



## Studying the effects of nano sintering additives on microstructure and electrical properties of potassium-sodium niobate piezoceramics

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### ABSTRACT

In this paper, lead-free (K<sub>0.48</sub>Na<sub>0.52</sub>)NbO<sub>3</sub> (KNN(48-52)) piezoelectric ceramics were made by the conventional solid-state sintering process. In order to decrease the sintering temperature and modify the dielectric, piezoelectric and ferroelectric properties, sintering additives of nano ZnO (n-ZnO), nano CuO (n-CuO) and nano SnO<sub>2</sub> (n-SnO<sub>2</sub>) were used. Phase structure and microstructure were analyzed by using X-ray diffractometry and scanning electron microscopy techniques, and the EDX analysis was used to study the ZnO distribution at grains and grain boundaries. The highest piezoelectric constant of  $d_{33} = 150$  pC/N was obtained for KNN(48-52) with 0.6 mol% n-ZnO at a sintering temperature of 1070°C, which is two times larger than the pure KNN(48-52) at the sintering temperature of 1112 °C. Additionally, the KNN(48-52) ceramics co-doped with 0.8 mol% n-ZnO, 0.5 mol% n-CuO and 0.8 mol% n-SnO<sub>2</sub>, showed dielectric and piezoelectric properties of  $d_{33} = 97$  pC/N,  $\tan\delta = 0.006$  and  $\epsilon_r = 172$  at the sintering temperature of 960 °C, which were much better than corresponding values for pure KNN at 1110 °C.

## 1. INTRODUCTION

In the past, innovations of actuators, sensors, and ultrasonic transducers have been the driving force behind new developments in piezoelectric ceramics. Lead-based compounds such as Pb (Zr, Ti) O<sub>3</sub> (PZT) have been the most widely used piezoelectric materials. However, due to the toxicity of lead, PZT is known as a hazardous substance for human health and environment. Accordingly, the piezoelectric society that has moved towards the green developments and environmental regulations are highly considered in the recent studies [1,2]. Among different lead-free materials, a solid solution of ferroelectric KNbO<sub>3</sub> and anti-ferroelectric NaNbO<sub>3</sub>, ((K<sub>0.5</sub>Na<sub>0.5</sub>) NbO<sub>3</sub>: KNN) has attracted much attention, due to good piezoelectric properties and a high Curie temperature [3-6]. Nevertheless, dense KNN ceramics are difficult to obtain; since their phase stability is limited to 1140 °C and have a narrow sintering temperature range (1100-1120 °C) [7, 8]. In order to surmount the densification problems, different advanced

processes such as spark plasma sintering or hot pressing were developed to promote the sintering, but they were not suitable for the massive production of piezoceramics with different shapes [9, 10]. Based on some recent studies, the piezoelectric properties of KNN-based ceramics have been promoted by the formation of new phase boundaries [11, 12] and the reduction of polarization anisotropy resulted in giant piezoelectricity in KNN-based ceramics [13]. Another strategy is the formation of new solid solutions by adding other perovskite compounds, or adding novel sintering aids such as ZnO [9, 14-16], CuO [17-23], and SnO<sub>2</sub> [24] to KNN ceramics [6-10]. Zuo et al. investigated the effects of adding some oxides such as Sc<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, CeO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, CdO, SnO<sub>2</sub> and ZnO [14, 25]. They concluded that SnO<sub>2</sub> enhanced the densification significantly at higher temperatures, and ZnO increased the densification and electrical properties. Park et al. [18] and Seo et al. [26] used CuO to decrease the sintering temperature and prevent the evaporation of alkali oxides during sintering. CuO not only decreased the sintering temperature to

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960°C [26], due to the hardening effect, but also decreased the piezoelectric coefficient of KNN [18]. In another study, Li et al. [27] investigated the dielectric and piezoelectric properties of ZnO and SnO<sub>2</sub> co-doped KNN ceramics and attributed the better piezoelectric properties to the presence of SnZnO<sub>3</sub> ferroelectric phase. Ahn et al. [28] studied the effect of ZnO and CuO on sintering and piezoelectric of PZT (APC 841) ceramics. Their results revealed that co-doping with CuO and ZnO decreased the sintering temperature, and excellent dielectric and piezoelectric properties were reported. None of these publications used nano oxides as sintering aids. In this paper, the effects of addition of nano sinter aids on the sintering temperature, microstructure and electrical properties of KNN (48-52) ceramics were studied. The reason for selection of nano sintering additives were explained in our previous paper [29], and the effects of n-ZnO on electrical properties of KNN (50-50) ceramics were investigated. In the recent study, the stoichiometric formula of KNN is slightly different. According to the interesting phase diagram of (K<sub>x</sub>Na<sub>1-x</sub>)NbO<sub>3</sub>, the best dielectric and piezoelectric properties were seen in the x values between 0.48 and 0.50 denote and the compositions with the Na/K ratios near the morphotropic phase boundary (MPB) [30]; However, once the x value is higher than 0.5 the materials enters the orthorhombic phase completely, which reduces the piezoelectric properties. Accordingly, better piezoelectric behavior was reported for KNN (48-52) [31-33]. As a result, to avoid getting far from the MPB region, this composition was studied in this work. Firstly, n-ZnO was added to KNN (48-52) to define the optimum amount of n-ZnO. Then, the concurrent addition of n-ZnO and n-CuO was investigated. Finally, co-doping with n-ZnO, n-CuO and n-SnO<sub>2</sub> was studied.

