DE GRUYTER Energy Harvesting and Systems 2015; 2(3-4): 149–152

Review

Lin-Lin Yao, Li-Xia Ji, Kong-Jun Zhu*, Jing Wang, Jing-Song Liu and Jin-Hao Qiu

Effect of A-Site Ion Excess on (K, Na)NbO_3 Thin Film Fabricated by Sol–Gel Non-alkoxide Process

Abstract: Lead-free (K, Na)NbO_3(KNN) ferroelectric films were fabricated on Ti substrates by sol–gel non-alkoxide process. Nb_2O_5 was used to prepare the soluble niobium source by citrate method. KNN thin films with perovskite phase were obtained by pyrolyzing at 500°C and annealing at 700°C. The influence of A-site ion excess on the phase, microstructure and electric properties of the films was investigated. X-ray diffraction and energy-dispersive spectroscopy (EDS) data indicate that the volatilization of K was severer than Na during the thermal treatment, and K excess is assisted to get pure perovskite phase. Meanwhile, the *P–E* loops and the dielectric curves manifest that K excess plays a role to improve the ferroelectric performance, while Na excess contributes to good dielectric property.

Keywords: KNN films, non-alkoxide, sol–gel process, A-site ion excess, electric property

DOI 10.1515/ehs-2014-0035

Introduction

Ferroelectric films have captured more and more attention due to the demand of the miniaturization of micromechanics and microelectronic components (Setter et al. 2006). Currently, the most widely used ferroelectric material is lead zirconate titanate (PZT)-based ferroelectric materials (Tseng et al. 2013; Park et al. 2014), which contain more than 60% harmful lead. For environment protection, lead-free ferroelectric materials have been receiving increasing attention (Shrout and Zhang 2007). Among these several lead-free ferroelectric materials (Jo et al. 2013; Wang et al. 2013; Wolny 2005; Yi and Ye 2007), (K, Na)NbO_3(KNN) with typical perovskite structure has been excepted as a promising candidate material because of its high Curie temperature and good electric properties.

Sol–gel method (Kang et al. 2011) is used to prepare KNN thin films because it allows high homogeneity, low temperature fabrication and the precise control of chemical composition. However, the ethanol niobium used as niobium source is easily deliquescent which brings much inconvenience for preparation. Moreover, it is difficult to get saturated *P–E* hysteresis loops and high piezoelectric properties due to large leakage current resulted from the volatilization of A-site alkaline ions during the thermal process. To decrease the volatilization of alkaline ions, Ahn et al. (2009) and Li et al. (2013) investigated the effect of alkaline ions excess to compensate for loss of K and Na, which exhibited relatively good electrical properties with single phase and low leakage current, while Lee et al. (2011) and Wang et al. (2014) certified that doping Mn can effectively improve electric performance by reduce the oxygen vacancies caused by the volatilization of A-site alkaline ions.

In this study, niobium pentoxide (Nb_2O_5) was used to prepare niobium hydroxide {$Nb(OH)_5$} regarded as the niobium source which has high activity. Besides, the effect of A-site alkaline ion excess on KNN thin films was investigated.

***Corresponding author: Kong-Jun Zhu,** State Key Laboratory of Mechanics and Control of Mechanical Structure, Nanjing University of Aeronautics and Astronautics, Nanjing, China,
E-mail: kjzhu@nuaa.edu.cn
Lin-Lin Yao, State Key Laboratory of Mechanics and Control of Mechanical Structure, Nanjing University of Aeronautics and Astronautics, Nanjing, China; College of Material Science and Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing, China, E-mail: Y001989@163.com
Li-Xia Ji, Linyi People's Hospital, Linyi 276003, China,
E-mail: LyxqyL@163.com
Jing Wang, State Key Laboratory of Mechanics and Control of Mechanical Structure, Nanjing University of Aeronautics and Astronautics, Nanjing, China, E-mail: wang-jing@nuaa.edu.cn
Jing-Song Liu, State Key Laboratory of Mechanics and Control of Mechanical Structure, Nanjing University of Aeronautics and Astronautics, Nanjing, China; College of Material Science and Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing, China, E-mail: jsliu@nuaa.edu.cn
Jin-Hao Qiu, State Key Laboratory of Mechanics and Control of Mechanical Structure, Nanjing University of Aeronautics and Astronautics, Nanjing, China, E-mail: qiu@nuaa.edu.cn

