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Effect of V_2O_5 addition on sintering behavior and electrical properties of lead-free $(Li_{0.06}Na_{0.47}K_{0.47})NbO_3$ ceramics

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$(Li_{0.06}Na_{0.47}K_{0.47})NbO_3$ (LNKN) ceramics with 0-2 mol% V_2O_5 has been prepared following the conventional solid state sintering method without cold-isostatic pressing (CIP) process. The effects of V_2O_5 addition on the sinterability and electrical properties of the LNKN ceramics were examined. Solid solution limit of V_2O_5 in LNKN is thought to be around 1 mol%. 1 mol% V_2O_5 addition is effective in decreasing the sinter temperature and increasing the density of LNKN to 95.3% of the theoretical density of LNKN ceramic (4.47 g/cm^3), while the optimized electrical properties, such as ε_r=493, tanδ=0.014, d_{33}=207 pC/N and k_p=0.43, are obtained.

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1. Introduction

$KNbO_3$-$NaNbO_3$ (KNN) system has attracted researcher's attention since Saito, *et al*, reported their work on the synthesized KNN-based ceramics with excellent piezoelectric performance comparable to the PZT-based ceramics [1]. KNN is one of the most important lead-free piezoelectric materials with perovskite structure. The hot pressed NKN ceramics (~99% of the theoretical density) was reported to possess a high Curie temperature (T_C ~ 420 °C), a large piezoelectric response (d_{33} ~ 160 pC/N), and a high electromechanical coupling coefficient (k_p ~ 45%). However, due to the volatility of potassium element and lack of pyroplastic behavior, the conventionally-sintered NKN ceramics showed relatively lower electrical properties, which prevent its researches and application [2-4]. Recent main focus has been conducted in the conventional solid state sintering method to prepare the dense NKN based ceramics [5-9]. Among these researches, doping into the system and its derivatives has been taken as a common and effective method. Guo, *et al,* reported that $0.98(Na_{0.5}K_{0.5})NbO_3$-$0.02BaTiO_3$ ceramics could reach to dense structure by a cold-isostatic pressing followed an ordinary sintering technique because of an increase in grain size[5]. Matsubara successfully synthesized $(K_{0.5}Na_{0.5})NbO_3$ (KNN)-based ceramics using $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$ as sintering aide due to its effect on the improvement of the sinterability of KNN ceramics [6]. Malic, *et al*, found that Ca and Sr doping could promote densification, decrease the phase transition temperatures of KNN ceramics [7]. Ichiki, *et al*, studied the effect of several doping elements on the electric properties of KNN ceramics [8].

V_2O_5 is a commonly-used sintering aide in ceramic process due to its low melting point. Many researches indicated that V_2O_5 doping could effectively improve the sintering behavior of ceramics [10-15]. Huang, *et al*, found that the density of V_2O_5-doped $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics can be increased beyond 95 % of its theoretical value by 1500 °C-sintering [10]. He believed that the densification effect is caused by the liquid-phase effect of V_2O_5 addition. Tzou, *et al*, studied the sintering behavior of $BiNbO_4$ and found that with 1wt% V_2O_5 added, the densification temperatures of $BiNbO_4$ ceramics decreased from 960 to 920 °C and the density increased from 83.6 to 98% of theoretical density [11]. The similar effects were also observed in other ceramic systems, including $ZnTiO_3$ [12], $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ [13], $Mg_4Nb_2O_9$ [14] and $Sr_{0.5}Ba_{0.5}Nb_2O_6$ [15] ceramics. However, the research about NKN based ceramics with V_2O_5 doped was scarcely reported.

In this work, the effects of V_2O_5 addition on the sintering behavior and dielectric properties of $(Li_{0.06}Na_{0.47}K_{0.47})NbO_3$ ceramics, which was reported with excellent piezoelectric performance [16], were investigated. The experiment results showed that the suitable addition of V_2O_5 could significantly improve the sintering behavior of LNKN ceramics while the electrical properties remains essentially constant. As 1 mol% V_2O_5 added, the optimal sintering temperature of the LNKN ceramics decreased to 1050 °C, and the density improved to 4.259 g/cm^3, and optimized electrical properties, such as ε_r=493, tanδ=0.014, d_{33}=207 pC/N and k_p=0.43, were also obtained.