## 2. EXPERIMENTAL

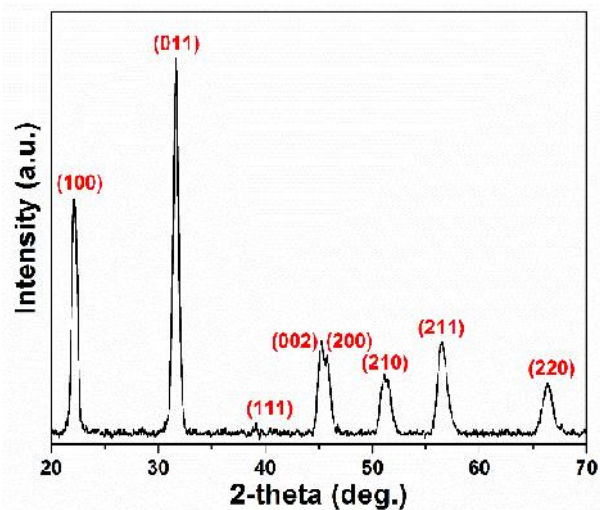
Pure KNN ceramics of (K<sub>0.48</sub>Na<sub>0.52</sub>)NbO<sub>3</sub> were prepared by conventional sintering process. The raw materials were Nb<sub>2</sub>O<sub>5</sub> (99.9%, Merck), nano ZnO (99.5%, ≤ 50nm, Noavaran Catalyst, Iran), nano CuO (99.9%, 40-80 nm, Advanced materials), nano SnO<sub>2</sub> (99.9%, 80 nm, Advanced materials, USA), K<sub>2</sub>CO<sub>3</sub> (99.9%, Merck, Germany) and Na<sub>2</sub>CO<sub>3</sub> (99.9%, Merck, Germany). The starting materials of KNN were weighted according to the stoichiometry, and then milled with zirconia balls in isopropyl alcohol (IPA) medium for 6 hours. After evaporation of IPA at 80 °C, the first calcination was done at 850°C for 4 hours. The powders were attrition milled with zirconia balls for 30 minutes, and then calcined once again in the manner of the first calcinations. The calcined powders were mixed with dispersed nano sintering aids (n-ZnO, n-CuO and n-SnO<sub>2</sub>) and PVB solution by attrition milling for 1 hour.

In the first stage, up to 2 mol% n-ZnO was added to KNN (0.4, 0.6, 0.8, 1, and 2 mol%), in the second part, n-ZnO

and n-CuO were mixed with KNN based on the formula KNN-xZnO-yCuO (x:y: 0.6: 0.5, 0.4: 0.4, 0.6: 0.5 mol%) and in the last part KNN-xZnO-yCuO-zSnO<sub>2</sub> composition with optimum amounts of n-ZnO (0.8 mol%) and n-CuO (0.5 mol%) (based on this study) and 0.8 mol% n-SnO<sub>2</sub> based on literature [27] were prepared. The powders were pressed into the disks of 10 mm in diameter and 1.5-2 mm in thickness. After burning off PVA at 600 °C, sintering process was then carried out at the temperature range of 930- 1110 °C. The density was measured with Archimedes method. The microstructure was investigated by a ZEISS S-360 scanning electron microscopy (SEM) and the crystal structure was identified by using X-ray diffraction (XRD) with Cu K $\alpha$  radiation utilizing a Bruker AXS D8 ADVANCE diffractometer. To measure the electrical properties, all the samples were carefully polished to reach parallel surfaces and then electroded using silver paste. In order to measure the piezoelectric properties the samples were polled by applying dc fields of 3kV/mm for 30 min in a silicon oil bath maintained at 100 °C. Using a LCR meter, capacitance and tan  $\delta$  were measured at 1 kHz before and after poling. The piezoelectric constant d<sub>33</sub> was measured by using a Berlincourt-type quasi-static meter at 100 Hz and the ferroelectric hysteresis loops were obtained by using a device based on Sawyer-Tower circuit.

## 3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD pattern of (K<sub>0.48</sub>Na<sub>0.52</sub>)NbO<sub>3</sub> powder double calcined at 850 °C for 4 hours. The pattern suggests the existence of pure perovskite phase of KNN with no signs of any secondary phases at this temperature.



