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Hydrothermal solvothermal synthesis potassium sodium niobate lead-free piezoelectric ceramics assisted with microwave

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Abstract Potassium–sodium niobate (Na, K)NbO_3 (NKN) powders were synthesized successfully by reducing holding time via microwave-assisted hydrothermal solvothermal method (MHSM). The obtained powders were characterized by X-ray diffraction and scanning electron microscope with special emphasis on the synthesizing temperature and holding time. The results indicate that the pure (Na, K)NbO_3 powders with single perovskite structure were obtained by being calcined at 200 °C for 30 min. The powder synthesized at 200 °C for 90 min has a fine morphology and an average grain size, and its ceramics were prepared after being sintered from 1000 to 1050 °C. The microstructure, piezoelectric and dielectric properties of the obtained NKN ceramics were investigated, by comparison, the same performance were also studied for the sample prepared from conventional powders. The sample sintered at 1050 °C show optimal values of $d_{33} = 128$ pC/N, $k_p = 35.0\%$, $\rho = 4.32$ g/cm^3, $\tan\delta = 0.021$ and $\varepsilon_r = 509$, respectively, and its Curie temperature (420 °C) is slightly higher than that (410 °C) of the conventional sample.

1 Introduction

With increasing of people's consciousness of environmental protection, lead zirconate–titanate piezoelectric ceramics (PZT) will be replaced due to the toxicity of lead oxide. Therefore, a lot of work has been done to find environment-friendly alternative materials. Among the lead-free piezoelectric compositions, potassium–sodium niobate [(Na, K) $NbO_{3,}$ NKN] is considered to be a promising alternative candidate because of its high curie temperature and relatively strong piezoelectricity [1–4]. However, NKN ceramic has a few disadvantages, of which the most serious one is poor sinterability, that is, pure NKN ceramic is difficult to sinter fully by traditional sintering method [5–8]. Two main reasons cause such problem, firstly, pour NKN can be decomposed beyond 1140 °C; secondly, K_2O and Na_2O easily evaporate at high temperature during sintering, which slightly changes the chemical stoichiometry of NKN ceramics. So it is difficult to obtain dense NKN ceramics using powders prepared from traditional solid state reaction.

One solution to obtain dense NKN ceramics is to use refined powder with enhanced sintering activity, prepared by chemical synthesis method, such as molten-salt method, sol–gel routine or hydrothermal process [7–9]. Among which hydrothermal method attracts more attention because it requires low temperature and gives pure ultrafine powders without further heat treatment. However, this method generally need dense alkali liquor and take long reaction time [10–12]. Hydrothermal solvothermal method, as a modified hydrothermal method, reduces the concentration of alkali liquor via the addition of isopropanol. Bai et al. have successfully synthesized NKN powders through hydrothermal solvothermal method by reducing the concentration of alkali liquor from 10 to 2 M [13]. Moreover, hydrothermal synthesis can be assisted by microwave heating, diminishing synthesis time by enhancing reaction kinetics. NKN, $KNbO_3$ (KN) and $NaNbO_3$ (NN) have been synthesized via this method [14–18]. Zhou and Zhang have successfully synthesized $K_{0.5}Na_{0.5}NbO_3$ powders by using the

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microwave-hydrothermal method at 160 °C for 7 h, respectively [19, 20]. Although, the reaction time was reduced as compared to the conventional hydrothermal route, it can be further reduced.

In this study, the microwave-assisted hydrothermal solvothermal method was utilized to synthesize NKN powders for lowing concentration alkali liquor and shorting holding time. The influences of temperature and holding time on the synthesized powders and the ceramics from which were detected by several techniques.

2 Experimental

Analysis-grade potassium hydroxide (KOH), sodium hydroxide (NaOH), niobium pentoxide (Nb_2O_5) and isopropanol (all of which were obtained from Sinopharm Chemical Reagent Co., Ltd, China) were used as starting materials. First, a mixed solution of KOH and NaOH with the KOH/NaOH ratio of 3:1 was adjusted to 5.0 mol/l. Then appropriate amounts of Nb_2O_5 and isopropanol were dispersed in the mixed hydroxide solution, and stirred for 30 min. The slurry was poured into a 100 ml Teflon lined reactor with a 60% filling ratio. The reactor was placed in HG-SC12 microwave synthesizer and the reaction was operated at 2.45 GHz. Several reaction temperatures and dwell times were studied. The studied temperature range was 170–230 °C and reaction time from 30 to 120 min. After the reaction was completed, the precipitates were filtered and washed several times with deionized water and dried at 110 °C for 6 h.

