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$0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ piezoelectric ceramics prepared from the solid state reaction modified with polyvinylpyrrolidone (PVP) of different molecular weights

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Abstract

Lead-free piezoelectric $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ (0.94KNN–0.06LN) ceramics were prepared by solid state reaction process modified by introducing polyvinylpyrrolidone (PVP) of different molecular weights in the starting raw materials. The chemical interaction between the metal cations and the PVP, particularly through the N in PVP, was observed. The effects of PVP for suppressing the loss of alkali ions, promoting the perovskite phase formation, and improving the piezoelectric properties were characterized and discussed. With molecular weight ranging from 55 K to 1300 K, PVP with lower molecular weight exhibited more significant effect. This study showed that introducing PVP in the starting raw materials may be an effective method for obtaining stoichiometric KNN–LN and other ceramics with volatile alkali ions.

Keywords: A. Powders; A. Solid state reaction; C. Piezoelectric properties; D. Perovskites; KNN–LN

1. Introduction

Currently, lead-based piezoelectric ceramics such as $PbZrO_3$–$PbTiO_3$ (PZT) have been widely used in our daily products including sensors, igniters, ultrasonic transducers and many other electronic devices. However, these PZT ceramics contain high content of toxic lead (>60% by weight) and are bringing health and environment concerns aggravated with their expanded applications. Therefore, it is urgent to source alternative piezoelectric green compositions to substitute the existing lead-based piezoelectric materials, particularly those ferroelectric ceramics with strong piezoelectric effects.

Several lead-free ferroelectric ceramic systems, including bismuth layer structure ferroelectrics (BLSFs) [1–4], tungsten bronze structure ferroelectrics (TBSFs) [5], modified $BaTiO_3$ (BT) [6], $(Bi_{0.5}Na_{0.5}TiO_3)$ (BNT) [7] and $K_{0.5}Na_{0.5}NbO_3$ (KNN) [8] ceramic ferroelectric families, have been intensively explored for piezoelectric applications and reported in the literature. Among these lead-free piezoelectric ceramic candidates, composition- and structure-modified KNN-based ceramics reported by Saito et al. [9] have drawn significant attentions, because piezoelectric properties comparable to those of PZT were found in their KNN-based ceramic. However, the high performance piezoelectric ceramics in their study had relatively low Curie temperature of about 253 °C only. Further studies by Guo and Kakimoto et al. [10] showed that the piezoelectric properties of KNN can be improved by introducing $LiNbO_3$ (LN) as additive, and the piezoelectric constant d_{33} values reached 200–235 pC/N while high Curie temperature around 452–510 °C could be maintained. Du et al. [11] also reported the microstructure, ferroelectric properties and mechanical quality factor Q_m of KNN–LN ceramics, and the highest d_{33} coefficient was obtained in the composition of $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ (0.94KNN–0.06LN), which is well consistent with the previously reported MPB (Morphotropic Phase Boundary) and later found to be temperature-dependent phase transition composition. Recently, many attentions have been paid to this promising KNN–LN system due to its high piezoelectric properties and also high Curie temperature [12–25].

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The starting materials for the alkali compositions in KNN–LN ceramic are commonly K_2CO_3, Na_2CO_3 and Li_2CO_3, which have a low melting point of 891 °C, 851 °C and 723 °C, respectively. During the calcination and sintering, the alkali components can become highly volatile at the elevated temperature and this makes it difficult to maintain chemical stoichiometry. The reported studies in the literature showed that addition of excess alkali components could help to maintain more alkali ions in the resulting ceramic. However, adding too much excess alkali elements could also cause other problems including difficulty in precisely controlling the chemical stoichiometry and excessive grain growth due to liquid phase sintering mechanism [26]. Therefore, it is desired to find another way to control the alkali volatility issue. Many studies on KNN–LN ceramics have focused on complex chemical doping and fine-tuning the processing condition. However, there is no substantial attention paid to modify the starting reactant powders with polymeric additives to suppress the alkali volatility problem.

