



High densification and dielectric properties of lead-free $(K_{0.5}Na_{0.5})NbO_3$ piezoelectric ceramics with optimum excess Na_2O and K_2O contents

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Abstract

Lead-free piezoelectric ceramics based on the $(K_{0.5}Na_{0.5})NbO_3$ (KNN) system were prepared by the solid-state reaction method. The effects of firing temperatures and excess Na_2O and K_2O on KNN ceramics were investigated. The samples were calcined between 750 and 950 °C for 4 h and the sintering range was between 1060 and 1140 °C. Impurities phases of Nb_2O_5 and K_2CO_3 appeared in all sintered samples, due to evaporation of some elements during in the sintering process. The average particle size and grain size increased with increased firing temperatures. After addition of excess Na_2O and K_2O with 0, 1, 2, 3, 4, 5 and 10 wt% in the system, the impurities phase did not appear in all samples. The porous microstructure gradually decreased with increased of excess Na_2O and K_2O up to 1 wt% and then slightly increased with higher than 1 wt% of excess Na_2O and K_2O . The density and dielectric constant can be improved by adding 1 wt% of excess Na_2O and K_2O . © 2015 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

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1. Introduction

Lead-free piezoelectric ceramics have attracted attention as new piezoelectric materials to replace PZT based ceramics because of environmental problem due to its high vapor pressure during sintering process. Recently, $(K_{0.5}Na_{0.5})NbO_3$ (KNN)-based lead-free piezoelectric ceramics are attracting attention which are characterized by high piezoelectric properties and high temperature of phase transition (~ 410 °C) [1–7]. These materials are widely used to develop sensors and actuators [8]. However, it was difficult to achieve the densification in pure KNN ceramic due to high reactivity with the volatilization of

K_2O and Na_2O during sintering process and difficulty in sintering an elaborate body [9–13].

Various fabricating techniques, such as hydrothermal method [14–16], hot-pressed sintering, spark-plasma sintering (SPS) have been utilized to improve the densification and properties of KNN lead-free materials. Hydrothermal synthesis and microwave sintering showed the maximum relative density 88% at the sintering temperature of 1040 °C [14]. Hot-pressed sintering method can improve the densification and presented maximum relative density of 98.9% at the sintering temperature of 1100 °C [15]. At low temperature of 920 °C, the theoretical density of 99% with enhanced properties was observed by SPS method [16]. However, all of these techniques are costly for production and unsuitable for practical application in industry [17,18]. The conventional solid-state reaction method is more economical for large batch processing of KNN ceramics which have been reported by several research groups [10,19,20]. Chen et al. [19] prepared KNN ceramic by solid-state reaction using a calcination temperature of 865 °C and sintering temperature of 1100 °C for 3 h. The

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maximum relative density of the ceramics was found at around 94.5% and this sample exhibited maximum dielectric constant of ~ 2400 . Birol et al. [10] sintered KNN ceramic at 1114 °C, the maximum theoretical density of $\sim 95\%$ and dielectric constant of 5500 were obtained. The obtaining of low density and low dielectric constant was caused from evaporation of K_2O and Na_2O during sintering process [9,11,13,20]. The deficiency of K_2O and Na_2O produce large pore in microstructure and has significant effect in other properties of KNN ceramics. The addition of excess K_2O and Na_2O is one of technique developed to counteract this problem.

The aim of this study is to improve sinterability, increase densification and dielectric properties by adding Na_2O and K_2O in excess in order to offset the volatile mass. Therefore, the optimum sintering temperatures and effects of excess Na_2O and K_2O on the crystal structure, microstructure and dielectric properties of KNN ceramics synthesized by solid-state reaction method were studied.

2. Experimental

$(K_{0.5}Na_{0.5})NbO_3$ (abbreviated as KNN) were prepared by the solid-state reaction method. Na_2CO_3 , K_2CO_3 and Nb_2O_5 were used as starting materials. The starting powders were weighed in the required stoichiometric ratio and then ball-milled in ethanol for 24 h. After the drying process, the mixed powders were calcined between 750 and 950 °C for 4 h. The crystal structure of the calcined powders was detected by X-ray diffraction. The calcined powders were mixed with polyvinyl alcohol and pressed into discs with a diameter of 15 mm under

120 MPa. These pellets were subsequently sintered between 1060 °C and 1140 °C for 2 h with a heating/cooling rate of 5 °C/min to discover the optimum sintering temperature. To compensate the evaporation of K_2O and Na_2O during calcination and sintering process, the K_2O and Na_2O were added. The amount of excess Na_2O and K_2O was subdivided into 0, 1, 2, 3, 4, 5 and 10 wt% at calcination and sintering temperatures of 900 and 1100 °C, respectively.