The obtained powders were mixed with 5 wt% polyvinyl alcohol (PVA) solution, and then uniaxially pressed into pellets of 10 mm in diameter and 1.0 mm in thickness under 80 MPa pressure. After burning out PVA, the green disks were respectively sintered at selected temperatures between 1000 and 1080 °C for 2 h in air to get dense ceramics. For electrical characterization, the samples were polished and coated with Ag paste on both parallel surfaces, and then fired at 550 °C for 30 min. Then samples were polarized along the thickness direction at 120 °C for 30 min at the polarizing electric field of 3 kV.

Density of samples was determined by the Archimedes method. The phase structure was determined using X-ray powder diffraction with a Cu *K* radiation ($\lambda = 1.5416$ Å) filtered through a Ni foil (Rigaku; RAD-B system, Tokyo, Japan). The microstructure of sintered samples was observed by a scanning electron microscope (SEM, S-450, HITACHI, Tokyo, Japan) and the powder by scanning electron microscope (SEM, S-360, Cambridge, English). The temperature dependence of the dielectric properties was examined using a programmable furnace with an *LCR* analyzer (TH2828S) in the temperature range of 20–530 °C The piezoelectric constant d_{33} was measured using a quasistatic piezoelectric coefficient testing meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). The planar electromechanical coupling coefficient k_p were calculated by the resonance–antiresonance method using a precision impedance analyzer (Agilent, 4294A) on the basis of IEEE standards.

3 Results and discussion

Figure 1 shows the XRD patterns between the 2θ range 20°–60° (a) and 31°–34° (b) of NKN powders synthesized by MHSM at different temperatures for 60 min. It can be seen from Fig. 1a that the samples synthesized above 200 °C show a pure perovskite structure, whereas the sample synthesized at 170 °C shows a little second phase peaks, which are indexed to the phase of $K_2Nb_8O_{21}$ (PDF#31-1060). Further increasing temperature diminished the diffraction peaks of $K_2Nb_8O_{21}$ phase, which suggests that the solid solubility of $K_2Nb_8O_{21}$ in NKN increases with increasing temperature. It is worth noting that the 2θ of mean diffraction peak, for instance, the (110) space, shifts to a lower angle with increasing synthesized temperature, as shown in Fig. 1b. The phenomena may be attributed to the fact that Na^+ reacts more readily with Nb_2O_5 than K^+ to form NKN, as reported in the literatures elsewhere [18, 21], at the low temperature of 170 °C, there is more Na ions enter into NKN lattice and generate Na-rich NKN solid solution, the redundant K will combine with Nb_2O_5 to form impurity phase $K_2Nb_8O_{21}$ and exist near grain boundary. With increasing synthesis temperature, more K ions will enter into the NKN lattice and cause the expansion of the crystal lattice due to the ionic radius of

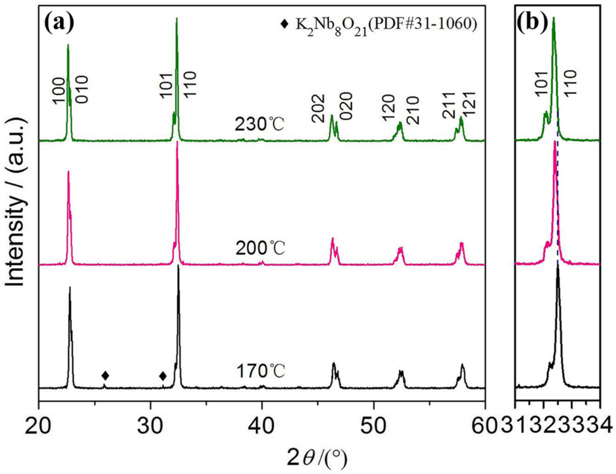

Fig. 1 XRD patterns between the 2θ range 20–60 (**a**) and 30–34 (**b**) of NKN powders synthesized by MHSM at different temperatures for 60 min

K^+ (1.33 Å) is larger than that of Na^+ (0.97 Å), which lead to the diffraction peak of (110) shifts to a low angle.