Polymers have been introduced in the process for preparing ferroelectric thin films with perovskite structure and complex oxide compositions by chemical solution approach. For example, poly(ethylene glycol) (PEG) and polyvinylpyrrolidone (PVP) were used to achieve perovskite $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PZN–PT) [27] and $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN–PT) [28] thin films by promoting perovskite phase crystallization at lowered temperature while effectively suppressing pyrochlore phase. Later it was also noted that PEG polymers showed similar effects when they were introduced in preparing bulk perovskite ceramics of $Pb(Ni_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PNN–PT) and (PMN–PT) [29,30]. Recently, lead-free KNN ceramic thin films prepared from polyvinylpyrrolidone (PVP)-modified precursor solution exhibited a substantially improved effective d_{33} of 61 pm/V under the clamping of the substrate [31], and further investigation revealed that the addition of PVP effectively promoted the crystallization of the KNN perovskite phase at reduced temperature, which had substantially suppressed the loss of alkali ions before the crystallization [32]. However, research on polymer-assisted ceramic processing has not been reported on lead-free piezoelectric KNN-based bulk ceramics derived from solid state reaction.

The objectives of this study are to examine the effects of PVP on the bulk KNN–LN ceramic prepared by conventional solid state reaction method and further to clarify the mechanism of the effects of PVP introduced in the bulk ceramic system.

2. Experimental procedure

The material compositions studied were $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ (0.94KNN–0.06LN). K_2CO_3 (99.5%), Na_2CO_3 (99.0%), Li_2CO_3 (99.999%), Nb_2O_5 (99.9%) (Alfa Aesar) were used as the starting raw materials, with 1 mol% of excess K, Na added. As the three carbonate powders were moisture sensitive, they were first dried prior to use to avoid compositional errors. The dried powders were then stoichiometrically weighted and mixed with 5 wt% of PVP of different molecular weights of 55×10^3, 360×10^3 and 1300×10^3 (abbreviated as PVP 55 K, PVP 360 K and PVP 1300 K, respectively). These mixed powders were then ball-milled in ethanol for 24 h. The crushed powders derived from the dried slurry after the ball-milling were then treated for 30 min with ultrasonic irradiation using a direct-immersion titanium horn. After the ultrasonication process, the slurry was dried and crushed again followed by calcinations at 850 °C for 5 h in an alumina crucible. After the calcined powders were ball milled for 4 h, and mixed with 4 wt% polyvinyl butyral (PVB) as a binder, they were uniaxially pressed into disks with a diameter of 10 mm and a thickness of about 1.3 mm.

The 0.94KNN–0.06LN disk samples were sintered at 1030 °C for 2 h in air. For comparison purpose, the 0.94KNN–0.06LN powder and ceramic without PVP addition were also prepared with the same procedures. The disk samples were carefully weighted before sintering (W_1) and also after sintering (W_2) (without taking into account the organic binder PVB in W_1 and W_2). The percentage of weight loss was calculated according to the equation below:

$$\%\ \text{Weight loss} = \left[\frac{W_2 - W_1}{W_1}\right] \times 100 \qquad (1)$$

The ceramic samples with different molecular weights of PVP and without PVP are abbreviated as KNN–LN-55 K, KNN–LN-360 K, KNN–LN-1300 K and KNN–LN respectively. The crystal structures of the samples were determined with X-ray diffraction (XRD) (D8-ADVANCED, Bruker AXS GmbH, Karlsruhe, Germany). The weight loss and heat flow analysis were conducted using thermogravimetry (TGA–DSC, SDT2960, TA Instruments, New Castle, DE). The infrared transmittance spectra were obtained using Fourier transform infrared spectroscopy (FTIR) (FT-IR Spectrum 2000, PerkinElmer, Waltham, MA) after the samples were mixed and pelletized with KBr. The ions valence states were characterized with X-ray photoelectron spectroscopy (XPS) (VG ESCALAB 2201-XL Imaging System, East Sussex, U.K.) using Al Kα source (1486.6 eV), with the binding energies (Bes) referenced to the C 1s at 284.5 eV.