The crystal structure of the samples was characterized by X-ray diffraction (XRD). The microstructure of each sample was observed using scanning electron microscopy (SEM). The grain size of each sample was measured by a mean linear

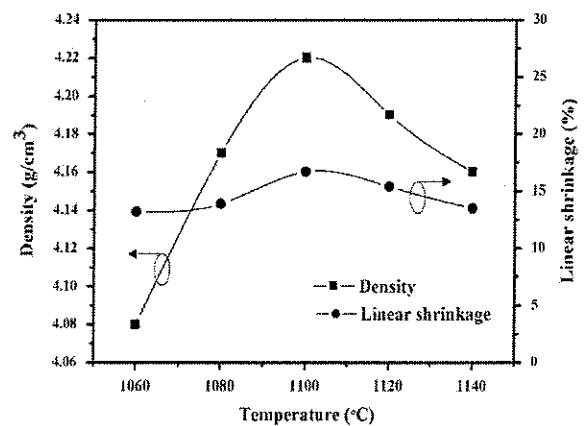


Fig. 2. Density and linear shrinkage of KNN ceramics with different sintering temperatures.

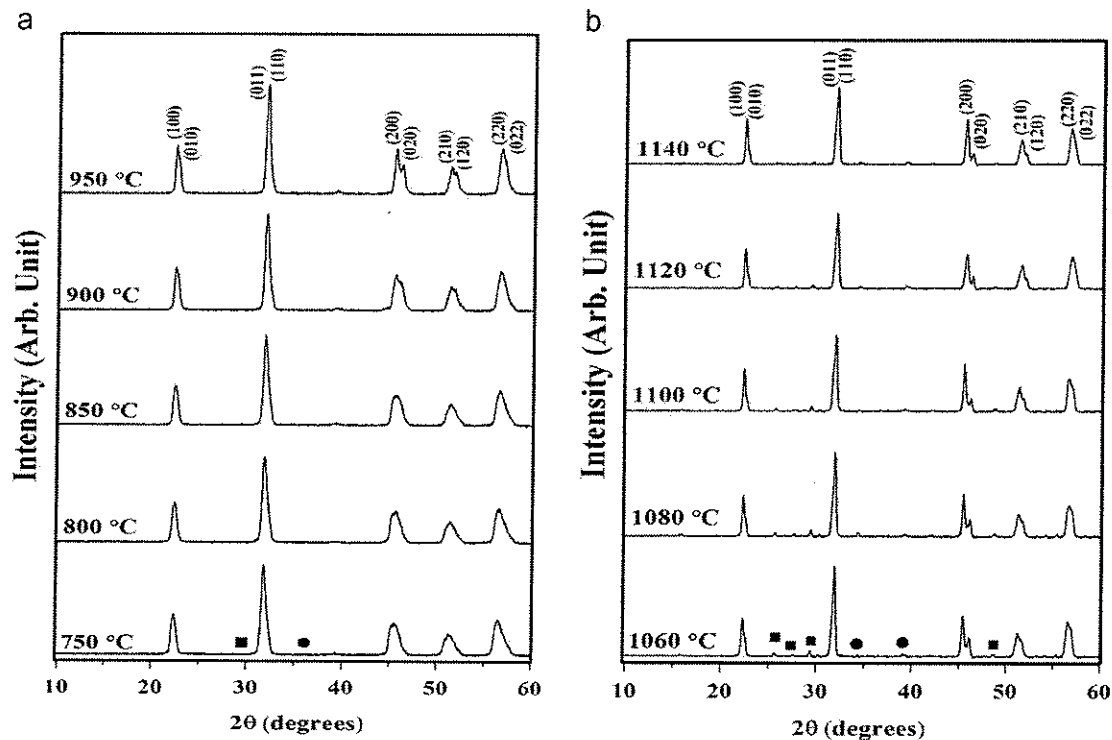


Fig. 1. XRD patterns of KNN (a) calcined powders and (b) sintered ceramics with different firing temperatures: (■) Nb_2O_5 , (●) K_2CO_3 .