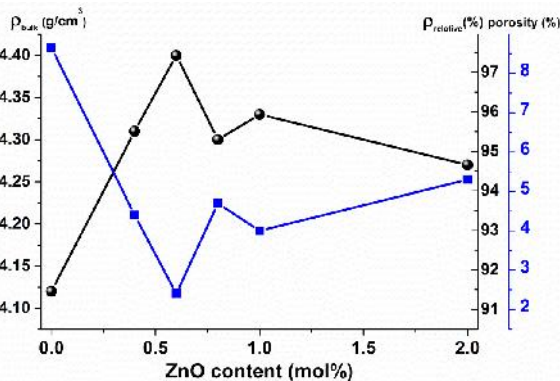
**Figure 1.** XRD pattern of (K<sub>0.48</sub>Na<sub>0.52</sub>)NbO<sub>3</sub> powder after double calcination at 850 °C for 4 hours

### 3.1. Effect of n-ZnO

Fig. 2 shows the variations in bulk density, relative density and porosity content of KNN (48-52) with n-ZnO content at a sintering temperature of 1070 °C. According to this graph, adding n-ZnO increased the density and KNN ceramic with 0.6 mol% n-ZnO reached the maximum density of 4.4 g/cm<sup>3</sup> with the minimum content of porosities (97% of the theoretical density, 4.51 g/cm<sup>3</sup> [34]).

The SEM micrograph of a thermally etched surface of KNN ceramics is demonstrated in Fig. 3. As it can be seen pure KNN has a porous structure at this temperature and nano ZnO addition has considerably changed the microstructure. The increase in the density of ZnO added KNN samples are related to the reduced number of small porosities in the microstructure of pure KNN. This phenomenon could be attributed to the better diffusion, due to the formation of ionic defects after ZnO incorporation into the KNN lattice. As can be seen in Fig.2, when ZnO content is more than 0.6 mol%, larger grains are developed and the density decreased. Furthermore, ZnO is considered as a sintering additive and should be used in small contents to improve the sintering behavior. Otherwise, the formation of some secondary phases with lower theoretical densities can reduce the density of KNN [35].

The FE-SEM micrograph of the fracture surface of KNN ceramics with 0.6 mol% n-ZnO is demonstrated in Fig. 4. As it is seen, KNN sample with n-ZnO additive has a dense microstructure with cuboid grains. In order to study the distribution of ZnO at grains and grain boundaries, the EDX analysis was used. The results of EDX analysis of grains and grain boundaries is shown in Table 1.



**Figure 2.** Variations in the density of KNN (48-52) samples with n-ZnO content at a sintering temperature of 1070 °C

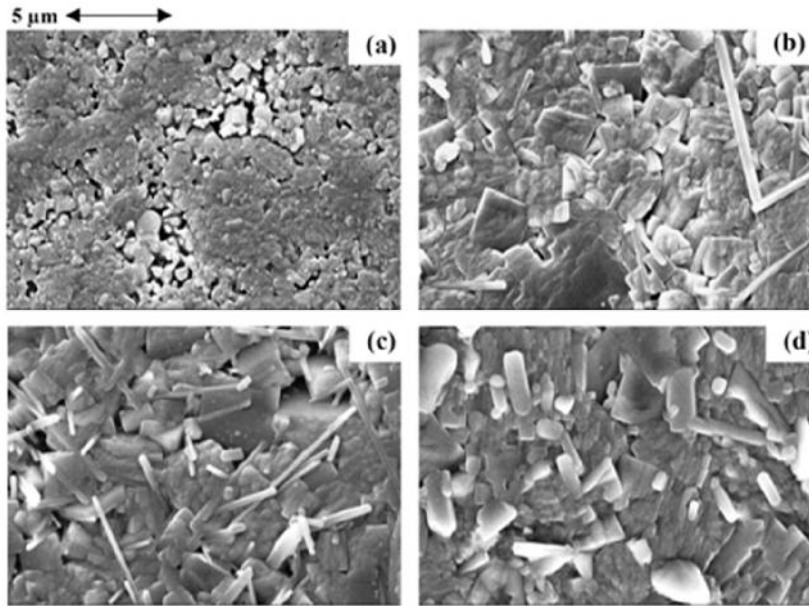
For pure KNN ceramics sintered at 1110 °C, the K/Na and (K+Na)/Nb ratios are less than the nominal composition. This result confirms the evaporation of alkaline oxides at this sintering temperature.

