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Effect of Nano and Micron WO_3 on Microstructure and Electrical Properties of Lead Free Potassium Sodium Niobate Piezoceramics

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A B S T R A C T

Lead free potassium sodium niobate (KNN) piezoceramics were synthesized via conventional solid state sintering route. Tungsten oxide (WO_3) with nano and micron particles was used as a donor dopant. Dielectric and piezoelectric properties of samples sintered in the temperature range of 1110°-1145°C were measured by precision LCR-meter and APC d_{33}-meter devices. SEM results revealed that micron WO_3 inhibited the grain growth of KNN ceramics and led to a finer microstructure. KNN with micron WO_3 had much finer microstructure and the sintering process terminated at higher temperature compared to pure KNN and KNN with nano WO_3. Nano and micron sized WO_3 affected the densification and electrical properties of KNN considerably. Additionally, KNN with nano WO_3 reached the maximum density at lower temperature compared to its counterpart. Finally, at 1125ºC KNN with 0.3 mol% nano sized WO_3 showed d_{33}, ε_r, tanδ, and Q_m of 75 pC/N, 345, 2%, and 50, respectively. For KNN sample with 0.3 mol% micron WO_3 at 1135ºC these values were 81 pC/N, 773, 3.3%, and 30, respectively.

1. INTRODUCTION

PZT based piezoelectric materials due to their outstanding properties are widely used in sensors and actuator devices. However, the production of these materials leads to environmental health hazards because of the toxicity of lead oxide and volatilization of Pb during calcination, as the main component [1]. Recent legislations all over the world induced a new surge in developing lead free and safe piezoelectric materials [2]. Three main classes of lead free piezoelectric ceramics are perovskite, tungsten bronze, and bismuth layered structure materials. Among these groups, alkali niobates of perovskite family are the best candidate to replace lead based piezoceramics [3].Potassium sodium niobate ($K_{1-x}Na_x$) NbO_3 (KNN) with compositions near morphotropic phase boundary (x=0.5 or 0.48) shows the best dielectric and piezoelectric properties [3]. However, it is difficult to obtain high density KNN ceramics by conventional sintering route. Additionally, KNN family has a narrow sintering temperature range of 1100-1120ºC. Even a small variation in stoichiometry results in the formation of secondary and unwanted phases which have considerable effects on microstructure and destructive effects on piezoelectric properties [4]. In recent years, new processing techniques such as hot press and spark plasma sintering have been used to improve densification of KNN, but these techniques are relatively expensive [5,6]. Another solution is modifying KNN ceramics and substituting a part of A or B sites of ABO_3 structure with other ions. Recently, many researchers reported solid solutions of KNN with different compounds, such as: $SrTiO_3$[7,8], $LiTaO_3$[9], $CaTiO_3$ [10], $LiNbO_3$[11-13], $LiSbO_3$[14,15], ($Bi_{0.5}Na_{0.5}$) TiO_3[16], $BaTiO_3$[17], etc. Among all these studies, Saito et al. replaced A and B sites of KNN structure with Li, Ta, and Sb and reported a new composition (LF4: ($K_{0.44}$ $Na_{0.52}$ $Li_{0.4}$) ($Nb_{0.86}$ $Ta_{0.10}$ $Sb_{0.04}$)) which is said to have piezoelectric properties comparable to PZT [18]. In some other research works, sintering aids such as ZnO [19] or CuO [20] was added to KNN and in these cases along with decreasing the sintering temperature the electrical and piezoelectric properties were modified.

In the present work, the effect of nano and micron WO_3 additives on sintering behavior, densification, microstructure, and electrical properties of KNN ceramics was investigated.

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2. MATERIALS AND METHOD

(K,Na) NbO_3 and (K,Na)($Nb_{1-x}W_x$)O_3(x=0.003) compositions were prepared via conventional solid state sintering route. Raw materials were Na_2CO_3 (99.9%), K_2CO_3 (99.5%), Nb_2O_5 (99.5%), nano WO_3 (99.5%, <100nm) and micron WO_3 (99%, <20μm). The surface area and crystal structure of nano and micron WO_3 powders were analyzed by BET (Belsorp mini ц, Bell, Japan) and X-ray diffraxtion (Siemens, D-500 system), respectively. The stoichiometric powders were mixed in a ball mill containing isopropyl alcohol and zirconia balls. The slurries were dried at 100ºC and then calcined at 950ºC for 4hrs to synthesize ($K_{0.5}$, $Na_{0.5}$)NbO_3, ($K_{0.5}$,$Na_{0.5}$) ($Nb_{0.997}W_{0.003}$(nano))O_3, and ($K_{0.5}$,$Na_{0.5}$) ($Nb_{0.997}W_{0.003}$(micron))O_3 powders represented by (KNN), ($KNNW_{3n}$) and ($KNNW_{3m}$), respectively. The mentioned calcined powders were then attrition milled for 2hrs. The resultant powders obtained from the above processes were granulated and pressed into disks of 10 mm diameter. The specimens were sintered at different temperatures in the temperature range of 1050°-1145ºC for 2hrs. The density of samples was measured in water by Archimedes' principle. They were polished and then electrodized by applying silver paste on both sides. The crystal structure of synthesized powders and sintered samples were characterized by XRD analysis. In order to calculate the lattice parameters, rietveld refinement was performed using MAUD software by using the CIF file of $KNbO_3$ [21]. The microstructure was investigated by scanning electron microscope (SEM) and the grain size was determined by averaging over the total number of grains. The electrical properties were measured using a precision LCR-meter (8110G, Taiwan), and the piezoelectric constants were measured by a Pennbaker d_{33} meter (model 8000, APC Inc., USA).