Table 1

Relative density, ϵ_r , $\tan\delta$, average particle size, average grain size, T_{O-T} and T_C of KNN ceramics.

Sintering temperature (°C)	Relative density (%)	ϵ_r (at T_c)	$\tan\delta$ (at T_c)	Excess K_2CO_3 and Na_2CO_3 (wt%)	Average particle size (μm)	Average grain size (μm)	Relative density (%)	T_{O-T} (°C)	T_c (°C)	ϵ_r (at T_c)	$\tan\delta$ (at T_c)
1060	90.6	2488	0.215	0	0.28	0.81	93.7	197.7	403.2	4382	0.14
1080	92.6	3789	0.208	1	0.39	1.24	98.0	199.0	406.2	6723	0.05
1100	93.7	4382	0.139	2	0.43	1.92	95.5	200.0	406.8	3951	0.06
1120	93.1	3570	0.260	3	2.06	2.87	95.1	199.3	411.7	3780	0.07
1140	92.4	3343	0.439	4	2.90	3.72	93.1	201.9	414.0	3650	0.08
				5	3.61	—	—	—	—	—	—
				10	4.46	—	—	—	—	—	—

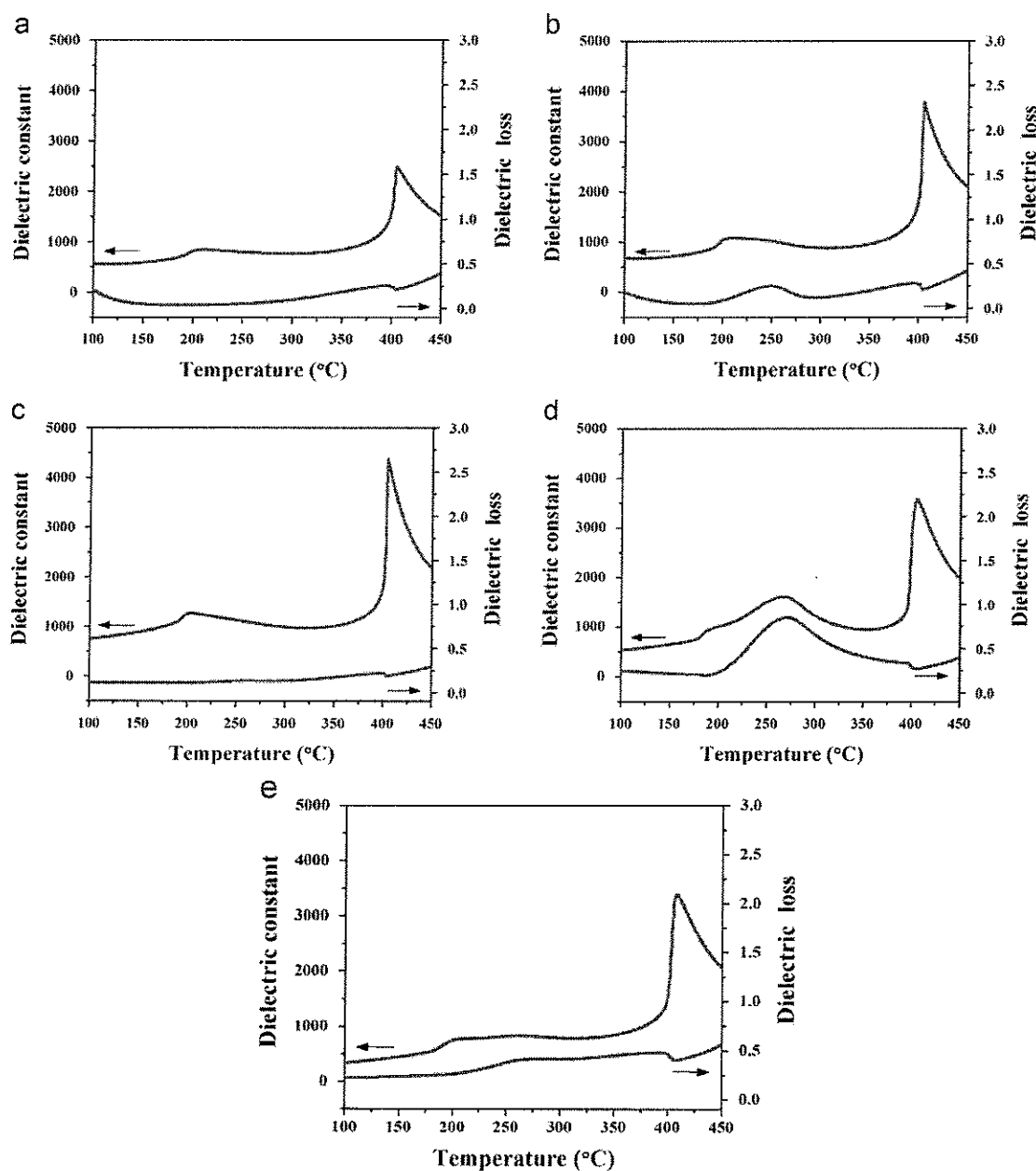


Fig. 3. Dielectric properties of KNN sintered ceramics with different sintering temperatures (a) 1060 °C; (b) 1080 °C; (c) 1100 °C; (d) 1120 °C and (e) 1140 °C.

intercept method from the SEM micrographs. For electrical measurements, two parallel surfaces of sintered ceramics were polished. Silver paste (Heraeus C1000) was deposited on both sides and fired in air at 650 °C for 30 min. Dielectric constant and loss of the ceramics for a wide variety of frequencies were measured using LCR meter (Agilent 4284A).

3. Results and discussion

The XRD patterns of calcined powders and sintered ceramics of KNN at various temperatures are shown in Fig. 1a and b. At low calcination temperatures (< 900 °C), the impurity phases of Nb_2O_5 and K_2CO_3 were found. The pure orthorhombic phase which is characterized by the splitting of (2 0 0) and (0 2 0) peaks was discovered in powders calcined ≥ 900 °C (Fig. 1a). After calcination at 900 °C, the powders were sintered between 1060 °C and 1140 °C, the impurity phases of Nb_2O_5 and K_2CO_3 were observed in all sintered samples.