By adding n-ZnO and decreasing the sintering temperature, (K+Na)/Nb ratio is approximately equal to the nominal composition. On the other hand, when n-ZnO added KNN ceramics, the amount of ZnO at grains and grain boundaries differ completely and ZnO is mostly located at grain boundaries, which can be facilitated the grain boundary motion and can be regarded as the reason for larger grains after n-ZnO addition. In addition, EDX analysis revealed that at grain boundaries of n-ZnO added KNN, the sodium content is decreased considerably and these regions probably are covered by some potassium and niobium-rich phases. Ryu et al. [36] showed that such potassium and niobium-rich compounds (K<sub>5.75</sub>Nb<sub>10.8</sub>O<sub>30</sub>) could form liquid phases, which result in exaggerative grain growth and lower electrical properties. Hence, it is suggested that n-ZnO forms a liquid phase at grain boundaries, which promotes the densification and grain growth [9, 37].

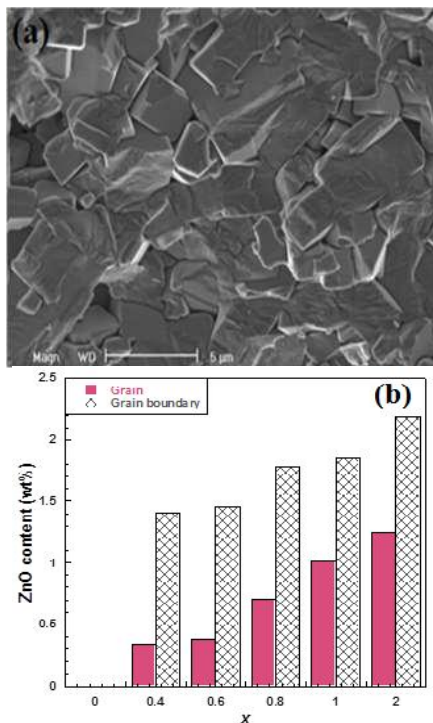
Variations of d<sub>33</sub>, ε<sub>r</sub>, and tanδ with sintering temperature is shown in Fig. 5, a-c. Adding n-ZnO, increased the piezoelectric coefficient and dielectric constant while decreased the dielectric loss. According to Fig. 5-a, piezoelectric coefficient, d<sub>33</sub> reached the maximum value of 150pC/N at x=0.6. This specimen showed the dielectric properties of ε<sub>r</sub>= 402 and tanδ= 0.02 (Fig. 4-b). According to Hayati et al. [38], the permittivity is mainly dependent on the density and a lesser degree on the grain size of the KNN samples. The increase in dielectric constant of n-ZnO added KNN ceramics can be attributed to the higher density and the larger grains of these ceramics [29]. The 90° domains are responsible for a higher dielectric constant in larger grains of KNN ceramics with n-ZnO additive [39]. HaO et al. [40] declares that the variations in grain size (t) influences the domain size (t) with the formula expressed as  $d = \left[ \left( \frac{\sigma}{\epsilon^* P_s} \right) t \right]^{1/2}$ , in which σ, ε\* and P<sub>s</sub> denote the energy density of the domain wall, spontaneous polarization and dielectric constant. Therefore, the larger grains, which facilitate the switching of domains walls, are the reason for the higher piezoelectric constant of n-ZnO modified KNN ceramics. Moreover, the lower dielectric loss of these samples is due to the easier domain wall motion in larger grains.

**TABLE 1.** data of EDX analysis of grains and grain boundaries of (K<sub>0.48</sub>Na<sub>0.52</sub>)NbO<sub>3</sub> ceramics with x mol% n-ZnO

	x (mol% of n-ZnO)	Sintering Temperature (°C)	Zn (wt %)	K/Na	(K+Na)/Nb
Nominal Composition	0	-	0	1.57	0.33
	0	1110	0	1.5	0.28
	0.4	1070	0.34	1.4	0.33
	0.6		0.38	1	0.34
	0.8		0.71	1.2	0.32
	1		1.01	1.2	0.32
	2		1.25	1.2	0.32
Grain Boundary	0	1110	0	2.4	0.25
	0.4	1070	1.41	1.4	0.31
	0.6		1.46	1.2	0.33
	0.8		1.78	1.6	0.3
	1		1.85	1.13	0.32
	2		2.19	1.13	0.33



**Figure 3.** SEM micrographs of polished and thermally etched surface of  $(K_{0.48}Na_{0.52})NbO_3+x$  mol% n-ZnO sintered at 1070°C for 2 hours, (a)  $x=0$ , (b)  $x=0.6$ , (c)  $x=1$ , and (d)  $x=2$ .



**Figure 4.** (a) SEM micrograph of the fracture surface of KNN+0.6 mol% n-ZnO, (b) the plot showing n-ZnO content at grains and grain boundaries of KNN+x mol% n-ZnO samples

### 3.2. Effect of n-ZnO and n-CuO

Fig. 6 shows the plots of variations in dielectric constant, dielectric loss and piezoelectric constant with sintering temperature for KNN-x mol% n-ZnO-y mol% n-CuO ceramics. According to Fig. 6-a, KNN-0.3 n-ZnO-0.5 n-CuO reached the highest value of room temperature dielectric constant ( $\epsilon_r=335$ ).