The SEM images of NKN powders synthesized at different temperatures for 60 min via MHSM and 850 °C for 4 h via conventional method are shown in Fig. 2. It is observed from Fig. 2a–c that the particle size increase slightly as the synthesized temperatures increases. The morphological investigations revealed that the presence of cuboid grains of about 1.2 µm (Fig. 2b) and 1.8 µm (Fig. 2c), estimated by the linear intercept method, for powders synthesized at 200 and 230 °C via MHSM, respectively. As seen in Fig. 2d, the powder calcined via conventional method has coarse particles and wider distribution than that synthesized by MHSM, in which the large particles are about 6–7 µm and the small ones < 0.5 µm.

The XRD patterns between the 2θ range 20°–60° (a) and 31°–34° (b) of NKN powders synthesized by MHSM at 200 °C for different holding times are shown in Fig. 3. It is possible to observe that all samples show pure perovskite-like structure without the evidence of secondary phases. A further increase in the holding time from 30 min to 120 min leads to splitting of (202)/(020) peak at $2\theta = 45–47$, which indicates the formation of single phase orthorhombic perovskite structure, as seen in Fig. 3a. Note that the 2θ of the mean diffraction peak of (110) space, as shown in Fig. 3b, has barely changed as the increase of holding time,

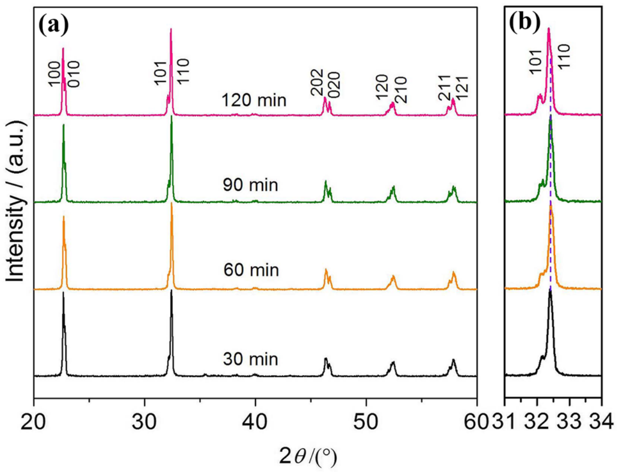

Fig. 3 XRD patterns between the 2θ range 20°–60° (a) and 31°–34° (b) of NKN powders synthesized by MHSM at 200 °C for different reaction time