The density and shrinkage of KNN ceramics with sintering temperature between 1060 °C and 1140 °C can be seen in Fig. 2. The density and shrinkage increased with increasing sintering temperatures from 1060 °C to 1100 °C, and reached a maximum value of 4.22 g/cm³ (93.7% of theoretical density, as listed in Table 1) and 17% respectively at 1100 °C which are higher than the previous work which has been reported [10,19]. The density and shrinkage decreased after further sintering at higher temperatures (1120–1140 °C) and are seen in Fig. 2. According to the melting phase of KNN is started at ~ 1120 °C [21], the decrease of density of KNN ceramics sintered at high temperature may cause from the higher rate loss of Na_2O and K_2O [9–13,20].

The dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$) of the KNN ceramics as a function of temperature are shown in Fig. 3 (a)–(e). All of the samples show two peaks at around 200 °C and 400 °C which corresponding to the phase transition from orthorhombic to tetragonal (T_{O-T}) and from tetragonal to cubic (T_C) [19]. At the lowest sintering temperature of 1060 °C, the ϵ_r and $\tan\delta$ are 2488 and 0.215. The dielectric constant of the samples increased when sintering temperature increased from 1060 to 1100 °C and showed maximum value of 4382. The lowest loss about 0.139 was observed from the sample sintered at 1100 °C, as seen in Table 1.

