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Isopropanol-assisted hydrothermal synthesis of (K, Na)NbO_3 piezoelectric ceramic powders

Likui Su · Kongjun Zhu · Jinhao Qiu · Hongli Ji

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Abstract (K, Na)NbO_3 particles were synthesized using the isopropanol-assisted hydrothermal method. The addition of isopropanol made it possible to prepare (K, Na)NbO_3 solid solutions under a mild hydrothermal condition of 2 mol/L alkali solution. The effects of the K/(K + Na) molar ratio, (K + Na)/Nb molar ratio in the starting suspensions, and annealing process on the phase evolutions of the (K, Na)NbO_3 solid solutions were investigated. The phases of the as-prepared particles were investigated by X-ray diffraction technique. The microstructure and composition were analyzed by scanning electron microscope and energy dispersive X-ray analysis. (K, Na)NbO_3 solid solutions were successfully synthesized by hydrothermal method with the addition of isopropanol through adjusting the K/(K + Na) molar ratio and (K + Na)/Nb molar ratio in the starting suspensions. The change of morphology is also in agreement with the phase evolution. The phase evolutions were discussed and the formation mechanism of the (K, Na)NbO_3 solid solutions was proposed.

Introduction

Piezoelectric ceramic plays an important role in the field of electrical devices as well as smart materials and structures, such as ultrasonic generators, filters, actuators, sensors, and so on. Lead-based ceramics, typically lead zirconium titanate (PZT) family, have been widely used during the last several decades because of their excellent piezoelectric and electromechanical properties [1]. However, due to the well-known fact that the toxic lead oxide is harmful to environment and human health, there is a rising concern about developing lead-free piezoelectric ceramics. Fortunately, high-electromechanical properties have also been found in potassium sodium niobate [(K, Na)NbO_3, (KNN)] solid solution systems [2–4]. Recently, KNN-based ceramics have received more attention as candidates to replace lead-based piezoelectric ceramics after Saito et al. [5] made a breakthrough in this kind of lead-free ceramics.

However, it is difficult to obtain dense KNN ceramics via conventional solid-state reaction technique because of Na_2O and K_2O evaporation during sintering process. In addition, the obtained specimens are hard to be poled due to the Na and K vacancy [2, 6]. Therefore, it is necessary to decrease sintering temperature in order to minimize the Na_2O evaporation and eventually improve the piezoelectric properties of the specimens by increasing their polling efficiency. Sintering aids such as $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$, CuO, and MnO_2 were added to decrease the sintering temperature in the past [6–8]. Moreover, ferroelectric and piezoelectric properties of $BaTiO_3$ ceramic strongly depend on small grain size and nanodomain [9–11]. It is well known that hydrothermal method is a wet-chemical technique for preparing the pure, fine, active, homogeneous crystalline powders, which has higher sinterability. Our previous work [12] revealed that $BaTiO_3$ lead-free ceramics sintered from hydrothermally synthesized powders exhibited excellent piezoelectric properties.

$KNbO_3$ and $NaNbO_3$ powders have been synthesized by hydrothermal method successfully [13–16]. However, the

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L. Su · K. Zhu (✉) · J. Qiu · H. Ji
Key Laboratory of Vehicle Structural Mechanics and Control of Ministry of Education, Nanjing University of Aeronautics and Astronautics, 210016 Nanjing, People's Republic China
e-mail: kjzhu@nuaa.edu.cn

K. Zhu
State Key Lab of Digital Manufacturing Equipment and Technology of China, Huazhong University of Science and Technology, 430074 Wuhan, People's Republic China

(K, Na)NbO$_3$ solid solution particles, especially those with the composition of K$_{0.5}$Na$_{0.5}$NbO$_3$, has seldom been reported. That is due to Na reacts more readily with Nb to form NaNbO$_3$ than K. It is well known that the supersaturation of the precursors in the starting suspension affect their reaction activity seriously. Therefore, the relative concentrations of K, Na, and Nb play an important role in the formation of (K, Na)NbO$_3$ solid solution particles. How to get pure KNbO$_3$–NaNbO$_3$ solid solution powders with accurate composition of K$_{0.5}$Na$_{0.5}$NbO$_3$ by hydrothermal method has been a well-concerning focus. Xing et al. [17, 18] reported that single crystalline (K, Na)NbO$_3$ powders had been prepared by hydrothermal method. However, Zhang et al.'s work [19] revealed that NaNbO$_3$ and KNbO$_3$ phases coexisted in the KNN powders. Their studies show that it is very difficult to prepare the pure K$_{0.5}$Na$_{0.5}$NbO$_3$ powder by hydrothermal method.