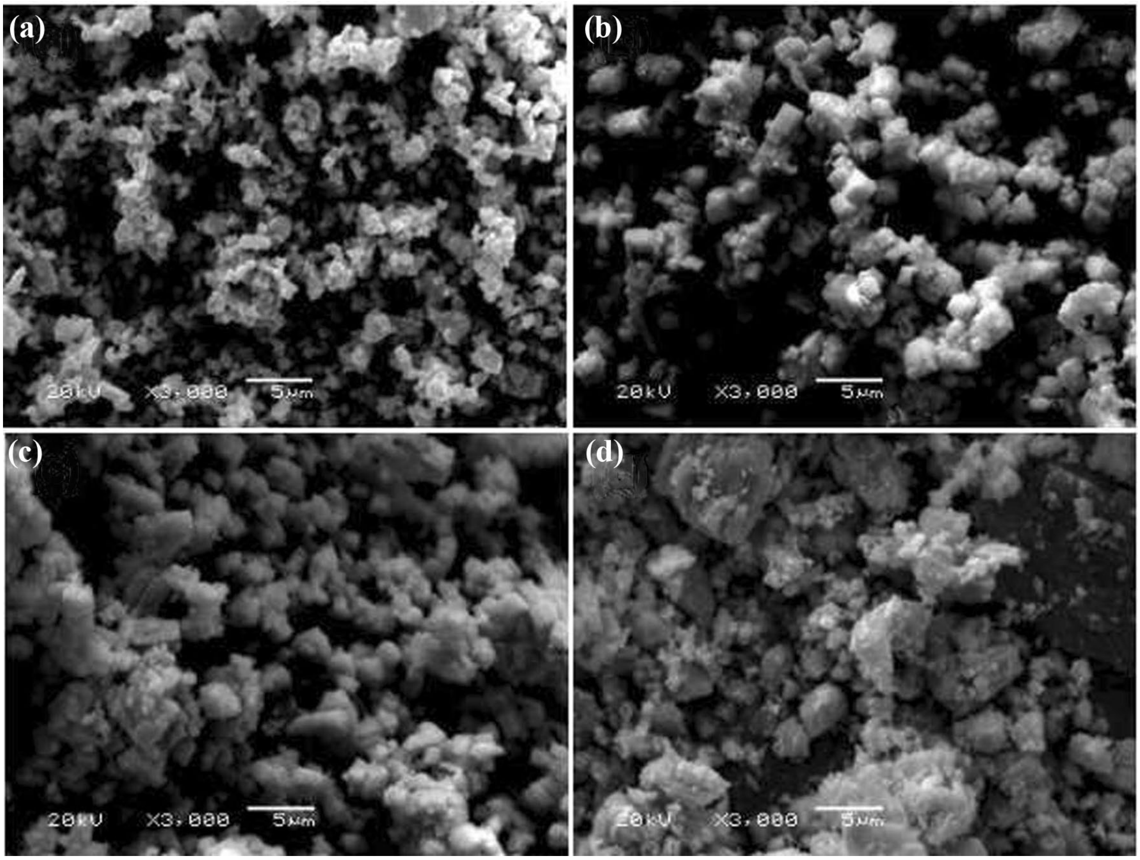

Fig. 2 SEM images of NKN powders synthesized by MHSM at different temperatures for 60 min : **a** 170 °C; **b** 200 °C; **c** 230 °C, and **d** synthesized by conventional method at 850 °C for 4 h

indicating that the effect of holding time on chemical composition is less than that of synthesized temperature, as shown in Fig. 1.

SEM images of NKN powders synthesized by MHSM at 200 °C for different holding time are presented in Fig. 4. It can be seen from Fig. 4a–c that the particle size increase from about 0.8 µm to about 2.1 µm as the holding time from 30 to 90 min, however, it is no more increase when the holding time further extending to 120 min. The particle shape present cubic-like when the holding time exceeds 90 min, which suggests that the desired reaction time is about 90 min. As the report in previous studies [18], it is difficult to avoid particles agglomeration due to the surface effect in the wet chemical methods, which would have negative impacts on subsequent sintering process. However, the obtained powders in this study show well dispersion, which probably because the addition of isopropanol plays a key role in the action of surfactant, and obstructs the coagulation of ultra-fines, which is consistent with the results reported by Bai [13].

The synthesis of NKN powders was considered to be difficult owing to the high volatility of K_2O and Na_2O during calcination at high temperature. The microwave hydrothermal method has given better results. Nevertheless, it is reported that this method demands a long holding time of 7 h to obtain well-crystallized powders [19, 20]. Rigoberto has studied the influence of temperature, pressure and KOH/NaOH concentration on the synthesis of NKN powders by microwave hydrothermal, and concluded that the correct temperature–pressure and alkaline ion concentration are necessary for fast synthesis of NKN powders [18].

In this paper, from Figs. 3 and 4, NKN phase is observed in XRD and SEM images for reactions carried out at 200 °C using 5 M KOH/NaOH for 30–120 min, which means that NKN powders have been synthesized at 200 °C for a short time of 30 min using MHSM. The reason for this may be ascribed to the addition of isopropanol, which can create higher pressure for the same reaction system due to its low boiling point (82 °C), which coincides with previous reports using hydrothermal solvothermal method [12, 13].