To compensate the evaporation of Na_2O and K_2O during calcination and sintering process, the excess of Na_2O and K_2O

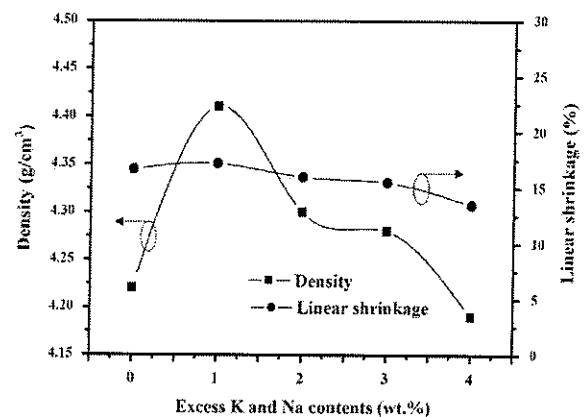


Fig. 5. Density and linear shrinkage of KNN ceramics with different amounts of excess Na_2O and K_2O .

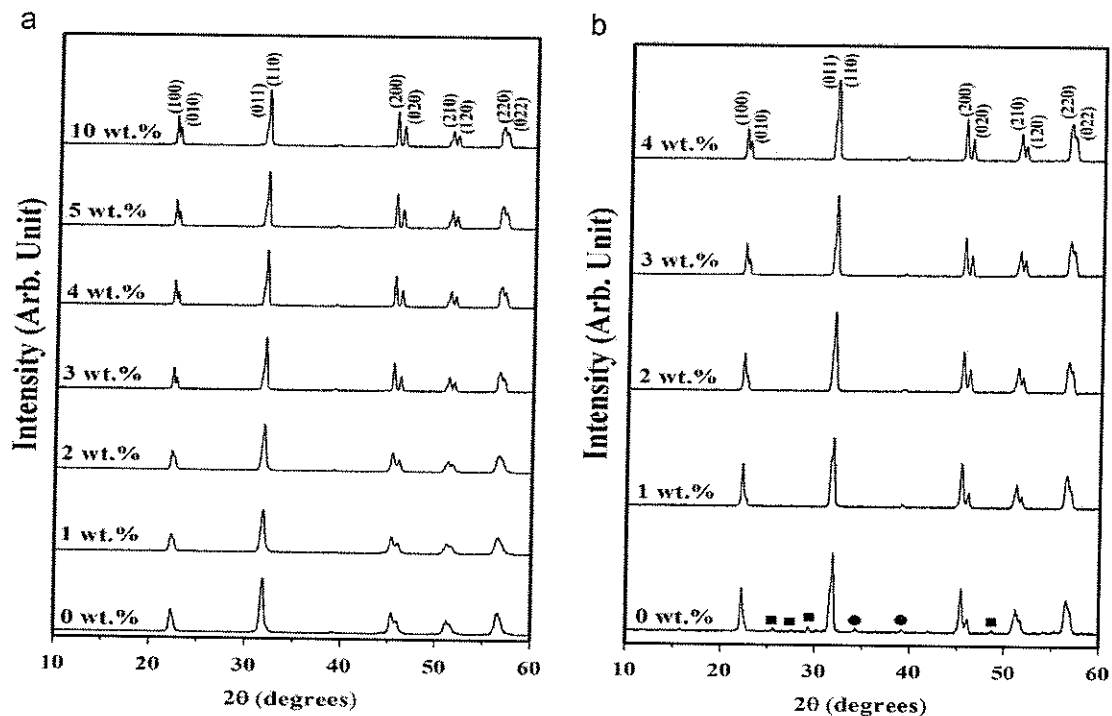


Fig. 4. XRD patterns of KNN (a) calcined powders and (b) sintered ceramics made from starting powders containing different amount of Na_2O and K_2O : (■) Nb_2O_5 , (●) K_2CO_3 .

were added in KNN during fabrication. The samples were calcined and sintered at 900 °C for 4 h and 1100 °C for 2 h, respectively. The X-ray diffraction patterns of KNN calcined powders at different amount of excess Na_2O and K_2O contents are shown in Fig. 4(a). The single orthorhombic perovskite phase without the impurity phase was observed in all excess Na_2O and K_2O samples. The peaks at (2 0 0) and (2 2 0) are clearly separated and shifted to high temperature region with increase in excess Na_2O and K_2O contents, which mean crystallite growth, lattice parameters and unit cell decreased.

