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Effects of excess amount of K and Na on properties of $(K_{0.48}Na_{0.52})NbO_3$ thin films

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Abstract

The excess amounts of K and Na in precursor solutions are very important for the phase structure and performance of $(K_{0.48}Na_{0.52})NbO_3$ (KNN) thin films because of their volatilization loss. However, there are no identical opinions have been reported that could describe which element is easily volatile. In this paper, different excessive amounts of K and Na are added simultaneously in precursor solutions, the lead-free KNN thin films are prepared by metallorganic compound decomposition (MOD) method. Through comparison of phase structures, dielectric properties, *J–E* characteristic and ferroelectric *P–E* hysteresis loops, the effects of chemical componential fluctuation of K and Na on properties of KNN thin films are discussed systematically.

Keywords: C. Electrical properties; Niobates thin films; MOD method; Excess K and Na

1. Introduction

Piezoelectric thin films are widely used as function materials, and they have been used extensively in transducer and sensor fields. Among all the piezoelectric materials, the most dominant one is still PZT which contains lead of more than 60%. Because of lead toxicity, people are working to find lead-free piezoelectric materials to replace PZT. Recently, sodium potassium niobate (KNN) piezoelectric material got an attention of the researchers because of its outstanding piezoelectric property, and is considered to be one of the main candidates for PZT piezoelectric. In KNN thin films, volatilization of alkali metal element is one of the most main reasons that affect the properties of KNN films. In order to improve the properties of KNN thin films, excess amounts of potassium and sodium are added, which can compensate the volatilization loss of alkali metal elements. Tanaka et al. [1] studied phase structure of KNN thin films prepared by sol–gel method with different K/Na ratios. After adding 10 mol% excess amount of Na, $K_4Nb_6O_{17}$ phase disappeared. So they thought that $K_4Nb_6O_{17}$ was a secondary-phase lacking Na. Lai and Li [2,3] also prepared KNN thin films by sol–gel method and reported that $K_2Nb_4O_{11}$ phase appeared in the films was a kind of phase lacking Na. Nakashima et al. [4] analyzed KNN thin films with different K/Na ratios through Raman Spectrum. They concluded that K was easier to volatilize than Na, and the reasonable value of total excess amount of K and Na was between 4 and 10 mol%. To sum up, there are no identical conclusions in publications, which is easily volatile for K and Na.

According to our opinions, under the same heat treatment conditions, the volatilization amount is different for K and Na. In this paper, we investigated the effects of different excess amount of K and Na on the properties of $(Na_{0.52}K_{0.48})$ NbO_3 (KNN) thin films.

2. Experimental procedures

Sodium acetate (CH_3COONa), potassium acetate (CH_3COOK) and niobium ethoxide ($Nb(OC_2H_5)_5$) were used as raw chemicals, and niobium ethoxide ($Nb(OC_2H_5)_5$) was synthesized in our laboratory [5]. 2-Methoxyethanol and acetic acid were selected as solvent. According to different ratios of elements, appropriate amounts of CH_3COONa and CH_3COOK were dissolved in mixed solution of 2-methoxyethanol and acetic acid, with continuous stirring for 30 min at room temperature. Acetylacetone was added into the solution to enhance the stability of $Nb(OC_2H_5)_5$, then $Nb(OC_2H_5)_5$ was mixed into the

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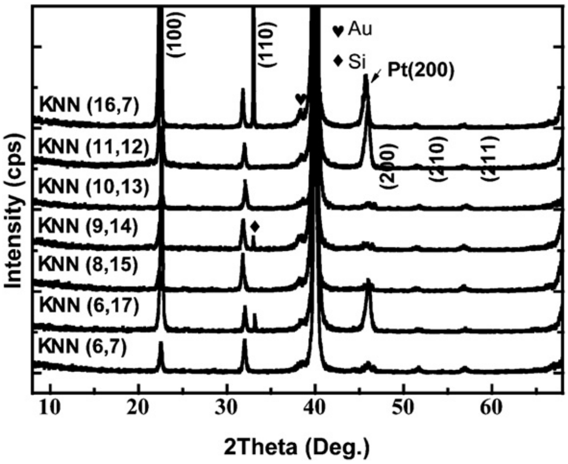

Fig. 1. XRD patterns of various KNN thin films sintered at 600 °C.

mixture with stirring at room temperature. The molar ratio of acetylacetone to $Nb(OC_2H_5)_5$ was 1:1. Finally, the mixture was heated at 120 °C for 30 min in rotary evaporators. The concentration of the KNN precursor solution is 0.3 M.

The KNN precursor was spin-coated on $Pt/TiO_2/SiO_2/Si$ substrates at 3000 rpm for 30 s. The wet films were dried at 200 °C for 2 min, pyrolyzed at 350 °C for 3 min and sintered separately at 450 °C, 500 °C, 550 °C, 600 °C, 650 °C, 700 °C for 5 min in the air using a rapid thermal annealing (RTA) furnace with a heating rate of 50 °C/s. In order to increase film thickness, these processes were repeated for 6 times. The thickness of various KNN thin films is about 250 nm.