2. Experimentation

In this work, the V_2O_5-doped LNKN ceramics were prepared by the conventional solid state sintering method. Chemical reagents, including Na_2CO_3 (99.9%), K_2CO_3 (99.9%), Li_2CO_3 (99.9%), Nb_2O_5 (99.9%) and V_2O_5 (99.7%), were weighed according to the formula $(Li_{0.06}Na_{0.47}K_{0.47})NbO_3$ + x mol.% V_2O_5 (x = 0, 0.5, 1, 1.5, and 2) and mixed in a nylon with ZrO_2 balls for 24 h using ethanol as a medium. The mixed oxide powders were calcined at 850 °C for 10 h. Then, the calcined powders were ball milled again with 2 wt.% poly vinyl alcohol (PVA) solution for 24 h. The granulated powders were dried and pressed under uniaxial 200 MPa pressure into pellets of 1.5 cm diameter. The pellets were sintered in a sealed alumina crucible in ambient atmosphere at selected temperatures in the range 1030 °C to 1080 °C, depending on their x, for 2 h. The sintered specimens were then lapped and electroded with a silver paste for dielectric measurements.

To check the densification of ceramics, the apparent density of the fired samples were measured by the Archimedes method using distilled water as a medium. The X-ray diffraction (XRD) analysis was performed in θ-2θ mode using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation, to examine the phase structure. The morphology of the ceramics was observed using a Hitachi model S-3500N scanning electron microscopy (SEM). The dielectric measurements were carried out on Agilent 4284A precision LCR meter. Prior to testing piezoelectric properties, the specimens were poled in a silicone oil bath at 150 ◦C by applying a dc field of 4 kV/ mm for 30 min and aged for 24 h. The piezoelectric coefficient d_{33} was measured using a ZJ-3D quasi-static piezoelectri d_{33} meter. The electromechanical coupling factor and k_p (kp) were estimated by the resonance and anti-resonance technique using a Agilent 4294A impedance analyzer.

3. Results and discussion

Fig. 1 shows the apparent densities of V_2O_5-doped LNKN ceramics as function of sintering temperature. As seen from the figure, the apparent density of ceramic for a fixed composition varies evidently as the temperature increases. For the undoped ceramics, the apparent density reaches a peak at temperature of 1070 °C, the optimal sintering temperature (OST), at which the maximal apparent density of 4.136 g/cm^3 arrives. As the V_2O_5 addition increased, the optimal temperature decreased. For the V_2O_5 addition less than 1.0 mol.%, the OST decreased while the maximal apparent density increased. When the V_2O_5 increased to 1.0 mol.%, the OST decreased to 1050 °C while the maximal density increased to 4.259 g/cm^3. It means that suitable V_2O_5 addition could effectively improve the sintering behavior of the LNKN ceramics. The densification was caused by the liquid-phase effect of V_2O_5 addition [10]. The liquid-phase effect could be related to two factors: the first is the low temperature melting of V_2O_5 at 670 °C; the second may be referred to the eutectic phenomena of V_2O_5 and other oxides. These phenomena would be favorable to the occurrence of liquid phase at a lower temperature and the promotion of the mass transfer during the sintering process, thus enhance the sintering behavior of LNKN ceramics. However, excess addition of V_2O_5 is disadvantage to the sintering of LNKN ceramics. As seen from Fig.1, as V_2O_5 increased to 1.5 and 2.0 mol.%, the maximal density at OST decreases gradually. When the V_2O_5 addition arrives at 2.0 mol.%, the maximal apparent density lowered to 4.219 g/cm^3. This may be resulted from the formation of second phase or cavities in the bulk.

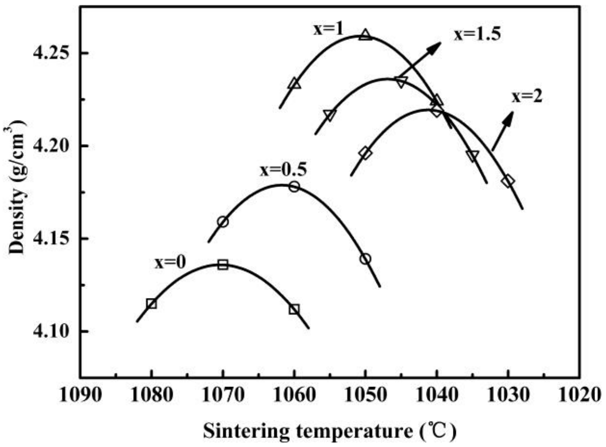

Fig. 1. The apparent densities of LNKN + x mol.% V_2O_5 ceramics ($0 \le x \le 2$) as function of sintering temperature

Fig. 2 shows the XRD patterns of LNKN ceramics sintered at optimum sintering temperature. As shown in Fig. 2, the undoped sample presents a single perovskite structure due to all the reflections could be assigned to orthorhombic $(Na,K)NbO_3$ phase as reported by Guo, *et al* [16]. As V_2O_5 adding into the LNKN ceramics, there appears two effects observed from the figure: one is the shift of the reflections to the larger diffraction angle, the another is the occurrence of the second phase when the addition exceed over 1.0 mol.%. As known, the V^{5+} ion possesses the smaller radius (0.68 Å) than that of Nb^{5+} (0.78 Å) [17]. Therefore, V^{5+} ion would prefer to enter into the perovskite lattice, thus cause the shrinkage and distortion of the lattice. Fig. 3 shows the changes of the reflection near 45º as function of V_2O_5 addition. Meanwhile, some new and weak reflections were observed as in Fig. 2. This could be attributed to the precipitation of

V_2O_5 or its solid solution due to the limited solution of V_2O_5 into the perovskite lattice of LNKN.