(K, Na)NbO$_3$ powders could be synthesized by hydrothermal method only when the alkaline concentration is as high as 6 mol/L [18]. In some case, the alkaline concentration is even as high as 10 mol/L [17]. Such high alkalinity conditions usually causes serious corrosion of reaction vessel and results in more difficult waste treatment, thereby making it an obstacle for the industrial manufacture of this material [20]. It is well known that when the temperature and pressure of solvent is above its critical point, it has a dissolving ability similar to that of normal liquids but has better transport properties (such as viscosity, diffusivity, thermal conductivity, etc.) [21, 22]; therefore, it is considered that the chemical reactions should be accelerated in supercritical environment [23]. In comparison with the critical conditions of water ($T_C = 374$ °C, $P_C = 218.3$ atm), both parameters of isopropanol ($T_C = 235.3$°C, $P_C = 47.0$ atm) are much lower than those of water. It has reported that the required alkaline concentration for glycothermal synthesis of KNbO$_3$ was reduced to 0.5 M using isopropanol as solvent [23]. In this study, we attempt to reduce the alkalinity with the addition of isopropanol into the solution to synthesize (K, Na)NbO$_3$ powders via hydrothermal method, and investigate the effects of relative concentration of K-, Na-, and Nb-source in the starting suspensions on the phase evolutions of the products.

Experimental procedure

The raw materials consisted of analysis-grade niobium pentaoxide (Nb$_2$O$_5$, Sinopharm Chemical Reagent Co., Ltd, China), potassium hydroxide (KOH, Sinopharm Chemical Reagent Co., Ltd, China), and sodium hydroxide (NaOH, Sinopharm Chemical Reagent Co., Ltd, China). First, KOH and NaOH were dissolved separately in distilled water to prepare 5 mol/L alkali solution. Then, they were mixed each other with different K/(K + Na) molar ratio, and formed a mixed alkali solution. Twenty milliliters of these mixed alkali solution and 30 mL of the isopropanol were transferred into a 90 mL Teflon-lined autoclave and stirred for 30 min. Therefore, the OH$^-$ concentration in the solution was 2 mol/L. During the stirring process, Nb$_2$O$_5$ powders were added and milky suspensions were obtained. The content of the reactants in detail was listed in Table 1. Then, the autoclave was heated in an oven at 240 °C for 8 h. After cooling, the white powders obtained were washed to neutrality using the method of air pump filtration and then dried at 80 °C in air.

In order to investigate the phase evolution, some of the as-prepared particles were post-treated at the different temperatures from 500 to 900 °C for 4 h.

The microstructures and morphologies of the as-prepared particles were characterized by scanning electron microscope (SEM; FEI Quanta 200, the Netherlands). Elemental analysis for Nb, K, and Na was performed using energy dispersive X-ray analysis (EDX; EDAX, America). The crystal structure of the as-prepared particles was identified

Table 1 The samples synthesized under the different conditions

Sample no.	Volume of alkali solution (5 mol/L)		Isopropanol (mL)	Nb$_2$O$_5$ (g)	K/(K + Na) molar ratio	(K + Na)/Nb molar ratio
	KOH (mL)	NaOH (mL)				
KNN01	12	8	30	2.66	0.60	5:1
KNN02	14	6	30	2.66	0.70	5:1
KNN03	15	5	30	2.66	0.75	5:1
KNN04	16	4	30	2.66	0.80	5:1
KNN05	17	3	30	2.66	0.85	5:1
KNN06	18	2	30	2.66	0.90	5:1
KNN07	15	5	30	1.33	0.75	15:1
KNN08	16	4	30	1.33	0.80	15:1
KNN09	15	5	30	0.44	0.75	30:1
KNN10	16	4	30	0.44	0.80	30:1
KNN11	17	3	30	0.44	0.85	30:1

by powder X-ray diffraction (XRD; Bruker D8 Advance, Germany) using Cu Kα radiation ($\lambda = 0.15418$ nm).