However, this composition had the highest amount of dielectric loss. The plots of piezoelectric constant in Fig. 6-c show an upward trend in  $x=0.6$ ,  $y=0.3$  and  $x=0.8$ ,  $y=0.5$  compositions with the highest value of 120 pC/N for KNN-0.8 n-ZnO-0.5 n-CuO sample sintered at 1040°C. Additionally, KNN samples with 0.4 mol% n-ZnO and 0.4 mol% n-CuO reached the maximum value of 100 pC/N at 1000°C and dropped down at higher sintering temperatures. Due to higher piezoelectric constants, KNN-0.8n-ZnO-0.5n-CuO composition was selected for further studies.

### 3.3. Effect of n-ZnO, n-CuO, and n-SnO<sub>2</sub>

Fig. 7 shows the SEM micrographs of KNN ceramics with sintering aids of n-ZnO, n-CuO, and n-SnO<sub>2</sub> at a sintering temperature of 960 °C.

According to Fig. 7a, for n-ZnO added KNN ceramic some cuboid grains have grown, but grain growth did not occur completely and the ceramic did not densify fully at this temperature. Fig. 7b demonstrates the microstructure of n-CuO-added KNN ceramic. The presence of irregular

faceted grains in this sample can be related to the possible liquid phase sintering of this sample.

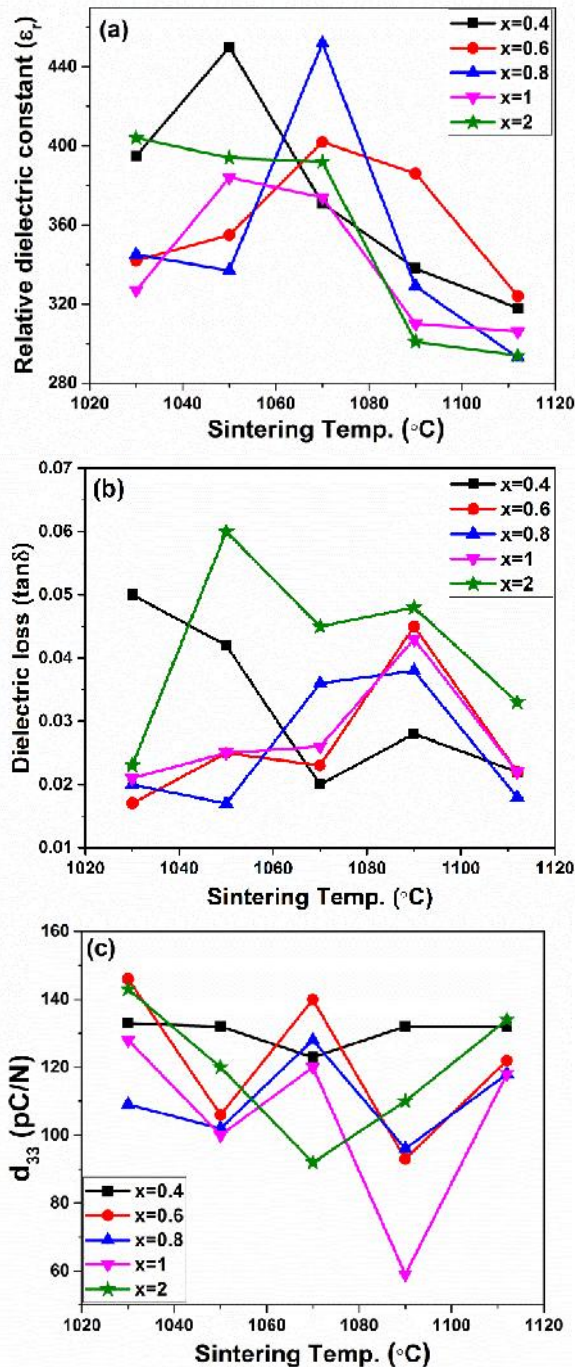


Figure 5. Variations of (a) dielectric constant, (b) dielectric loss and (c) piezoelectric coefficient with sintering temperature for n-ZnO added KNN (48-52) ceramics