For electrical characterization, the ceramic disk samples were coated with silver paste on both sides after polishing, followed by firing at 550 °C. All the samples were poled at 120 °C for 30 min under direct current field of 30 kV/cm for piezoelectric measurement. The piezoelectric constant, d_{33} was measured using a piezo-d_{33} meter (ZJ-4B, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). The planar electromechanical coupling factor k_p was obtained by resonance–antiresonance method by impedance analyzer (HP4294A, Agilent Technologies Inc.).

3. Results and discussion

Fig. 1 presents the X-ray diffraction (XRD) patterns of the 0.94KNN–0.06LN ceramic samples sintered at 1030 °C for 2 h. It can be seen from Fig. 1 that all the samples with and without PVP showed single-phase perovskite structure with an orthorhombic symmetry. The XRD peaks of orthorhombic

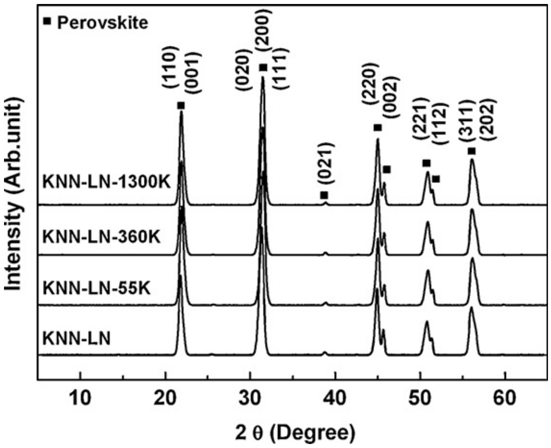

Fig. 1. X-ray diffraction (XRD) patterns of the 0.94KNN–0.06LN ceramic samples with PVP of different molecular weights and without PVP, sintered at 1030 °C for 2 h.

phase are indexed in reference to those of $KNbO_3$ (JCPDS No. 32-0822).

Fig. 2 shows the mole ratio between measured (K + Na) according to energy dispersive X-ray spectroscopy (EDX) and theoretically calculated (K + Na), together with weight loss according to Eq. (1) for the 0.94KNN–0.06LN ceramic samples without PVP and with PVP of different molecular weights. The mole ratio in Fig. 2 was calculated according to Eq. (2) below:

$$\text{Mole ratio} = \frac{(\mathrm{K}+\mathrm{Na})(\text{measured})}{(\mathrm{K}+\mathrm{Na})(\text{calculated})} \qquad (2)$$

As shown in Fig. 2, there was significant deficiency of (K + Na) in the resulting 0.94KNN–0.06LN ceramic without PVP and the addition of PVP in the ceramic process substantially retained more (K + Na), although it was still below the theoretical amount. It is an established fact that maintaining the composition stoichiometry in KNN–LN system is very difficult due to strong alkali volatility at elevated temperature. Moreover, the formation of orthorhombic phase can lead to deficient potassium and sodium in the KNN–LN system as reported by Liu et al. [25] and we also observed this as shown in Fig. 1. Although 1 mol% excess alkali components were added in our experiments to compensate the alkali ions losses, was still insufficient. On the other hand, adding too much excess alkali components could lead to stoichiometric imbalance in the final product and cause excessive grain growth due to liquid phase sintering [26]. In the mean time, it was observed that the weight loss during sintering as determined according to Eq. (1) was suppressed with PVP introduced with the starting reactants. It is believed that the effect in suppressing most of (K + Na) evaporation could happen during calcinations as our previous study showed that the major loss of alkaline components happened before the formation of perovskite phase [32]. By introducing PVP in the ceramic process, the starting reactants could form perovskite phase more completely during calcinations as compared to the 0.94KNN–0.06LN ceramic without PVP in which more unreacted reactants remained during the calcination. Thus further (K + Na) evaporation could continue to happen during the sintering. These results clearly indicate that (K + Na) alkali volatility was substantially suppressed by the addition of PVP polymer in the solid state reaction process for preparing the bulk KNN–LN ceramic.