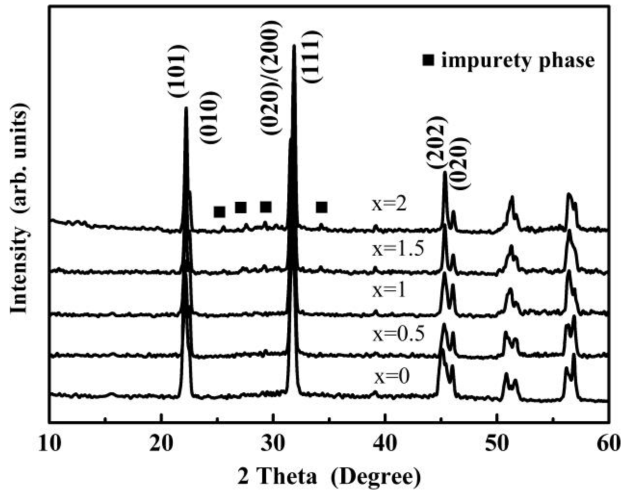

Fig. 2. The XRD patterns of LNKN + x mol.% V_2O_5 ceramics sintered at optimum sintering temperature

Fig. 3 shows the SEM photographs of the fracture surface for the LNKN ceramics with different V_2O_5 addition. As seen from Fig. 3a, the undoped sample shows the worsened sintering behavior: some particles still present a status of agglomeration while some grains have developed to a size of about 20 μm. However, the sample with V_2O_5 addition of 0.5 mol.% gives an adequately-developed grains with a size of 10 μm (Fig. 3b), which means the addition of V_2O_5 promote the development of the grains. However, further increase of V_2O_5 addition induces the decrease of grain size and the occurrence of the cavity in the grains as shown in Fig.3c and 3d. It may be related with the precipitation of excess V_2O_5 addition the grain boundary. The EDX analysis for LNKN ceramics with 0.5 and 2.0 mol.% V_2O_5 addition affirmed the suggestion of the V_2O_5 precipitation in the grain boundary as shown in Table 1. Obviously, there is no distinct difference of V_2O_5 content for sample with 0.5 mol.% V_2O_5 addition in grain bulk and boundary. But for the sample with 2.0 mol.%, the difference of the V_2O_5 content in different position is so significant that can not be explained by the measuring error. In a word, small addition of V_2O_5 will dissolve into the perovskite lattice and improve the sintering behavior of LNKN ceramics, which will affect the dielectric properties of LNKN ceramics.

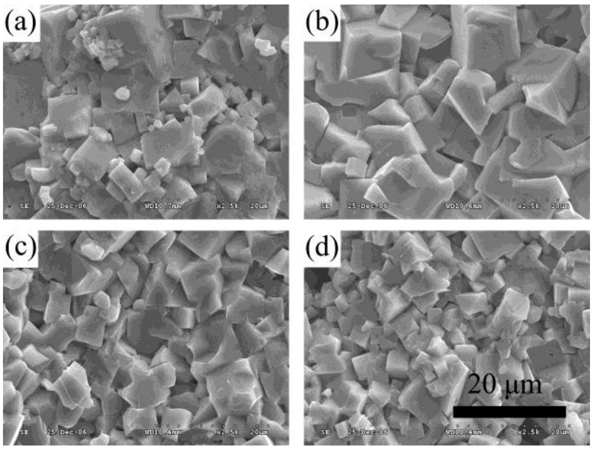

Fig. 3. SEM photographs of the fracture surface for LNKN ceramics undoped(a) and doped with V_2O_5: 0.5 mol.% (b), 1.0 mol.% (c) and 2.0 mol.% (d)

Table 1. EDX analysis of element contents in LNKN ceramics with 0.5 and 2.0 mol.% V_2O_5 addition measured at the boundary or bulk position

V_2O_5 addition / Element	0.5 mol.%		2.0 mol.%	
	Bulk(A)	Boundary(B)	Bulk(C)	Boundary(D)
O	39.57	41.46	57.40	54.35
Na	11.85	11.41	8.33	7.64
K	14.48	13.86	8.76	8.52
V	0.38	0.53	0.74	7.02
Nb	33.71	32.74	24.77	22.47