3. RESULT AND DISCUSSION

The surface area of micron and nano WO_3 powders were measured to be 0.6516 and 10.3120 m^2/g, which are equal to the particle sizes of 3.9μm and 81nm, respectively.

XRD patterns of pure KNN, $KNNW_{3m}$ and $KNNW_{3n}$ powders have been shown in Figure 1 after calcination at 950ºC. All compositions have pure orthorhombic perovskite structure and no secondary phase is observed, implying that W^{6+} ions diffused into the KNN lattices. $KNbO_3$ with PDF number 00-032–0822 in the ICDD database was used as a reference because of being isostructural with KNN [21].

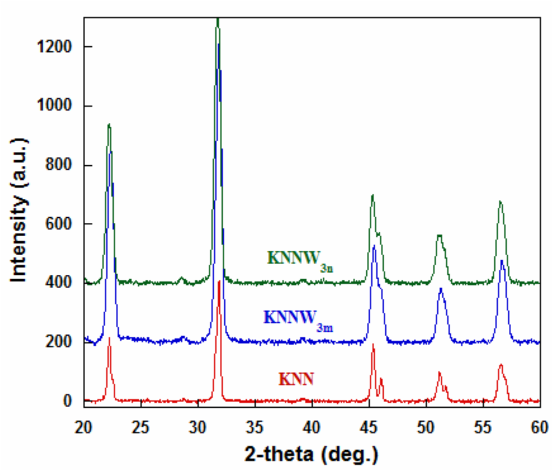

Figure 1. XRD patterns of KNN, $KNNW_{3m}$ and $KNNW_{3n}$ powders after calcinations at 950ºC.

SEM micrographs of Figure 2 imply that pure KNN, $KNNW_{3m}$ and $KNNW_{3n}$ particles are in submicron range and there is no considerable difference between them.

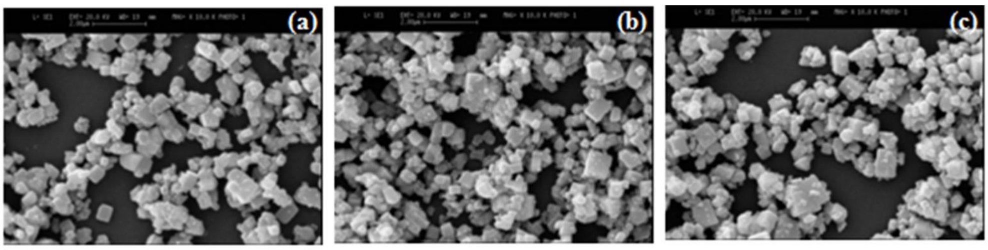

Figure 2. SEM micrographs of the powders (a) KNN, (b) $KNNW_{3m}$, (c) $KNNW_{3n}$ calcined at 950ºC for 4h.

According to the XRD patterns of Figure 3, by adding nano and micron sized WO_3, the diffraction peaks slightly shifted to higher angles and it was more obvious in $KNNW_{3m}$. The increase of lattice volume in $KNNW_{3m}$ and $KNNW_{3n}$ can be attributed to the smaller ionic radius of W^{+6} ions (60pm) in comparison with Nb^{5+} ions (64pm) [22-25].

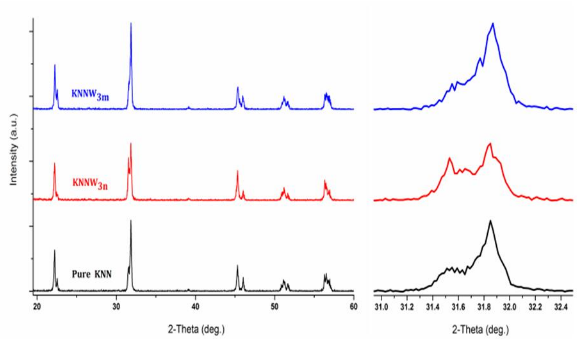

Figure 3. XRD patterns of KNN ceramics sintered at 1115ºC.