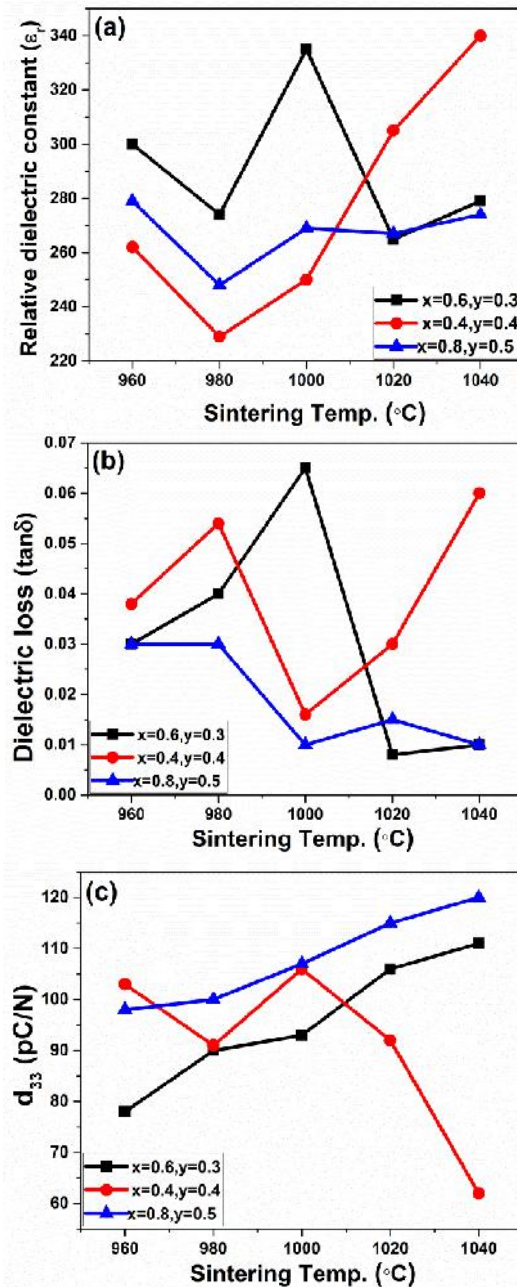
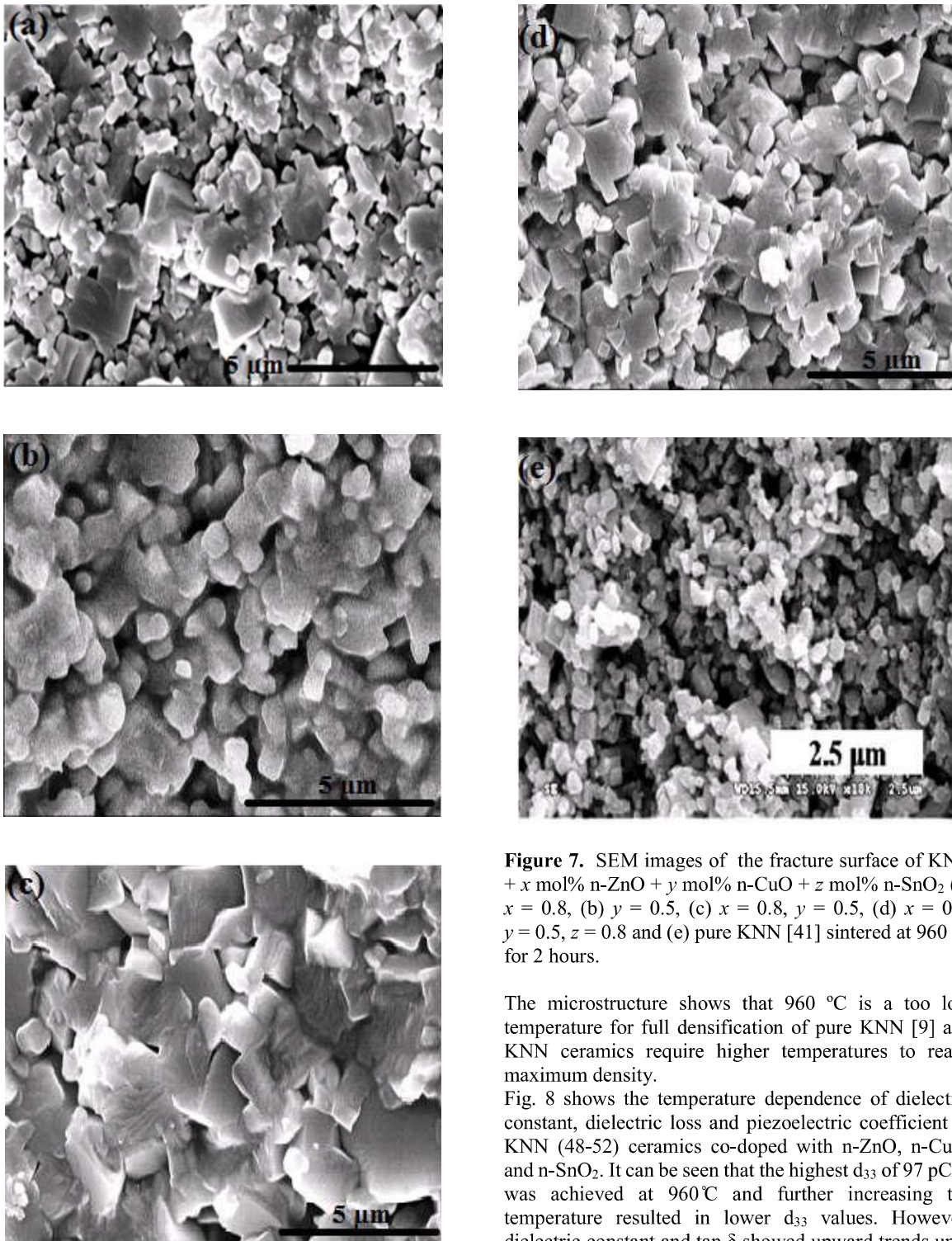