The results in Fig. 2 also show that the molecular weight of PVP played an important role on the effect of suppressing alkali volatility. The least weight loss after sintering process occurred at KNN–LN-55 K ceramic, corresponding to PVP with a relatively smaller molecular weight of 55 K. With the molecular weight of PVP increased to 360 K and 1300 K in KNN–LN-360 K and KNN–LN-1300 K samples, respectively, the weight loss kept increasing. Therefore, appropriate molecular weight of the polymer additives should be considered for effectively suppressing the volatilization of alkali metal ions and weight loss for the preparation of KNN–LN bulk ceramics.

The piezoelectric coefficient d_{33} and electromechanical coupling factor k_p of 0.94KNN–0.06LN ceramic samples with PVP of different molecular weights are given in Fig. 3. As

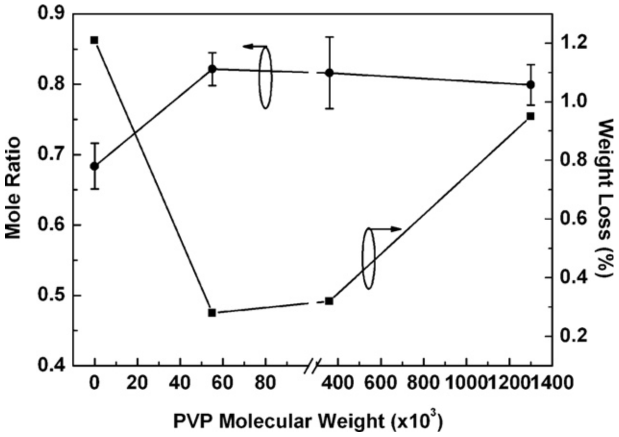

Fig. 2. Mole ratio between measured (K + Na) according to energy dispersive X-ray spectroscopy (EDX) and theoretically calculated (K + Na); and weight loss of 0.94KNN–0.06LN ceramic samples with PVP of different molecular weights and without PVP, sintered at 1030 °C for 2 h.

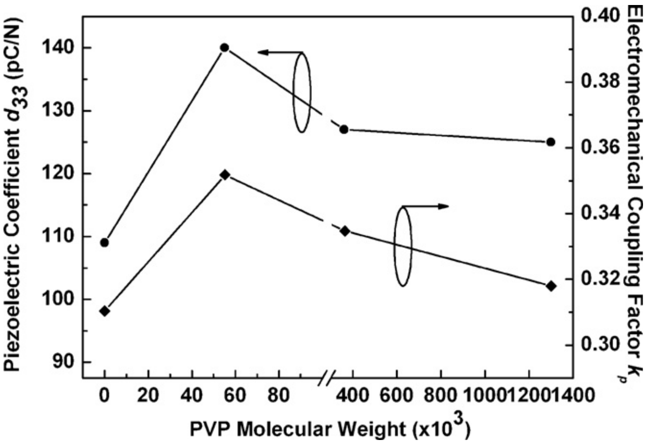

Fig. 3. Piezoelectric coefficient d_{33} and planar electromechanical coupling factor k_p of 0.94KNN–0.06LN ceramic samples with PVP of different molecular weights and without PVP, sintered at 1030 °C for 2 h.

shown in Fig. 3, d_{33} and k_p were increased from 109 pC/N and 0.31 in 0.94KNN–0.06LN sample without PVP to 140 pC/N and 0.35 respectively in KNN–LN-55 K sample with PVP 55 K. With the molecular weight of PVP increased to 360 K and 1300 K, KNN–LN-360 K and KNN–LN-1300 K samples still showed superior piezoelectric properties compared to 0.94KNN–0.06LN sample without PVP, but inferior to those of KNN–LN-55 K. These results showed that improved piezoelectric properties were achieved in 0.94KNN–0.06LN ceramic with the addition of PVP 55 K and with minimized alkali volatilization. However, with the PVP molecular weight further increased to 360 K and PVP 1300 K, the piezoelectric properties degraded again, which was consistent with the observed result of corresponding alkali loss.