Experimental Procedure

To prepare the KNN precursor solution, high active $Nb(OH)_5$ obtained by dissolving Nb_2O_5 into hydrofluoric acid (HF), potassium carbonate (K_2CO_3) and sodium carbonate (Na_2CO_3) were used as niobium source, potassium source, sodium source, respectively. Besides, citric acid and ethylene glycol were acted as chelating agent and esterifying agent, respectively. To study the effect of alkaline ions excess on the films, different alkaline metal excess were added into the precursor solution, that is 20 mol% K excess ($K_{0.6}Na_{0.5}NbO_3$), 20 mol% Na excess ($K_{0.5}Na_{0.6}NbO_3$), meanwhile the molar ratio of $n(K + Na)/n(Nb)$ was fixed at 1.1. The concentration of the final solution was adjusted to approximately 0.25 mol/L.

To obtain KNN thin films, the precursor solutions were spin coated on 1 cm × 1 cm Ti substrate with the rate of 3,000 rpm for 30 s. The wet films were dried at 150°C for 5 min on a hot plate. Subsequently, the dried gel films were pyrolyzed at 500°C for 10 min using a muffle furnace. The coating–drying–pyrolysis circle was repeated for several times to obtain a desire thickness. Finally, these films were annealed at 700°C for 30 min.

The crystallographic phases of the prepared thin films were identified by X-ray diffraction (XRD; Bruker D8 Advance, Germany) analysis using Cu-K_α radiation ($\lambda = 0.15418$ nm). The chemical composition was analyzed by energy-dispersive spectroscopy (EDS). The morphologies of the thin films were characterized by FESEM (Hitachi-S4800, Japan). The ferroelectric property was analyzed using a ferroelectric test system (Radiant Technologies, USA) at room temperature. The dielectric constant was measured using an impedance analyzer (4294A, Agilent Technologies, USA).

Results and Discussion

Figure 1 shows the XRD patterns of KNN thin films annealed at 700°C with different A-site ions excess. The KNN thin films are pure perovskite phase, except a Na-rich phase (i.e. $Na_2Nb_4O_{11}$) appears when the Na excess is 20 mol%, as shown in Figure 1(b) and (c). The emergence of Na-rich phase is attributed to the loss of stoichiometric resulted from the volatilization of potassium ions. While no similar situation occurs to the 20 mol% K excess thin films, it is deduced that K volatilized easier than Na. Besides, the XRD pattern of KNN thin film with no alkali ion excess is also shown in Figure 1(a); this film shows a weaker KNN perovskite phase consisted of a weak Na-rich phase, which also indicates K is easier to volatilize.

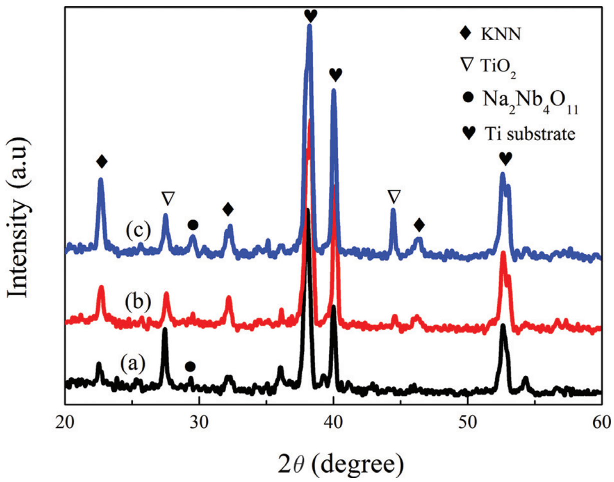

Figure 1: XRD patterns of KNN thin films with different A-site ions excess: (a) no alkali ion excess, (b) 20% K excess and (c) 20% Na excess.

Table 1: EDS data of KNN thin films with different A-site ion excess (data inside the parentheses represent the theoretical values).

Sample	K/Na	(K + Na)/Nb
20 mol% K excess	1.47 (1.2)	0.79 (1.1)
20 mol% Na excess	0.36 (0.83)	1.07 (1.1)

The EDS data is shown in Table 1; the values of $n(K)/n(Na)$ are 1.47, 0.36 of $K_{0.6}Na_{0.5}NbO_3$ and $K_{0.5}Na_{0.6}NbO_3$ thin films, respectively. Compared to the theoretical values, the composition of the $K_{0.5}Na_{0.6}NbO_3$ sample has much inaccuracy. On the other hand, the values of $n(K+Na)/n(Nb)$ are 0.79 and 1.07, respectively. Compared to the theoretical value 1.1, the $K_{0.6}Na_{0.5}NbO_3$ has large deviation. All these illustrated that the volatilization of K is severer so that the values of $n(K)/n(Na)$ and $n(K+Na)/n(Nb)$ are gravely deviated from the theoretical values, which correspond to the results of XRD.

