density as well as piezoelectric and ferroelectric properties. The $K_4CuNb_8O_{23}$ (KCN) second phase that formed in NKN–5LT–2Cu ceramics enhanced the sintering by making liquid phases. When a small amount of CuO was added, the densities of the samples were 4.44 g/cm^3. The NKN–5LT–2Cu ceramics sintered at 940 °C and 960 °C show excellent properties of k_p = 37.8%, k_t = 50.7%, and k_{33} = 58.9% with hardness characteristics of $E_c = 34.6$ kV/cm and $P_r = 22.6$ μC/cm^2. The k_t value of NKN–5LT–2Cu ceramics is very high, making if a promising lead-free ceramic for surface acoustic wave devices (SAW devices) and a wide range of electromechanical transducers.

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