Results and discussion

Effects of K/(K + Na) molar ratio

It has been reported in the reference [19] that Na reacted more readily with Nb to form $NaNbO_3$ than K. In our previous study, we found that the as-prepared particles was $NaNbO_3$, almost no K element coexist in the structure, when the K/(K + Na) molar ratio in the starting suspension was below 0.5. In order to obtain (K, Na)NbO_3 solid solution, vK/(K + Na) molar ratio from 0.6 to 0.9 in the starting suspension were decided in this study. The reaction equation under hydrothermal conditions could be written as follow:

$$KOH + NaOH + Nb_2O_5 \rightarrow 2(K_xNa_{1-x})NbO_3 + H_2O.$$

KOH, NaOH, and Nb_2O_5 act as K-source, Na-source, and Nb-source, respectively. The x value in $(K_xNa_{1-x})NbO_3$ solid solution changes with the $K^+/(K^+ + Na^+)$ molar ratios in the starting solution. The phase transition of the as-prepared particles with various K relative concentration while (K + Na)/Nb molar ratio maintained at 5:1 in the starting suspension was investigated by the XRD method and the patterns are shown in Fig. 1. The patterns of the samples KNN01 and KNN02 are similar to that of orthorhombic $NaNbO_3$ (JCPDS, 33-1270), while the patterns of samples KNN05 and KNN06 are similar to that of orthorhombic $KNbO_3$ (JCPDS, 32-0822). That means the structure of KNN01 and KNN02 are similar to that of $NaNbO_3$, while the structure of KNN05 and KNN06 are similar to that of $KNbO_3$. Based on the compositions shown in Table 2, the samples KNN01 and KNN02 are Na-rich (K, Na)NbO_3 solid solutions, while the samples KNN05 and KNN06 are K-rich (K, Na)NbO_3 solid solutions. In the patterns of KNN03 and KNN04, an interesting phenomenon was seen whereby both Na-rich and K-rich (K, Na)NbO_3 solid solutions were observed in the products. This indicates that a Na-rich (K, Na)NbO_3 phase coexists with K-rich (K, Na)NbO_3 phase in these two samples. In other words, the KNN03 and KNN04 samples are the mixtures of Na-rich (K, Na)NbO_3 solid solution and K-rich (K, Na)NbO_3 solid solution rather than a complete (K, Na)NbO_3 solid solution. The compositions and the phases of the products in detail have been listed in Table 2. The composition results are well in agreement with the XRD results.

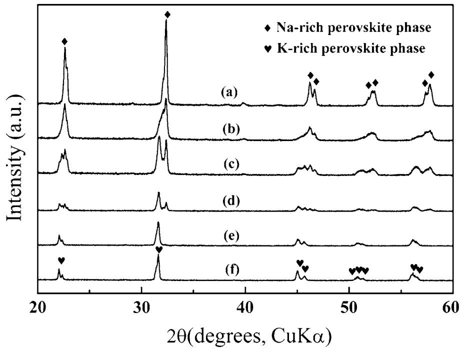


Fig. 1 XRD patterns of (K, Na)NbO_3 particles prepared from the starting suspensions with the different K/(K + Na) molar ratios: *a* 0.60, *b* 0.70, *c* 0.75, *d* 0.80, *e* 0.85, *f* 0.90 when the (K + Na)/Nb molar ratio is 5:1

Table 2 K/Na molar ratio and the possible phase in the resultant (K, Na)NbO_3 powders

Sample	K/Na molar ratio	Phase
KNN01	2:98	Na-rich (K, Na)NbO_3
KNN02	9:91	Na-rich (K, Na)NbO_3
KNN03	–	Mixture of Na-rich and K-rich phase
KNN04	–	Mixture of Na-rich and K-rich phase
KNN05	77:23	K-rich (K, Na)NbO_3
KNN06	80:20	K-rich (K, Na)NbO_3
KNN09	11:89	Na-rich (K, Na)NbO_3
KNN10	14:86	Na-rich (K, Na)NbO_3
KNN11	72:28	K-rich (K, Na)NbO_3

During the hydrothermal synthesis of KNN03 and KNN04 samples, even though Na reacts faster with Nb to form $NaNbO_3$ than K to form $KNbO_3$, the K concentration is higher than that in the starting solutions for synthesis of KNN01 and KNN02. As a result, a mixture of Na-rich (K, Na)NbO_3 solid solution and K-rich (K, Na)NbO_3 solid solution is obtained. However, in the KNN01 and KNN02 samples, the reaction between Nb and Na is dominant all through the hydrothermal reaction because the Na/K molar ratio is higher than that of KNN03 and KNN04 samples. Therefore, the KNN01 and KNN02 samples are single-phase Na-rich (K, Na)NbO_3 solid solutions. Oppositely, the KNN05 and KNN06 samples are single-phase K-rich (K, Na)NbO_3 solid solutions due to higher K/Na molar ratio.