Figure 2 shows the SEM images of KNN thin films with different alkali excess. The films are dense, while

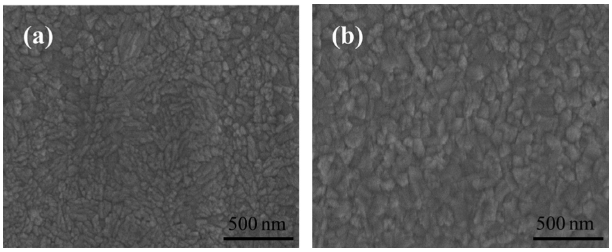

Figure 2: SEM images of KNN thin films with various alkaline ions excess: (a) 20% K excess and (b) 20% Na excess.

the grain size of $K_{0.6}Na_{0.5}NbO_3$ is smaller, which indicates that K excess can restrain the growth of the grains. The possible reason is that the volatilization of excessive K ions promotes a large amount of Ti ions diffuse from the substrates into the films which accumulate around the grain boundaries and restrain the growth of grains (Goh, Yao, and Chen 2009).

Figure 3 shows the *P–E* hysteresis loops and dielectric constant (*K*) of $K_{0.6}Na_{0.5}NbO_3$, $K_{0.5}Na_{0.6}NbO_3$ and $K_{0.5}Na_{0.5}NbO_3$ thin films. The loops of the $K_{0.6}Na_{0.5}NbO_3$ and $K_{0.5}Na_{0.6}NbO_3$ films are typical and integrated, and the $K_{0.6}Na_{0.5}NbO_3$ shows better ferroelectricity. However, the $K_{0.5}Na_{0.5}NbO_3$ can't obtain an integrated *P–E* hysteresis loop. It indicates that A-site ions excess can improve the ferroelectric property.

The leakage current density of the KNN films is plotted against electric field and is shown in Figure 4. The current density of $K_{0.6}Na_{0.5}NbO_3$ film is slightly lower than $K_{0.5}Na_{0.6}NbO_3$ film which is in accordance with the results of the *P–E* hysteresis loops. However, the current density also looks good at high electric field which is different from the other reports (Abazari and Safari 2010; Wu and Wang 2009), it may be resulted from the existence of TiO_2 phase, it reduces the electrical conductivity of the substrates, which finally affects the quality of the interface between the KNN film and the metal electrode.

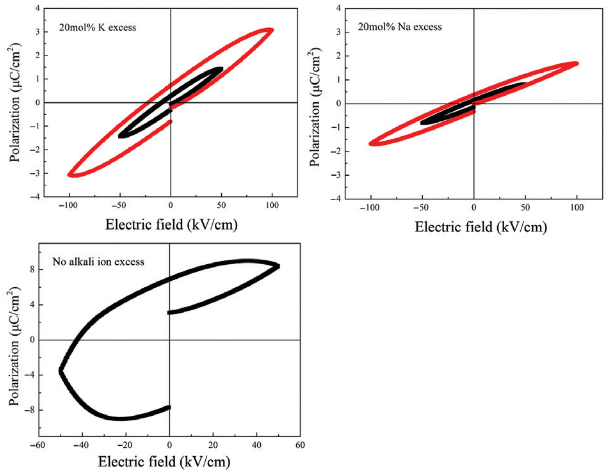

Figure 3: The *P–E* hysteresis loops of KNN thin films with different A-site ions excess measured at 1 KHz (thickness of the films was 200 nm).

Figure 5 shows dielectric constant (*K*) and dielectric loss of $K_{0.6}Na_{0.5}NbO_3$ and $K_{0.5}Na_{0.6}NbO_3$ thin films. The $2P_r$ and K of $K_{0.6}Na_{0.5}NbO_3$ thin film are 1.6 μC/cm^2 and 242 at 1 KHz, respectively, which are found slightly higher than that of $K_{0.5}Na_{0.6}NbO_3$, where the $2P_r$ and K are 0.53 μC/cm^2 and 185 at 1 KHz, respectively. However, the dielectric constant of $K_{0.6}Na_{0.5}NbO_3$ thin film decreases sharply at low frequency, which is attributed to the secondary phase of $Na_2Nb_4O_{11}$, as well as the non-ferroelectric TiO_2 phase, while the $K_{0.5}Na_{0.6}NbO_3$ thin film keeps falling slowly as the frequency increased. Moreover, the dielectric loss of the $K_{0.5}Na_{0.6}NbO_3$ thin film is smaller as the frequency increases.