Figure 6. the plots of (a) variations in dielectric constant, (b) dielectric loss and (c) piezoelectric coefficient with temperature for KNN (48-52)-x mol% n-ZnO-y mol% n-CuO ceramics

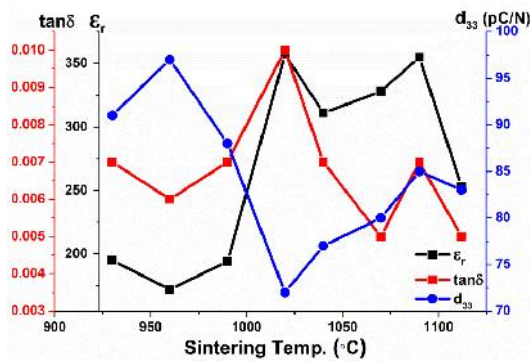
According to Fig. 7c, co-doping with n-ZnO and n-CuO resulted in larger grains and in n-ZnO, n-CuO, and n-SnO<sub>2</sub> co-doped sample of Fig. 7d, SnO<sub>2</sub> prevented the densification and grain growth at this temperature. SEM image of pure KNN is demonstrated in Fig. 7e.



**Figure 7.** SEM images of the fracture surface of KNN +  $x$  mol% n-ZnO +  $y$  mol% n-CuO +  $z$  mol% n-SnO<sub>2</sub> (a)  $x = 0.8$ , (b)  $y = 0.5$ , (c)  $x = 0.8$ ,  $y = 0.5$ , (d)  $x = 0.8$ ,  $y = 0.5$ ,  $z = 0.8$  and (e) pure KNN [41] sintered at 960 °C for 2 hours.

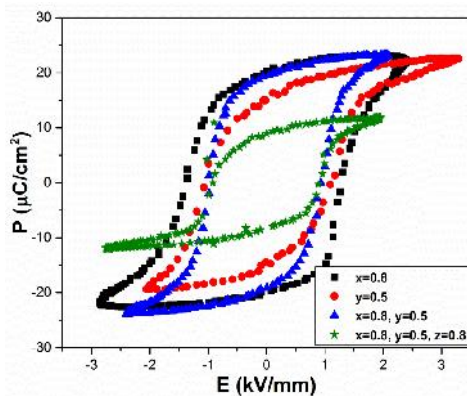
The microstructure shows that 960 °C is a too low temperature for full densification of pure KNN [9] and KNN ceramics require higher temperatures to reach maximum density.

Fig. 8 shows the temperature dependence of dielectric constant, dielectric loss and piezoelectric coefficient of KNN (48-52) ceramics co-doped with n-ZnO, n-CuO, and n-SnO<sub>2</sub>. It can be seen that the highest  $d_{33}$  of 97 pC/N was achieved at 960°C and further increasing the temperature resulted in lower  $d_{33}$  values. However, dielectric constant and  $\tan \delta$  showed upward trends until 1040 °C and afterward they decreased.



**Figure 8.** the plots of dielectric constant, dielectric loss and piezoelectric coefficient KNN (48-52) ceramics with 0.8 mol% n-ZnO, 0.5 mol% n-CuO and 0.8 mol% n-SnO<sub>2</sub> additives

Fig. 9 shows the ferroelectric hysteresis loops of n-ZnO, n-CuO, and n-SnO<sub>2</sub> added KNN ceramics at a sintering temperature of 960 °C and the summary of ferroelectric properties is demonstrated in Table 2.



**Figure 9.** Ferroelectric hysteresis loops of KNN (48-52) +  $x$  mol% n-ZnO +  $y$  mol% n-CuO +  $z$  mol% n-SnO<sub>2</sub> sintered at 960 °C for 2 h

Adding 0.5 mol % n-CuO decreased the remnant polarization of KNN to 7.879  $\mu\text{C}/\text{cm}^2$ , but with the addition of 0.8 mol% n-ZnO,  $P_r$  reached the amount of 19.309  $\mu\text{C}/\text{cm}^2$ . The increased  $P_r$  of n-ZnO and n-ZnO-n-CuO added KNN ceramics is attributed to their larger grains. Larger grains facilitate the domain wall switching and smaller coercive fields are expected. Additionally, based on the Avrami model proposed by Orihara [42], larger grains have higher contribution in polarization rotation which is one of the mechanisms of increasing the piezoelectric properties. As it is seen in table 2, co-doping with n-ZnO, n-CuO, and n-SnO<sub>2</sub>, increased the coercive field and lowered the remanent polarization.