Figure 4 reveals the effect of sintering temperature on XRD patterns and lattice parameters of $KNNW_{3n}$ and $KNNW_{3m}$ ceramics. According to Figure 5, the variations of lattice volume in $KNNW_{3m}$ are more than that in $KNNW_{3n}$ ceramics, moreover, Figure 5 represents the lattice contraction in both $KNNW_{3n}$ and $KNNW_{3m}$ ceramics which occurs by increasing sintering temperature from 1100° to 1130°C. on the one hand, the lattice contraction can occur due to the substitution of W^{6+} ions for Nb^{5+} ions, which results in K^{1+} /Na^{+1} vacancies for charge compensation, but on the other hand, the evaporation of alkali oxided at higher sintering temperatures can lead to lattice contraction as well [26, 27].

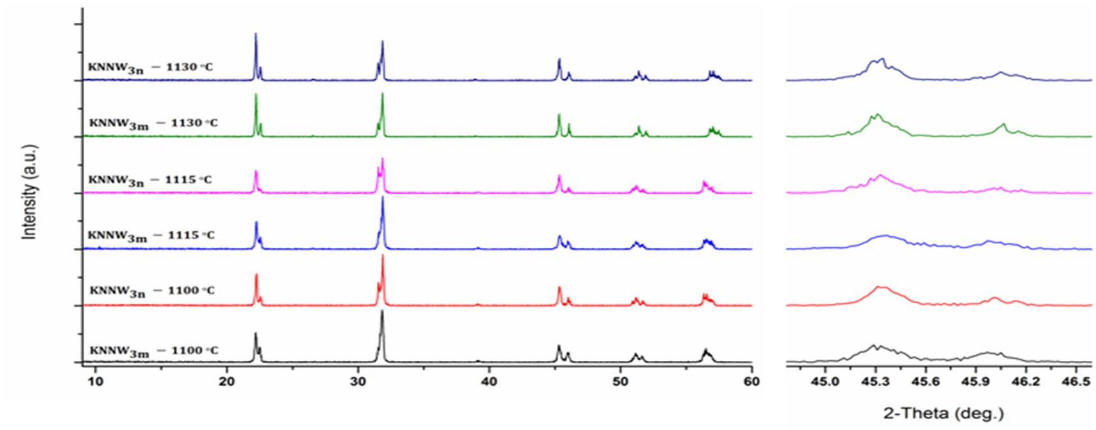

Figure 4. XRD patterns of $KNNW_{3m}$ and $KNNW_{3n}$ ceramics sintered at 1100-1130ºC.

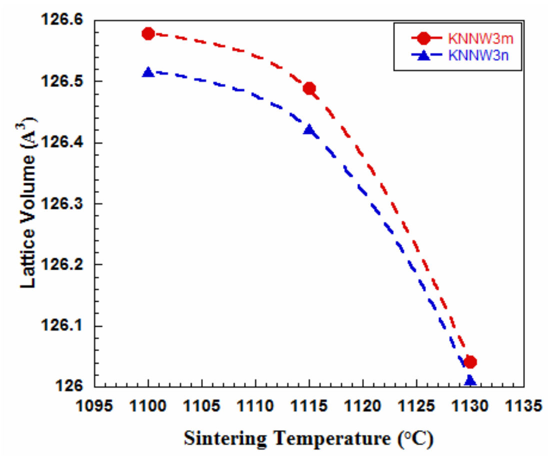

Figure 5. Variations in lattice volume with sintering temperature for $KNNW_{3m}$ and $KNNW_{3n}$ ceramics.

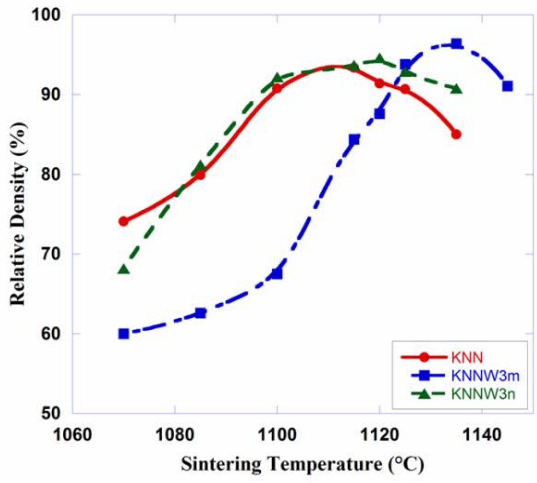

Figure 6. The variations in density of KNN ceramics with sintering temperature.