It is interesting to study the interaction between PVP and metal cations in the system. Fig. 4 shows the Fourier transform infrared (FTIR) spectra of uncalcined 0.94KNN–0.06LN powders mixed with PVP of different molecular weights and pure PVP with molecular weight of 55 K. The peak at 1658 cm^{-1} in pure PVP 55 K is assigned to the C=O stretching band of PVP [33]. When PVP was added in KNN–LN system, regardless of the molecular weight, the C=O peak shifted to a higher wavenumber; 1663 cm^{-1} for KNN–LN-55 K and 1661 cm^{-1} for both KNN–LN-360 K and KNN–LN-1300 K. The shifting of C=O peak shows that there could be some interactions between metal ions and PVP. According to literature, there are two possible interactions between PVP and metal cations; the donation of electrons lone pair from the carbonyl oxygen to the metal cations or electron transfer from nitrogen in the five-membered nitrogen-containing ring to the metal cations [34,35]. These two interactions may affect the polarizability of the oxygen in the C=O. It is known from Nakamoto [36] that a positive band shifts (shift to higher wavenumber) of amides' C=O stretching band in FTIR indicates electron transfer from nitrogen to the metal ions while a negative band shift (shift to lower wavenumber) indicates donation of electrons lone pair from the carbonyl oxygen to the metal ions. The shift of C=O peak to higher wavenumber in KNN–LN with different molecular weights of PVP as shown in Fig. 4 shows that metal cations are likely interact with nitrogen in PVP.

Although the shift of C=O stretching band in FTIR in Fig. 4 is evident, it is not very significant. XPS study was further conducted to examine the interactions of metal ions with PVP. Fig. 5 presents the XPS spectra of N 1s in pure PVP 55 K, uncalcined powders of KNN–LN-55 K and KNN–LN. In KNN–LN, no N 1s peak is observed in binding energy range between 395 eV and 403 eV. In pure PVP 55 K, only one peak is observed at 399 eV, which is corresponding to the nitrogen in the five-membered ring of PVP [37]. When PVP 55 K was mixed with uncalcined KNN–LN, two peaks at 399 eV and 400.7 eV were observed. According to the literature, the smaller peak at the higher binding energy of N 1s is attributed to the –N$^+$– species [38]. This suggested again that metal cations could have interacted with the nitrogen in PVP. This is reasonable because when positively charged K$^+$ or Na$^+$ is attracted to the nitrogen in PVP, electrons from the nitrogen could move towards K$^+$ or Na$^+$, which could cause the decrease of electron density in nitrogen and hence increase its binding energy [39]. Referring to Fig. 2, the interaction between the nitrogen of PVP and the K/Na helped to retain K and Na in the KNN–LN bulk ceramic.

Fig. 6 shows the XRD patterns of 0.94KNN–0.06LN ceramic powders with PVP of different molecular weights calcined at 500 °C for 5 h. The decomposition of these carbonates started around 420 °C [40] and therefore all the samples were calcined at 500 °C to examine the formation of perovskite phase at the initial reaction stage. The formation of perovskite phase could depend on the decomposition of the starting alkali carbonates to oxides and their reaction with Nb$_2$O$_5$ oxides. By examining the XRD peaks of Nb$_2$O$_5$ in Fig. 6, it can be noted that the formation of perovskite phase

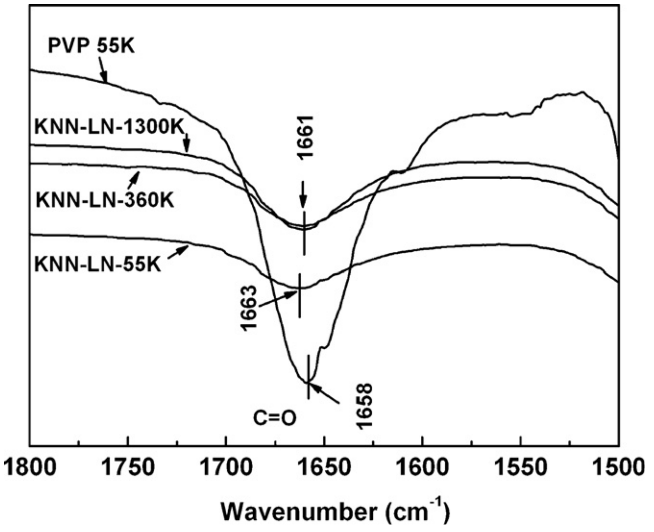

Fig. 4. Fourier transform infrared spectroscopy (FTIR) curves of uncalcined KNN–LN powders mixed with PVP of different molecular weights, in comparison with PVP 55 K.