It is demonstrated that the KNN film shows better ferroelectric property as the K/Na is close to 1. In contrast, high concentration of oxygen vacancies will be formed when the (K + Na)/Nb is seriously deviated to 1, which is the main reason for the poor electric properties.

However, all the ferroelectric *P–E* hysteresis loops of KNN thin films as shown in Figure 3 are not fully saturated as compared with previous reports (Lu et al. 2014). The possible reasons are as follows. The mass formation of oxygen vacancies due to the volatilization of A-site ions, which also result in loss of stoichiometry, causes

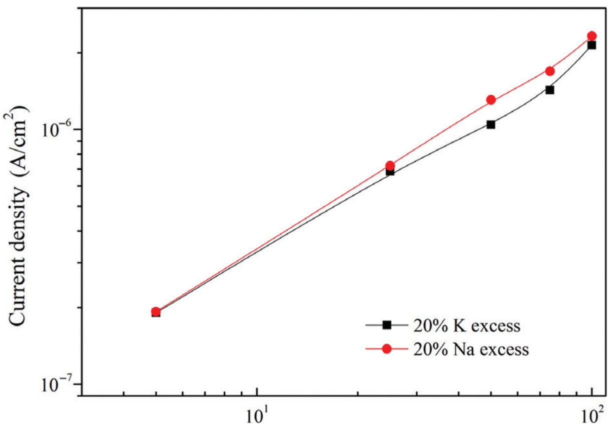

Figure 4: The leakage current density curves of $K_{0.6}Na_{0.5}NbO_3$ and $K_{0.5}Na_{0.6}NbO_3$ films.

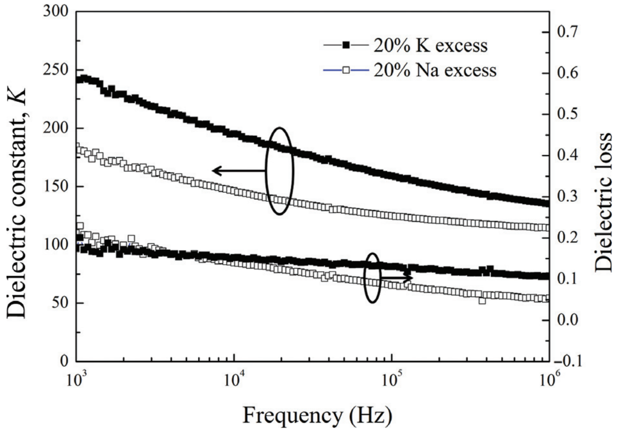

Figure 5: Plots of dielectric constant and dielectric loss versus frequency for $K_{0.6}Na_{0.5}NbO_3$ and $K_{0.5}Na_{0.6}NbO_3$ thin films.

serious leakage current. Besides, the oxygen vacancies together with other defects such as the Ti ions diffused into the films during the thermal process have pining effect on domain walls, which make it harder for the domain walls to turn over (Jin, Li, and Zhang 2014).

Conclusions

In conclusion, the KNN thin films were successfully fabricated by sol–gel non-alkoxide process with citrate precursor solution. The excess of A-site ions can improve the ferroelectricity. Single perovskite phase was obtained as the potassium ions have 20% excess. The volatilization of alkali metals resulting in high concentration of oxygen vacancies has a great influence on the electric properties of KNN thin films. As the K/Na is close to 1, the films show better ferroelectric performance. On the other hand, the films have higher stability of dielectric property as the (K + Na)/Nb is close to 1. That is, K excess is conducive to improve the ferroelectric performance, while Na excess contributes to good dielectric property.

Funding: This work was supported by the National Nature Science Foundation of China (NSFC Nos. 51172108 and 51202118) and the Doctoral Fund of the Ministry of Education of China (Grant No. 20120002120012). This project was funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD) and the NUAA Fundamental Research Funds (Nos NN2012018 and NP2013301).

References

Abazari, M., and A. Safari. 2010. "Leakage Current Behavior in Lead-Free Ferroelectric (K, Na)NbO_3-$LiTaO_3$-$LiSbO_3$ Thin Films." *Applied Physics Letters* 97 (26):262902.