Fig. 4 shows the dielectric constant ε_r and dielectric loss tanδ of LNKN ceramics measured at 100 kHz as function of V_2O_5 content. It is observed that the suitable V_2O_5 doped benefits the improvement of dielectric properties. The optimal ε_r of 493 and tanδ of 0.014 were reached at the 1.0 mol.% addition of V_2O_5, which could be attributed to the increase of ceramic density and the development of the grain growth. However, when the V_2O_5 addition increase over 1.0 mol.%, the dielectric constant of the ceramic decreases markedly and the dielectric loss increases significantly, which could be resulted from the precipitation of V_2O_5 in grain boundary and the occurrence of cavity in the grain bulk, which result in the worsening of the dielectric behavior. The similar effect of the V_2O_5 addition was also observed in the piezoelectric performance. Fig. 5 shows the piezoelectric coefficient d_{33} and the electromechanical coupling factor k_p of LNKN ceramics as function of V_2O_5 addition. As seen from the figure, both d_{33} and k_p show a similar variation with V_2O_5 addition. When d_{33} and k_p are rapidly increased with V_2O_5 addition until 1.0 mol.%. The optimized values for d_{33} of 207 pC/N and k_p of 0.43 were obtained at the 1.0 mol.% addition of V_2O_5, and further V_2O_5 addition above 1.0 mol.% leads to a rapid decrease in the piezoelectric properties, which corresponds well with the changes of ε_r and tan δ.

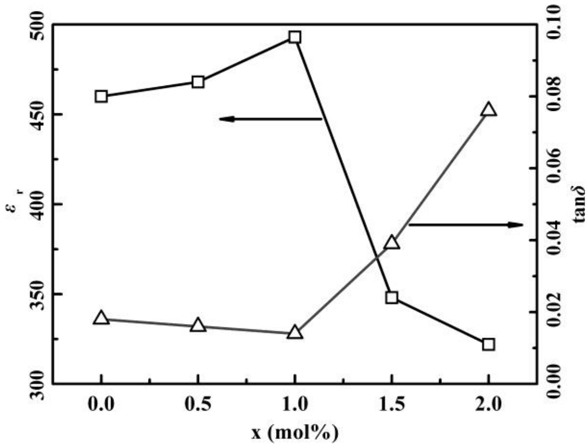

Fig. 4. The dielectric constant and dielectric loss of LNKN + x mol.% V_2O_5 ceramics measured at 100 kHz

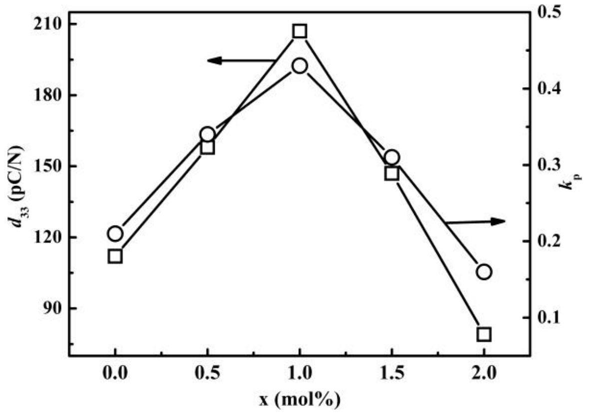

Fig. 5. The piezoelectric d_{33} and the electromechanical coupling factor k_p of LNKN + x mol.% V_2O_5 ceramics

4. Conclusions

Using the conventional solid state sintering method without cold-isostatic pressing (CIP) process, V_2O_5-doped LNKN ceramics have been synthesized and their sintering behavior and electrical properties have been investigated in this study. The experiment results show that, for the small V_2O_5 addition less than 1.0 mol.%, the grains grow gradually into well-developed morphology, and small addition of V_2O_5 into the system simultaneously lowers the sintering temperature and enhances the bulk density of the ceramics due to the effect of liquid phase sintering induced by V_2O_5. As the V_2O_5 addition arrives at 1.0 mol.%, the optimal sintering temperature lowered to 1050 ºC from1070 ºC for the undoped sample while the bulk density increased to 4.259 g/cm^3, which is 95.3% of the theoretical density. Combining the effect of the bulk densification and grain development, the optimized electrical properties, such as ε_r=493, tanδ=0.014, d_{33}=207 pC/N and k_p=0.43, are obtained with1.0 mol.% V_2O_5 addition. However, when the addition exceeds over 1.0 mol.%, the density of LNKN ceramics decrease and excess of V_2O_5 precipitated in the grain boundary, thus the electrical properties deteriorate markedly.

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