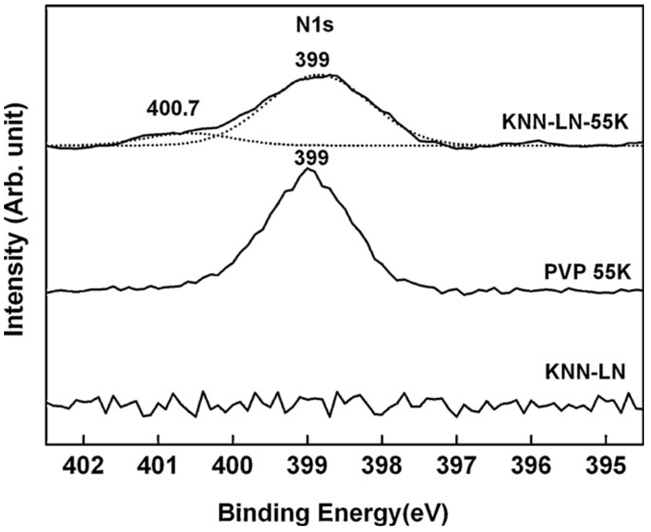

Fig. 5. XPS spectra of N 1s for uncalcined powders of PVP 55 K, KNN–LN-55 K and KNN–LN.

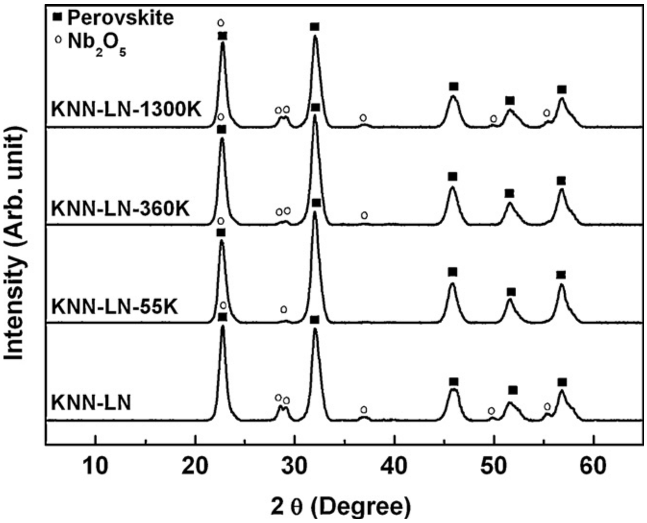

Fig. 6. X-ray diffraction (XRD) patterns of 0.94KNN–0.06LN powders with PVP of different molecular weights and without PVP, calcined at 500 °C for 5 h.

was promoted most effectively with PVP 55 K in KNN–LN-55 K with the least residual Nb_2O_5, and the increase in the molecular weight from 55 K to 1300 K limited the effect of PVP on promoting the formation of the perovskite phase with more unreacted Nb_2O_5 at 500 °C.