Figure 5 shows the microstructures of the ceramic samples prepared from the powders synthesized by MHSM at 200 °C for 90 min (Fig. 5a–c) and conventional method (Fig. 5d). It can be seen from Fig. 5a–c that all samples show a cubic-like grain shape. The specimen sintered at 1000 °C has a porous microstructure with small grains

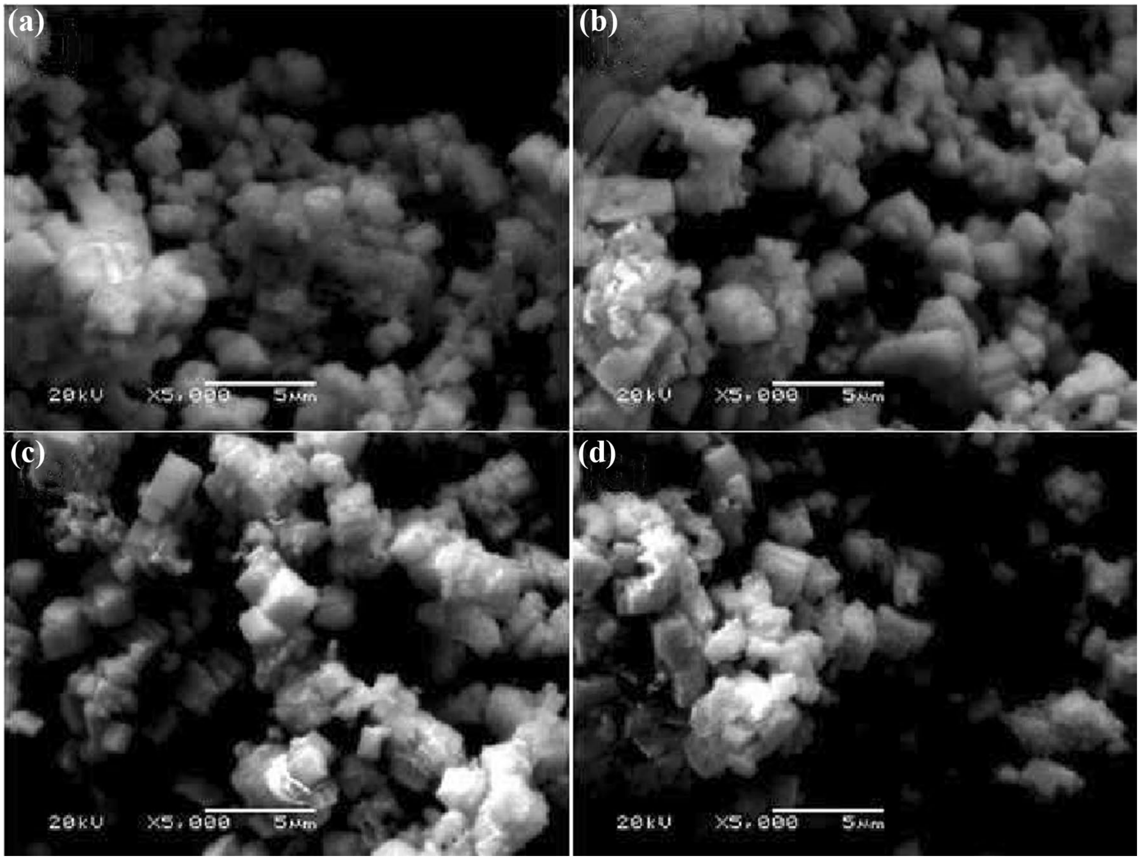

Fig. 4 SEM images of NKN powders synthesized at 200 °C for different reaction time: **a** 30 min; **b** 60 min; **c** 90 min; **d** 120 min