After the samples were sintered at 1100 °C, impurity phases of Nb_2O_5 and K_2CO_3 could be observed in the sample without excess Na_2O and K_2O contents (0 wt%), as seen in Fig. 4(b). Meanwhile, the impurity phase did not appear in the samples with excess Na_2O and K_2O contents (1–4 wt%) and present a single orthorhombic phase. This indicated that the excess Na_2O and K_2O helped maintain compositional control in KNN ceramics. For the sintered ceramic samples with excess Na_2O and K_2O of 5 and 10 wt%, the green body could not be formed.

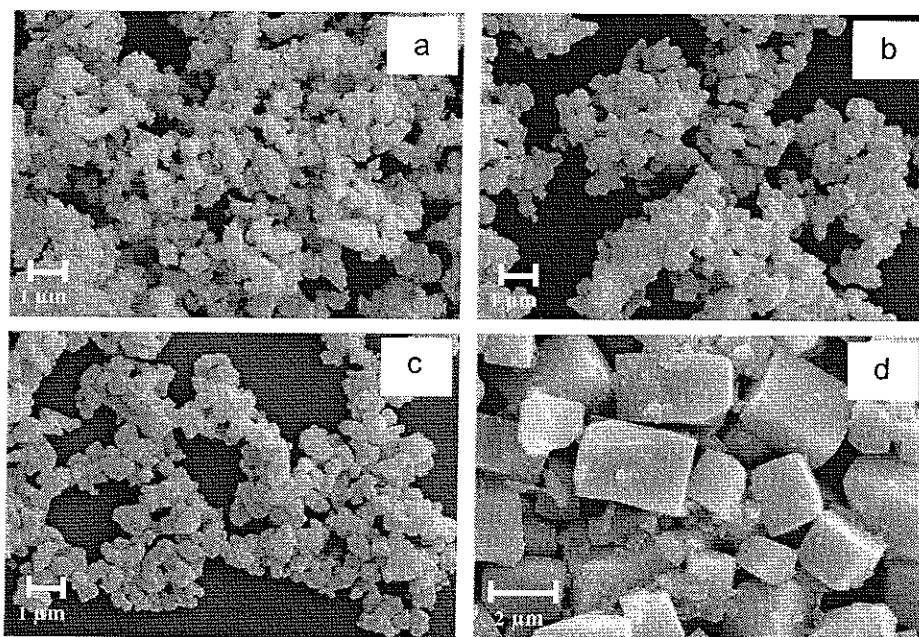


Fig. 6. SEM photomicrographs of KNN calcined powders with excess Na_2O and K_2O , (a) 0 wt%; (b) 1 wt%; (c) 2 wt% and (d) 4 wt%.

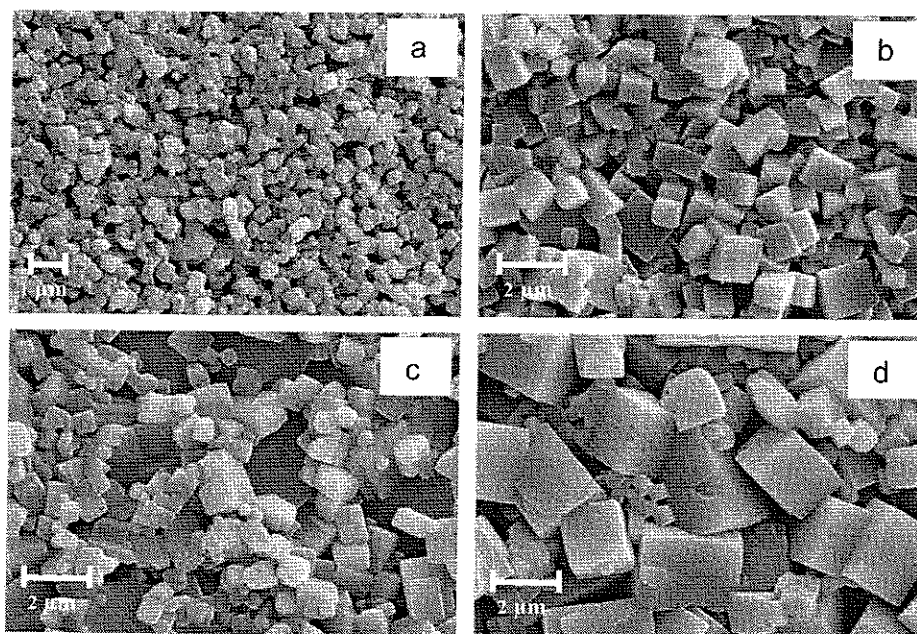


Fig. 7. SEM photomicrographs of KNN sintered ceramics with excess Na_2O and K_2O , (a) 0 wt%; (b) 1 wt%; (c) 2 wt% and (d) 4 wt%.