Fig. 7 presents the XPS spectra of K 2p for 0.94KNN–0.06LN ceramic powders with PVP of different molecular weights calcined at 500 °C for 5 h. The samples calcined at 500 °C for all samples with and without PVP showed two peaks for K 2p with binding energies (BE) at 295 eV and 292 eV labeled as K $2p_{1/2}'$ and K $2p_{3/2}'$, respectively, which were attributed to K ions before crystallized into perovskite phase. Another two peaks for all the samples, labeled as K $2p_{1/2}$ and K $2p_{3/2}$, which shifted by ~1.5–1.6 eV toward lower binding energy (BE) from K $2p_{1/2}'$ and K $2p_{3/2}'$, respectively, were attributed to the ions in KNN perovskite phase [32,41] As evident in Fig. 7, the peaks of K $2p_{1/2}'$ and K $2p_{3/2}'$, which were very intensive in KNN–LN samples, were almost eliminated in KNN–LN-55 K. This XPS analysis result also strongly indicated the effect of PVP 55 K for promoting the formation of perovskite structure in the solid state reaction for preparing the KNN–LN bulk ceramic. However, with the increase of molecular weight of PVP as in KNN–LN-360 K and KNN–LN-1300 K samples, more K ions could not form the perovskite structure at 500 °C. The XPS analyses on the amount of residual unreacted K ions are consistent with the XRD results on the residual unreacted Nb_2O_5 in all the samples without PVP and with PVP of different molecular weights.

Fig. 8 shows the XPS spectra of O 1s for 0.94KNN–0.06LN ceramic powders with PVP of different molecular weights calcined at 500 °C for 5 h. By analyzing the C=O peaks at 500 °C, the information about the decomposition of carbonates in the samples could be obtained. It was noted that the carbonates decomposed faster for KNN–LN-55 K samples as compared to KNN–LN-360 K, KNN–LN-1300 K and KNN–LN samples, as shown in Fig. 8.

Previously, our group observed that the alkali ions in KNN material were much more volatile during the preparation at the moderate temperature before the formation of the perovskite phase than after the formation at high temperature [32]. Once the alkali ions entered the lattice of the perovskite structure, they would be much more stable. Therefore, we believe retaining the alkali ions at the moderate temperature is critical to obtaining high quality KNN–LN ceramic. The results here showed the interactions between PVP and alkali ions, and further exhibited the role of introducing PVP for retaining the alkali composition in KNN–LN ceramic. Thus introducing PVP in the starting raw materials may be an effective method for obtaining stoichiometric KNN–LN and other ceramics with volatile alkali ions.

In order to understand other effects of the different molecular weight, the thermal decompositions of PVP powders with different molecular weights were characterized using TGA–DSC, as shown in Fig. 9. The TGA showed the

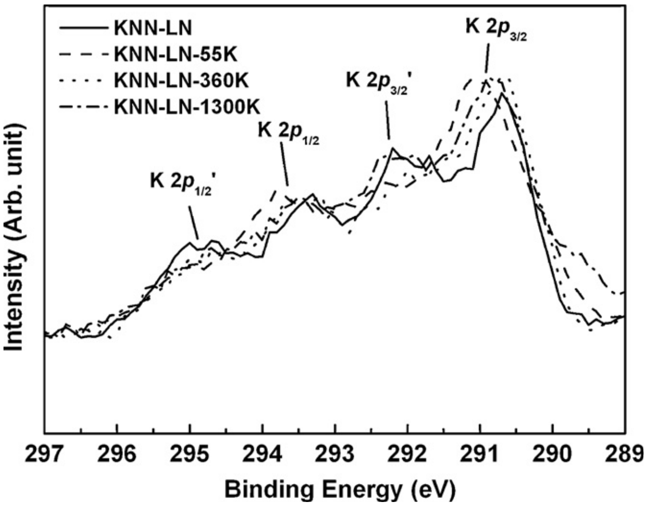

Fig. 7. XPS spectra of K 2p for 0.94KNN–0.06LN ceramic powders with PVP of different molecular weights and without PVP, calcined at 500 °C for 5 h.