Figure 6 shows the variations in density of pure and WO_3 doped KNN with sintering temperature.

This Figure reveals the increase of density values of samples by increasing sintering temperature. By increasing the sintering temperature over optimum amounts, the density of samples decreased due to the evaporation of alkali elements. As Figure 6 further represents, the decrease in density of KNN samples occurred at higher sintering temperatures by adding nano and micron sized WO_3. $KNNW_{3m}$ reaches the maximum density of 96.4% at higher sintering temperature of 1130ºC compared to $KNNW_{3n}$ with relative density of - 95.7% at 1120ºC.

Figure 7 compares the SEM micrographs of various KNN samples sintered at different temperatures. KNN samples obtained finer grains by adding micron WO_3 compared to nano WO_3. Additionally, the sintering process was slower in $KNNW_{3m}$ samples and the densification and grain growth terminated at higher temperatures for these samples. This was in complete agreement with data of density for $KNNW_{3m}$ sample which had a low value of 84.4% at 1115 ºC and reached the maximum density of 96.4% at 1140ºC.

At temperature of 1115ºC, contrary to pure KNN (Figure 7a) and $KNNW_{3n}$ (Figure 7c), the microstructure of $KNNW_{3m}$ (Figure 7b) is still porous and requires more grain growth which completed at higher temperatures. Also at temperature of 1135ºC, contrary to $KNNW_{3n}$ sample (Figure 7g), $KNNW_{3m}$ (Figure 7f) obtained a dense and pore free microstructure without any abnormal grain growth and finally, at 1135ºC (Figure 7h) the samples melted and the density decreased.

In the case of nano WO_3, the microstructure completed at 1125ºC (Figure 7e), and after 1135ºC the samples melted. Table 1 summarizes the data of electrical properties for pure and WO_3 doped KNN. At sintering temperature of 1125ºC, $KNNW_{3n}$ showed d_{33}, ε_r, tanδ, and Q_m of 75 pC/N, 345, 2%, and 50, respectively. For $KNNW_{3m}$ sample at 1135ºC these factors were 81 pC/N, 773, 3.3%, and 30, respectively. Due to higher density of $KNNW_{3m,}$ it has a higher dielectric constant compared to $KNNW_{3n}$, while the latter has higher mechanical quality factor.

Additionally, the d_{33} piezoelectric constant of $KNNW_{3m}$ was higher than that of $KNNW_{3n}$, and at some temperatures it was the same as pure KNN. Actually, grain size is an important factor in piezoelectric ceramics and WO_3 doped samples had smaller grains compared with pure KNN and the piezoelectric coefficients of these samples hardly reached that of pure KNN ceramics. On the other hand, despite larger grain size of $KNNW_{3n}$ ceramics, they had lower d_{33} values compared with $KNNW_{3m}$ which can be related to the lower density of the former.

4. CONCLUSION

Microstructure and electrical properties of conventionally synthesized lead free potassium sodium niobate (KNN) ceramics were modified by adding nano and micron WO_3. The addition of WO_3 prohibited the grain growth and resulted in a finer microstructure in comparison with pure KNN. Micron WO_3-doped KNN had finer microstructures and the sintering process completed at higher temperatures compared with nano WO_3-doped KNN.

Finally, at sintering temperature of 1125ºC nano WO_3-added KNN obtained the highest electrical properties of d_{33}=75 pC/N, ε_r=345, tanδ=0.02, and Q_m=50. However, micron WO_3-added KNN obtained the highest electrical properties of d_{33}=81 pC/N, ε_r=773, tanδ=0.033, and Q_m=30 at sintering temperature of 1140ºC.

TABLE 1. Electrical properties of $KNNW_{3m}$ and $KNNW_{3n}$ ceramics sintered at 1115-1145°C for 2h.

Sintering Temperature (°C)	**$KNNW_{3n}$***				**$KNNW_{3m}$**			
Ʋ	**ε_r**	**tanδ**	**Q**	**d_{33}**	**ε_r**	**tanδ**	**Q**	**d_{33}**
1110	403	0.034	29	53	283	0.05	18	59
1115	419	0.024	41	61	383	0.028	35	71
1120	349	0.024	41.4	54	432	0.16	17	73
1125	345	0.02	50	75	638	0.069	19.5	74
1135	365	0.07	14	32	749	0.04	25	83
1140	-	-	-	-	773	0.033	30	81
1145	-	-	-	-	364	0.06	16	31

*Pure KNN sintered at 1115°C (ε_r=538, tanδ=0.033, Q=30 and d_{33}=80 pC/N)

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