Ahn, C. W., S. Y. Lee, H. J. Lee, et al. 2009. "The Effect of K and Na Excess on the Ferroelectric and Piezoelectric Properties of $K_{0.5}Na_{0.5}NbO_3$ Thin Films." *Journal of Physics D: Applied Physics* 42 (21):215304.

Goh, P. C., K. Yao, and Z. Chen. 2009. "Titanium Diffusion into $(K_{0.5}Na_{0.5})NbO_3$ Thin Films Deposited on Pt/Ti/SiO_2/Si Substrates and Corresponding Effects." *Journal of the American Ceramic Society* 92 (6):1322–7.

Jin, L., F. Li, and S. Zhang. 2014. "Decoding the Fingerprint of Ferroelectric Loops: Comprehension of the Material Properties and Structures." *Journal of the American Ceramic Society* 97 (1):1–27.

Jo, W., J. Daniels, D. Damjanovic, et al. 2013. "Two-Stage Processes of Electrically Induced-Ferroelectric to Relaxor Transition in 0.94 $(Bi_{1/2}Na_{1/2})TiO_3$-0.06$BaTiO_3$." *Applied Physics Letters* 102 (19):192903.

Kang, C., J. H. Park, D. Shen, et al. 2011. "Growth and Characterization of $(K_{0.5}Na_{0.5})NbO_3$ Thin Films by a Sol–Gel Method." *Journal of Sol-Gel Science and Technology* 58 (1):85–90.

Lee, S. Y., C. W. Ahn, A. Ullah, et al. 2011. "Effect of Mn Substitution on Ferroelectric and Leakage Current Characteristics of Lead-Free $(K_{0.5}Na_{0.5})(Mn_xNb_{1-x})O_3$ Thin Films." *Current Applied Physics* 11 (3):S266–S269.

Li, G., X. Wu, W. Ren, et al. 2013. "Effect of Excessive K and Na on the Dielectric Properties of (K, Na)NbO_3 Thin Films." *Thin Solid Films* 548:556–9.

Lu, T., K. Zhu, J. Liu, et al. 2014. "Lead-Free (K, Na)NbO_3 Thin Films Derived from Chemical Solution Deposition Modified with EDTA." *Journal of Materials Science: Materials in Electronics* 25 (2):1112–16.

Park, K. I., J. H. Son, G. T. Hwang, et al. 2014. "Highly-Efficient, Flexible Piezoelectric PZT Thin Film Nanogenerator on Plastic Substrates." *Advanced Materials* 26 (16):2514–20.

Setter, N., D. Damjanovic, L. Eng, et al. 2006. "Ferroelectric Thin Films: Review of Materials, Properties, and Applications." *Journal of Applied Physics* 100 (5):051606.

Shrout, T. R., and S. J. Zhang. 2007. "Lead-Free Piezoelectric Ceramics: Alternatives for PZT?." *Journal of Electroceramics* 19 (1):113–26.

Tseng, H. J., W. C. Tian, W. J. Wu, and P. Z. T. Flexible. 2013. "Thin Film Tactile Sensor for Biomedical Monitoring." *Sensors* 13 (5):5478–92.

Wang, H., X. Zhai, J. Xu, et al. 2013. "Effects of CuO Doping on the Structure and Properties Lead-Free KNN-LS Piezoelectric Ceramics." *Journal of Materials Science: Materials in Electronics* 24 (7):2469–72.

Wang, L., W. Ren, P. Shi, et al. 2014. "Effects of Thickness on Structures and Electrical Properties of Mn-Doped $K_{0.5}Na_{0.5}NbO_3$ Films." *Journal of Alloys and Compounds* 582:759–63.

Wolny, W. W. 2005. "Application Driven Industrial Development of Piezoceramics." *Journal of the European Ceramic Society* 25 (12):1971–6.

Wu, J., and J. Wang. 2009. "Phase Transitions and Electrical Behavior of Lead-Free $(K_{0.50}Na_{0.50})NbO_3$ Thin Film." *Journal of Applied Physics* 106 (6):066101–066101–3.

Yi, Z. G., and J. H. Ye. 2007. "Band Gap Tuning of $Na_{1-x}La_xTa_{1-x}Co_xO_3$ Solid Solutions for Visible Light Photocatalysis." *Applied Physics Letters* 91 (25):254108–254108-3.