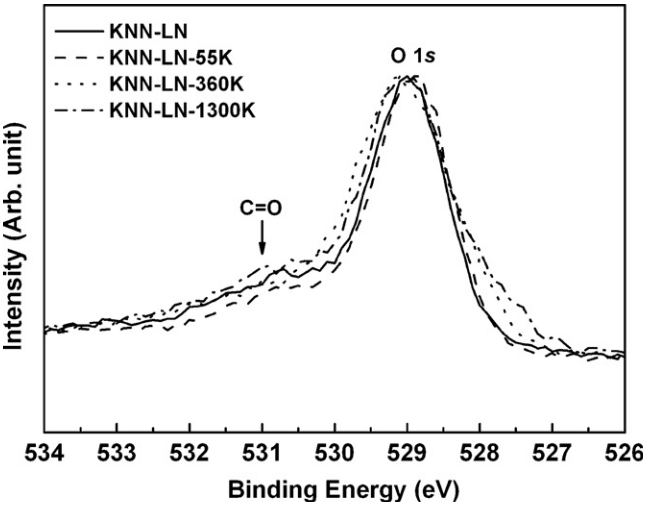

Fig. 8. XPS spectra of O 1s for 0.94KNN–0.06LN ceramic powders with PVP of different molecular weights and without PVP, calcined at 500 °C for 5 h.

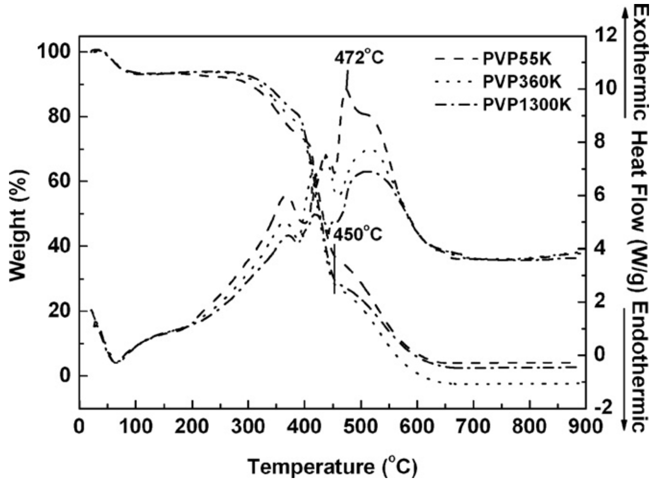

Fig. 9. Thermogravimetry–differential scanning calorimetry (TGA–DSC) curves for PVP powders of different molecular weights.

decomposition of PVP 55 K, PVP 360 K, and PVP 1300 K mainly happened between 300 and 550 °C. By observing the exothermic peaks, PVP 55 K had more intense exothermic peak at 472 °C with much higher heat flow generated as compared to PVP 360 K and PVP 1300 K. According to literature [42], thermal degradation of PVP is the depolymerization of polymeric main chain into monomer beginning from both ends of the linear polymer chain. For a given mass, PVP 55 K has more chain ends than PVP with higher molecular weight. Therefore, PVP 55 K could break more quickly than PVP 360 K and PVP 1300 K to facilitate the exothermic pyrolysis process. The short polymer chain means less endothermic decomposition and more heat generated. This intense heat generated between around 450 and 472 °C for PVP could act as in situ heat source to promote the perovskite phase formation. It is believed that the more in situ heat generated from PVP 55 K would more significantly promote the decomposition of carbonates and enhance the perovskite phase formation as confirmed by the XRD and XPS results shown in Figs. 6–8.

4. Conclusions

0.94KNN–0.06LN ceramics were prepared by solid state reaction process modified by introducing PVP in the starting raw materials. Our experimental results revealed that the addition of PVP suppressed the loss of alkali ions and promoted the perovskite phase formation. Further characterization and analyses showed the chemical interaction between the metal cations and the PVP, particularly through the N in PVP. The heat generated by the decomposition of PVP could act as an in situ heat source to promote the decomposition of the raw carbonates and the formation of the perovskite phase formation. With molecular weight ranging from 55 K to 1300 K, PVP with lower molecular weight exhibited more significant effect. Ceramic samples obtained with PVP 55 K addition under normal air sintering exhibited an improved piezoelectric constant d_{33} of 140 pC/N and a planar electromechanical coupling factor k_p of 0.35. This study showed that introducing PVP in the starting raw materials may be an effective method for obtaining stoichiometric KNN–LN and other ceramics with volatile alkali ions.

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