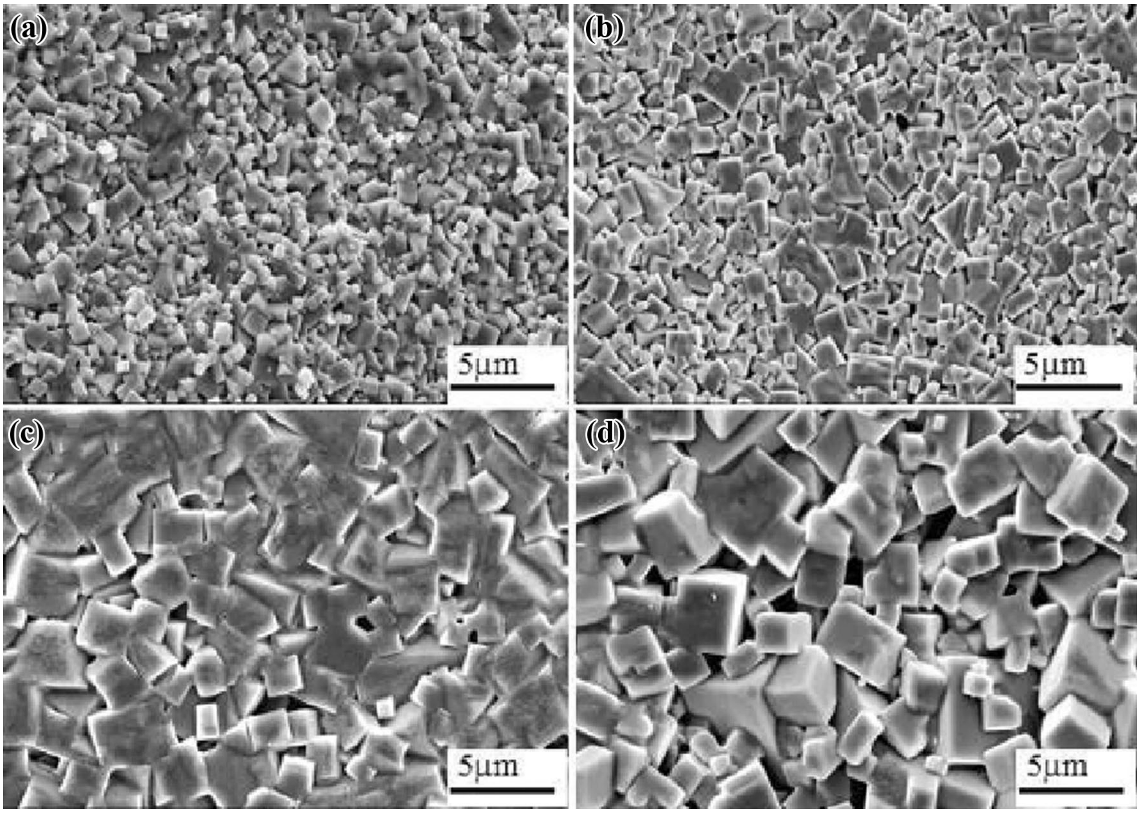

Fig. 5 SEM images of NKN samples sintered at different temperature for 2 h: **a** 1000 °C; **b** 1020 °C; **c** 1050 °C; and **d** from the powder synthesized by conventional method, 1080 °C

(approximately average of 0.5 μm in size), as seen in Fig. 5a, indicating an insufficient growth of the grains due to the low sintering temperature. As the sintering temperature is increased, the microstructure becomes much denser and the grains grow much larger, the mean gain size of the samples sintered at 1020 and 1050 °C is about 1.5 and 2.6 μm, respectively, as seen in Fig. 5b, c. Figure 5d shows the microstructure of the sample sintered at 1080 °C, which from the powders synthesized by conventional method. It can be observed that the sample is composed by cubic-like grains, and some pores generate at grains boundaries. The image also reveals a bimodal grain size distribution, which may be attributed to the exaggerated grain grow process, as it was reported in NKN-based piezoelectric ceramics [22].

The density and electrical properties of NKN samples sintered at different temperature for 2 h are summaried in Table 1. As observed in this table, the piezoelectric coefficient (d_{33}), electromechanical (k_p) and density (ρ) increase with increasing sintering temperature from 1000 to 1050 °C. The d_{33}, k_p, and ρ of the sample sintered at 1000 °C are 82 pC/N, 25%, and 3.80 g/cm^3, and reach a maximum values of 128 pC/N, 35%, and 4.32 g/cm^3, respectively, at densification sintering temperature of 1050 °C. However, the sample sintered at 1080 °C, which from the powder synthesized by conventional method, shows a poor values of $d_{33} = 85$ pC/N, $k_p = 31\%$, and $\rho = 4.18$ g/cm^3, respectively. It is reported that piezoelectric properties were closely related to densification and grain size distribution in NKN-based lead-free ceramics [22, 23], for the sample sintered at 1080 °C, the detrimental

Table 1 Summary of physical and electrical properties of NKN samples sintered at different temperature for 2 h