In addition, the 2θ values in the patterns of the KNN01 shown in Fig. 1a are higher than that of KNN06 shown in Fig. 1f. Because the ionic radius of K^+ (1.33 Å) is larger than that of Na^+ (0.97 Å), the distance between the crystal faces in the KNN06 samples is larger than that in the KNN01 samples, and as a result the 2θ values of the KNN06 samples decrease according to the Bragg rule $d = \lambda/(2\sin\theta)$. The patterns intensity of the KNN01 is stronger than that of the KNN06. This owes to the higher reaction activity of Na than K. This is consistent with the results that Na reacted more readily with Nb to form $NaNbO_3$ than K [19].

The similar results are also reported in other studies [17, 18], but the samples were prepared from suspensions with higher alkalinity of 10 mol/L [17] or 6 mol/L [18]. In this study, due to the addition of isopropanol in the starting suspensions, the samples can be successfully synthesized by hydrothermal method in a milder condition of 2 mol/L alkali solution. The supercritical point of isopropanol is 235 °C, while that of water is 374 °C; therefore, the addition of isopropanol may decrease the supercritical point of reaction solution and accelerate the reaction rate. As a result, the suspensions reacted more readily even though the alkalinity is as low as 2 mol/L.

Figure 2 shows SEM photographs of the KNN01, KNN03, and KNN06 samples. The KNN01 sample, Na-rich (K, Na)NbO_3 solid solution, is cubic particles as shown in Fig. 2a, while the KNN06 sample with K-rich (K, Na)NbO_3 phase is irregular with a flat-like morphology as shown in Fig. 2c. $KNbO_3$ is ferroelectric and one single domain has only one single polar axis, and thus $KNbO_3$ particles are easy to form aggregation. On the contrary, $NaNbO_3$ is antiferroelectric because two contrary polar axes exist in one single domain, and $NaNbO_3$ particles are bigger owing to the higher crystallinity, thus the $NaNbO_3$ particles are difficult to form aggregation [18]. Figure 2b shows the morphology of KNN03 sample. When two phases coexist in the as-prepared particles, the small irregular grains agglomerated together. This could be explained that the two phases of Na-rich (K, Na)NbO_3 phase and K-rich (K, Na)NbO_3 phase with similar crystal structure grow in one system, which results in a lower growth rate and the irregular aggregation is formed. The compositions of different grains were checked by EDX method as shown in Fig. 3. Figure 3a shows the composition of the crisscross 1 in Fig. 2b. The K/Na molar ratio is below 1, and it is suggested that the grain 1 is Na-rich (K, Na)NbO_3 solid solution. Figure 3b shows the composition of the crisscross 2 in Fig. 2b. The K/Na molar ratio is above 1, and it is suggested that the grain 2 is K-rich (K, Na)NbO_3 solid solution. It indicates that there are two different phases in the KNN04 sample. This result is in agreement with that of XRD.

Effects of (K + Na)/Nb molar ratio

As shown in Fig. 1, the KNN03 and KNN04 samples are the particles with two phases coexisted. For the purpose of