Considering the ionic radii and the valance of Zn<sup>2+</sup> (0.74 nm), Cu<sup>2+</sup> (0.73 nm) and Sn<sup>4+</sup> (0.69 nm), they would enter the B-sites of Nb<sup>5+</sup> (0.64 nm) in KNN structure inducing a hard piezoelectric behavior, therefore, P-E loops with smaller  $P_r$  and larger  $E_c$  are expected.

**TABLE 2.** Ferroelectric properties of KNN (48-52) +  $x$  mol% n-ZnO +  $y$  mol% n-CuO +  $z$  mol% n-SnO<sub>2</sub> sintered at 960 °C for 2 h, obtained from hysteresis loops

$x/y/z$	$E_c$ (kV/mm)	$P_r$ ( $\mu\text{C}/\text{cm}^2$ )	Ref
0/0/0*	12	20	[43]
0/0/0	10	9	[18]
0.8/0/0	8.989	19.309	This work
0/0.5/0	8.509	17.879	This work
0.8/0.5/0	9.317	19.103	This work
0.8/0.5/0.8	8.909	8.923	This work

\*This sample was sintered at 1115 °C [43]

As a result, at 960 °C, the P-E loops of KNN ceramics with n-CuO and n-ZnO additives was similar to pure KNN at its optimum sintering temperature (1115°C [43] ), hence, these nano oxides lowered the sintering temperature of KNN (48-52) without deteriorating the ferroelectric properties. However, SnO<sub>2</sub> addition decreased the remanent polarization of n-ZnO and n-CuO added KNN samples, which is in agreement with the literature [27].

Table 3 compares the electrical properties of KNN ceramics sintered with additives of n-ZnO, n-CuO, and n-SnO<sub>2</sub> at a sintering temperature of 960 °C. The density and porosity values are also summarized in this table. Adding 0.5 mol% n-CuO led to the highest  $d_{33}$  of 115 pC/N, and maximum  $\epsilon_r$  and minimum  $\tan\delta$  are belonged to 0.8 mol% n-ZnO added KNN and KNN ceramic with 0.8 mol% n-ZnO, 0.5 mol% n-CuO, and 0.8 mol% n-SnO<sub>2</sub>, respectively. Although Co-doping with n-ZnO, n-CuO, and n-SnO<sub>2</sub> at 960 °C did not improve the  $d_{33}$  considerably, lowered the dielectric loss to 0.006.

At such a low sintering temperature (960 °C), p-KNN had a low density and the poling process was ineffective, but the piezoelectric coefficient of a co-doped sample was higher than pure KNN sintered at 1110 °C, which could be attributed to the homogeneous microstructure and the optimum grain size of this sample [28]. As it can be seen, the number of porosities are decreased after co-doping, and the KNN sample with n-ZnO, n-CuO, and n-SnO<sub>2</sub> had the highest value of density, which is in agreement with the homogenous microstructure in SEM image of Fig 6-d.

#### 4. CONCLUSION

In this study, nano sintering additives were added to KNN (48-52) piezoceramics to decrease the sintering temperature below 1000 °C, to avoid the evaporation of alkali oxides of KNN, and to modify the electrical properties. Among all sintered ceramics, KNN + 0.6 mol % n-ZnO has shown the highest  $d_{33}$  of 150 pC/N,  $\epsilon_r = 402$  and  $\tan\delta = 0.02$  at a sintering temperature of 1070°C. EDX analysis of this sample confirmed the segregation of n-ZnO at grain boundaries, which resulted in larger grains and better piezoelectric properties. Beside, concurrent addition of 0.8 mol% n-ZnO and 0.5 mol% n-CuO have improved the electrical properties of pure KNN and  $d_{33}$  values of 98-120 pC/N were obtained in the sintering temperature of 960-1040 °C. Finally, the co-doping with n-ZnO, n-CuO and n-SnO<sub>2</sub> improved the electrical properties of pure KNN at a sintering temperature of 960 °C.

**TABLE 3.** Summary of electrical properties of n-ZnO, n-CuO, and n-SnO<sub>2</sub> added KNN ceramics at a sintering temperature of 960 °C

Composition			Sintering Temperature (°C)	$d_{33}$ (pC/N)	$\tan\delta$	$\epsilon_r$	$\rho$ (g/cm <sup>3</sup> )	Porosity content (%)
% n-ZnO	% n-CuO	% n-SnO <sub>2</sub>						
0	0	0	1110	88	0.045	384	4.09	9.31
0.8	0	0	096	90	0.055	342	4.03	10.6
0	0.5	0		114	0.05	174	4.21	6.65
0.8	0.5	0		98	0.03	279	4.19	7.09
0.8	0.5	0.8		97	0.006	172	4.23	6.2
0.8	0.5	0.8						

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