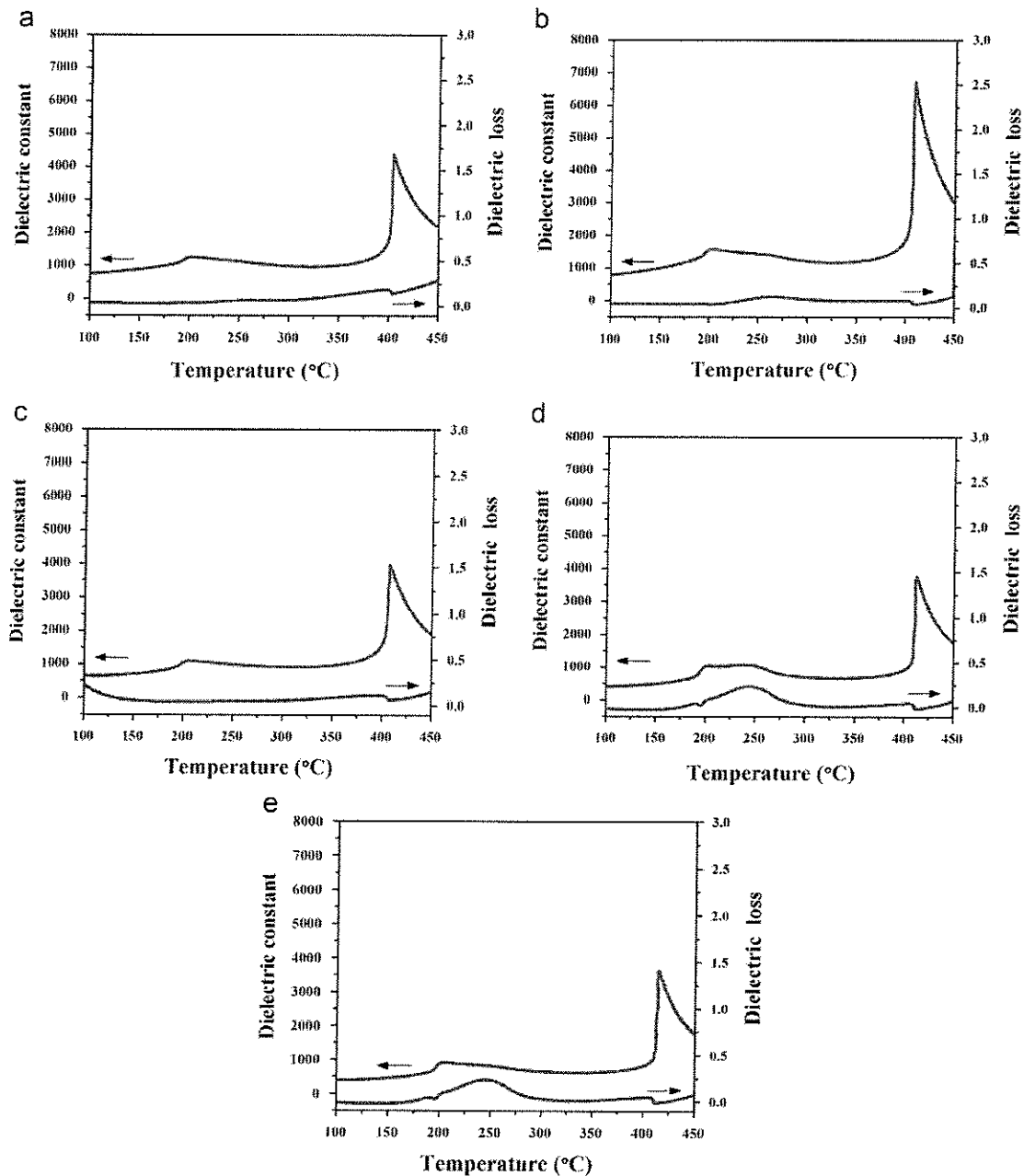


Fig. 8. Dielectric properties of KNN sintered ceramics with amounts of excess K_2O and Na_2O (a) 0 wt%; (b) 1 wt%; (c) 2 wt% (d) 3 wt% and (e) 4 wt%.