Sintering temperature (°C)	d_{33} (pC/N)	k_p (%)	ρ (g/cm^3)	tanδ (@10 KHz)	ε_r (@10 KHz)
1000	82	25	3.80	0.036	452
1020	112	28	4.22	0.028	488
1050	128	35	4.32	0.021	509
1080 (CM)	85	31	4.18	0.014	611

effect on piezoelectric properties may be attributed to low density and bimodal grain size distribution. Interestingly, the decrease in dielectric loss (tanδ) and increase in relative dielectric constant (ε_r) can be observed by increasing sintering temperature from 1000 to 1080 °C (CM). It has been reported that tanδ and ε_r are highly dependent on density of NKN-based ceramics, but the case is not consistent with which here. The reason may be attributed to the bigger grain size of the sample sintered at 1080 °C (CM). According to previous studies, the bigger gains may exhibit less internal stresses inside the gains, which makes the motion of domain walls easily and subsequently higher dielectric properties. Kumar and Palei attributed the low ε_r of NKN-based sample with small gains to the grain boundary width [24]. They explained that the decrease in grain size leads to a increase in the thickness of more insulating gain boundary layer and concluded that ε_r increase with increasing grain size. The tanδ decrease with the increase of sintering temperature may be attributed to the difficulty in domain wall motion that results from the smaller grain size [25].

The temperature dependence the relative dielectric constant (ε_r) for the NKN ceramics sintered at 1050 °C (MHSM) and 1080 °C (CM) measured at 10 KHz, are shown in Fig. 6. It can be seen that two phase transitional peaks could be observed for both samples, corresponding to the orthorhombic-tetragonal ($T_{O\text{–}T}$) and tetragonal–cubic (T_C) transitions, respectively, indicating that both samples show orthorhombic structure at room temperature, which coincides with the XRD results, as shown in Figs. 1 and 3. The $T_{O\text{–}T}$ and T_C for the sample sintered at 1080 °C (CM) are 200 and 410 °C, respectively, which is in agreement with that obtained in pure NKN ceramics [26]. However, both the $T_{O\text{–}T}$ and T_C of the sample sintered at 1050 °C (MHSM) slightly shift to high temperature, reaching to 210 and 420 °C, respectively. The reason for this may be due to the difference between the gain sizes, as reported by Wu [27]. Besides, the maximum dielectric constant for 1080 °C (CM) sintered sample is higher than that sintered at 1050 °C (MHSM), which is according to room temperature values presented in Table 1. Feizpour et al. have reported a similar behavior for temperature dependence of dielectric constant for pure NKN ceramics synthesized with microwave method and conventional method [28].

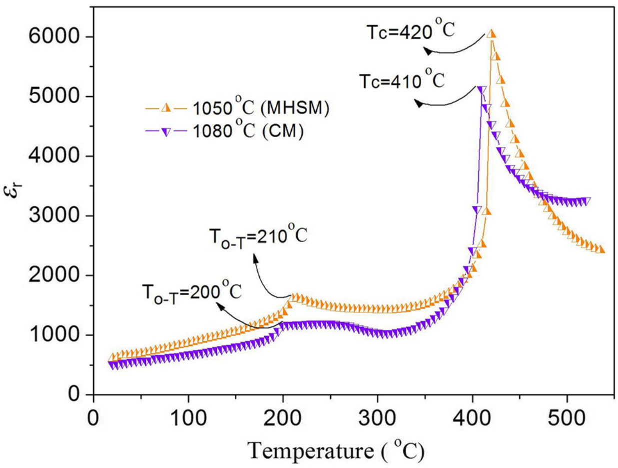

Fig. 6 Temperature dependence of the ε_r (100 KHz) for NKN ceramics sintered at 1050 °C (MHSM) and 1080 °C (CM)

4 Conclusion

The single phase orthorhombic perovskite KNN powder has been successfully synthesized using MHSM, which lower the concentration of alkali liquor from 10 to 5 M and shorten holding time from 24 to 0.5 h. Compared with the powders synthesized with conventional method, the powders synthesized with MHSM have fine and homogeneous grain sizes, and its sintered samples exhibit higher density and better piezoelectric properties than that prepared by ordinary synthesized method. Enhanced piezoelectric coefficient d_{33} and electromechanical coupling coefficient k_p of the sample sintered at the optimal temperature of 1050 °C are 128 pC/N and 35.0%, respectively.

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