The crystal structure of KNN films was identified by Rigaku D/MAX2400 X-ray diffractometer with Cu *Kα* radiation. The dielectric properties were measured using an Agilent 4294A precision impedance analyzer, and the ferroelectric *P–E* hysteresis loops were measured using aixACCT TF Analyzer 2000 system. Current voltage (*I–V*) characteristics were examined with a semiconductor characterization system (4200-SCS, Keithley).

3. Results and discussion

Based on $(K_{0.48}Na_{0.52})$ NbO_3 (KNN) composition for preparation of the films, keeping total excess value at 23 mol% for both K plus Na. The sample conditions are listed in Table 1. In addition, the KNN thin films sintered at 600 °C possesses better property, so comparison is done only for the films sintered at 600 °C.

Table 1
Formula ratios with different excess amount of K and Na for KNN thin films.

Number	Formulas for short	Formulas
No. 1	KNN(6,7)	$(K_{0.48}Na_{0.52})NbO_3$ + K 6 mol% + Na 7 mol%
No. 2	KNN(6,17)	$(K_{0.48}Na_{0.52})NbO_3$ + K 6 mol% + Na 17 mol%
No. 3	KNN(8,15)	$(K_{0.48}Na_{0.52})NbO_3$ + K 8 mol% + Na 15 mol %
No. 4	KNN(9,14)	$(K_{0.48}Na_{0.52})NbO_3$ + K 9 mol% + Na 14 mol%
No. 5	KNN(10,13)	$(K_{0.48}Na_{0.52})NbO_3$ + K 10 mol% + Na 13 mol%
No. 6	KNN(11,12)	$(K_{0.48}Na_{0.52})NbO_3$ + K 11 mol% + Na 12 mol%
No. 7	KNN(16,7)	$(K_{0.48}Na_{0.52})NbO_3$ + K 16 mol% + Na 7 mol%

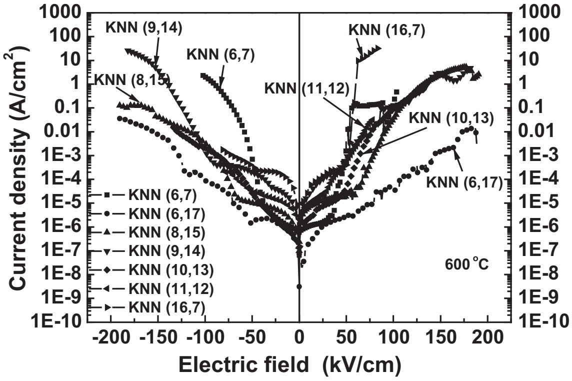

Fig. 3. *J–E* curves of various KNN thin films.

The XRD patterns of the KNN thin films with different excess amounts of K and Na are shown in Fig. 1. It can be seen that all of KNN thin films possess a pure KNN phase. Electrical properties of these KNN thin films are listed in Table 2. Dependence of dielectric property on frequency is shown in Fig. 2. Fig. 3 shows the curves of leakage current density (*J*) and electric fields (*E*). Fig. 4 shows the *P–E* hysteresis loops and *J–E* curves of *P–E* hysteresis loops.

From Table 2 and Fig. 3, it can be seen that KNN(6,17) film with more excess Na has the smallest value of dielectric loss (2%), and its leakage current density reaches to minimum and increases slowly with increasing electric fields. Compared with

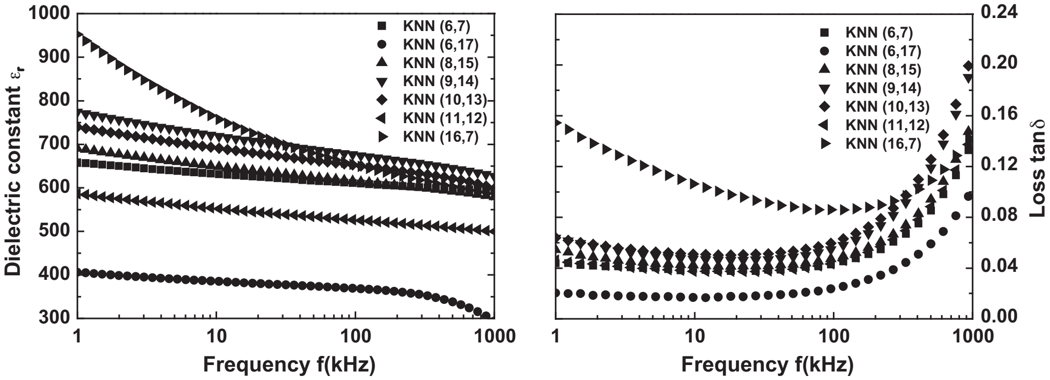

Fig. 2. Frequency dependency of dielectric properties various KNN thin films.