The density and shrinkage of KNN ceramics with various amounts of Na_2O and K_2O excess are shown in Fig. 5. The density increased with increase in excess Na_2O and K_2O , reaches a maximum value at 1 wt% excess Na_2O and K_2O (98.0% of theoretical density, as listed in Table 1), and slightly decreases above 1 wt% excess Na_2O and K_2O . The density result with excess Na_2O and K_2O at 1 wt% is higher than the density result without excess Na_2O and K_2O which were reported by previous work [10,19].

The SEM photomicrographs of calcined powders of KNN with various excess Na_2O and K_2O are shown in Fig. 6. The sample without excess Na_2O and K_2O contents showed aggregates with irregular shape. At higher amount of excess Na_2O and K_2O

contents, the powder becomes more quadrate in shape. The average particle size increased from 0.28 μm to 0.44 μm with increase of excess Na_2O and K_2O contents, as listed in Table 1. Fig. 7 reveals the SEM photomicrograph of KNN sintered pellets. Generally, an arrangement of particles will form during liquid phase sintering process and take place rapidly [17,22]. The process must have sufficient liquid phase concentration to allow an easy rearrangement of the grains. Consequently, the amount of Na_2O and K_2O should be proportionally related with densification. In this system, the microstructure presented small grains and high porosity in the samples without excess Na_2O and K_2O contents. It means that the ceramic evolution had insufficient liquid phase of Na_2O and K_2O in the sintering process. At excess 1 wt% of Na_2O

and K₂O, the grain size gradually increased, porous microstructure decreased and quadrate structure morphology with relative uniform grain size were observed. At higher amount of Na₂O and K₂O contents (>1 wt%), the microstructure presented high porosity with wide grain size distribution. Well morphology was observed in 1 wt% of excess Na₂O and K₂O sample due to adequate amount of Na₂O and K₂O liquid phase which could be formed between the grain boundary. In the case of >1 wt% of excess Na₂O and K₂O, the immoderate amount of Na₂O and K₂O liquid phase can be produced initial rapid densification but a lower final densification as a result of void formation of Na₂O and K₂O. The microstructure in SEM result corresponding to the results of density, as can be seen in Table 1. The average grain size increased from 0.81 to 3.72 μm with increasing of excess Na₂O and K₂O, as listed in Table 1.

The dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$) of the KNN ceramics with various excess Na₂O and K₂O contents are shown in Fig. 8. The dielectric constant showed two peaks in all samples. Both of T_{O-T} and T_C shifted to high temperature region with increase of excess Na₂O and K₂O contents, as listed in Table 1. The dielectric properties were increased by excess Na₂O and K₂O of 1 wt%, with the highest ϵ_r and lowest $\tan\delta$ value of ~ 6723 and 0.05. At above 1 wt% of excess Na₂O and K₂O contents, the ϵ_r decreased and $\tan\delta$ increased and are listed in Table 1. The optimum amount of excess Na₂O and K₂O results in better dielectric properties as compared with previous work [10,14,19].

4. Conclusions

The firing temperature and excess Na₂O and K₂O contents have a strong influence on the phase formation, microstructure and dielectric properties of KNN ceramics. The optimal calcination and sintering condition were found at 900 °C for 4 h and 1100 °C for 2 h, respectively. The pure perovskite phase with orthorhombic symmetry was observed in all samples with excess Na₂O and K₂O. The average particle size and grain size increase with an increase of excess Na₂O and K₂O. Appropriate amount of the liquid phase can decrease porosity and increased densification in KNN ceramic system. The density and dielectric properties of KNN ceramics prepared by solid-state reaction method can be improved by addition of 1 wt% Na₂O and K₂O. The results will help to guide the design and development of new (K,Na)NbO₃-based lead-free piezoceramics.

Conflict of interest statement

The authors declare no competing financial interest.

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