Table 2
Dielectric properties and leakage current density of various KNN thin films.

	KNN(6,7)	KNN(6,17)	KNN(8,15)	KNN(9,14)	KNN(10,13)	KNN(11,12)	KNN(16,7)
ε_r (at 1 kHz)	658	405	690	774	739	586	952
tan δ	0.04	0.02	0.05	0.06	0.06	0.05	0.15
J (A/cm^2) at ±50 kV/cm	2.8×10^{-3}	2.1×10^{-6}	1.7×10^{-5}	5.1×10^{-4}	3.6×10^{-5}	3.3×10^{-5}	3.8×10^{-4}
J (A/cm^2) at ±80 kV/cm	2.4×10^{-1}	2.6×10^{-5}	1.2×10^{-3}	1.6×10^{-2}	8.3×10^{-3}	1.6×10^{-2}	1.4×10^{1}

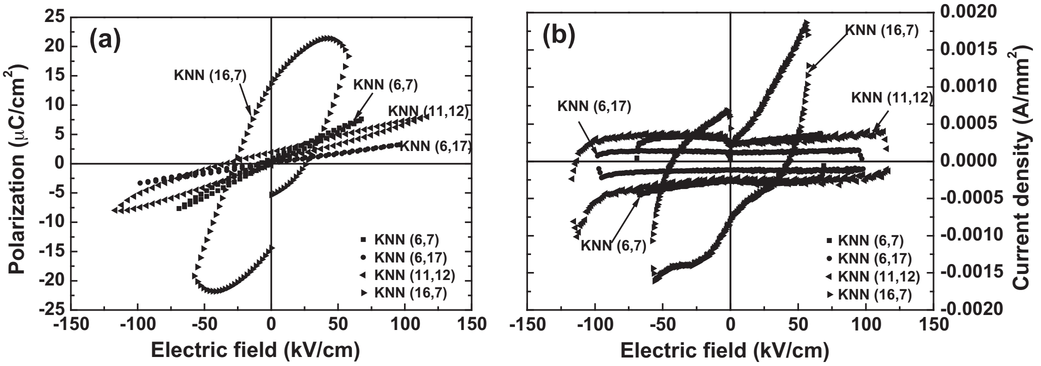

Fig. 4. *P–E* hysteresis loops (a) and *J–E* loops (b) various KNN thin films.

KNN(6,17), KNN(6,7) film with equal excess K and less 10 mol% excess Na shows smaller dielectric loss of 4% but the value of leakage current density increase sharply with increasing electric fields. It implies that the large *J* values resulted from severe lack of Na. This viewpoint is the same as that of Tanaka et al. [1].

The properties among KNN(8,15), KNN(9,14), KNN(10,13) and KNN(11,12) thin films have little differences. In Fig. 2 and Table 2, the dielectric losses of four samples are in the range of 5–6%, leakage current increases obviously with increasing electric fields. These results indicate that the properties deteriorate with K increase and Na decrease compared with KNN(6,17) film. Especially, for KNN(16,7) sample, the value of dielectric loss reaches to 15% under 1 kHz frequency, and dielectric constant descends sharply with increasing frequency. Moreover, the value of J increase faster with increasing electric fields (see Fig. 3) and its fat *P–E* hysteresis loop proves property degradation again in Fig. 4. It is a reasonable reason that bad property of the KNN(16,7) film is result from K residue on crystal boundary and lake of Na in crystal structure.

From the above results, some discussions can be made: first, the critical values of excess K and Na are different because of larger volatility of Na. Second, although properties of the KNN(6,17) thin films are better than that of other KNN thin films, the leakage current density increase obviously at higher voltage, and the J value of 2.1×10^{-6} A/cm^2 under ±50 kV/cm is still larger for application. This indicates that values of excess amount of K and Na in KNN(6,17) formula may be not optimal value. Third, no matter how much excessive amount of K and Na is in the precursors, all of the XRD patterns of KNN thin films in Fig. 1 show a pure phase. There may be two reasons: one is XRD measuring accuracy, that 5% secondary-phase cannot be apperceived. The other one is the existence of amorphous K and Na oxide. Fourthly, the current peaks produced by electric domain rotation in *P–E* hysteresis loops cannot be found from the current loops. This phenomenon is relative to a large leakage current probably. A slim *P–E* hysteresis loop proves that the KNN thin films have a weak ferroelectricity. In a word, the properties of KNN thin films are affected by many issues, such as intrinsical structure characteristics, vacancy and residua due to inappropriate compensation of alkali metals, interface, stress, thin thickness, etc.

4. Conclusions

There is a different critical value for excess K and Na in KNN system. The excess amount of Na should be more than K because Na is easier to volatilize than K. When the excess values of Na and K are 17 mol% and 6 mol% separately, the property of the KNN thin films becomes better in our experiments.

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