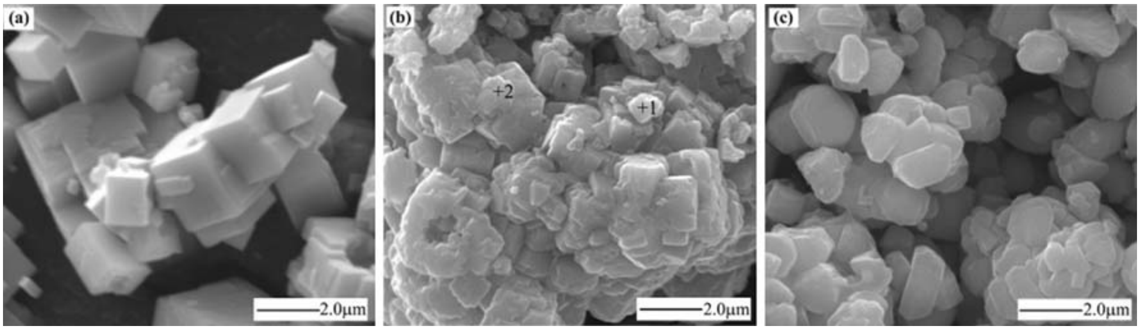
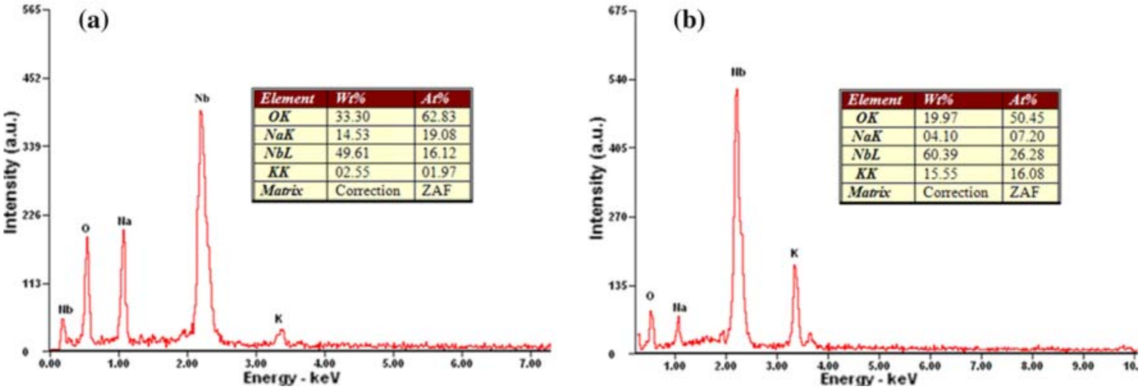


Fig. 2 SEM images of the samples prepared from the starting suspensions with the different K/(K + Na) molar ratios: **a** 0.60, **b** 0.75, and **c** 0.85 when the (K + Na)/Nb molar ratio is 5:1



Element	Wt%	At%
OK	33.30	62.83
NaK	14.53	19.08
NbL	49.61	16.12
KK	02.55	01.97
Matrix	Correction	ZAF

Element	Wt%	At%
OK	19.97	50.45
NaK	04.10	07.20
NbL	60.39	26.28
KK	15.55	16.08
Matrix	Correction	ZAF

Fig. 3 EDX analysis of the grains in the Fig. 2b: **a** crisscross 1; **b** crisscross 2

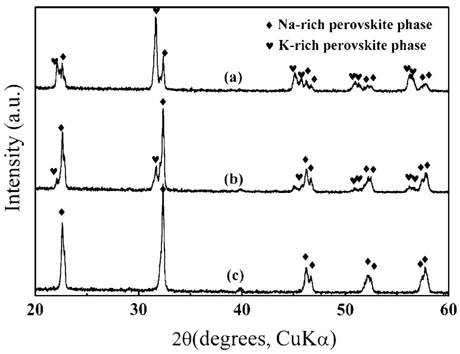


Fig. 4 XRD patterns of (K, Na)NbO_3 particles prepared from the starting suspensions with the different (K + Na)/Nb molar ratios: *a* 5:1, *b* 15:1, *c* 30:1 when K/(K + Na) molar ratio is 0.8

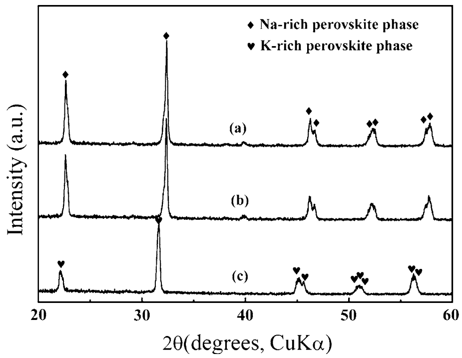


Fig. 5 XRD patterns of as-prepared (K, Na)NbO_3 particles from starting suspensions with the different K/(K + Na) molar ratios: *a* 0.75, *b* 0.80, *c* 0.85 while the (K + Na)/Nb molar ratios is 30:1

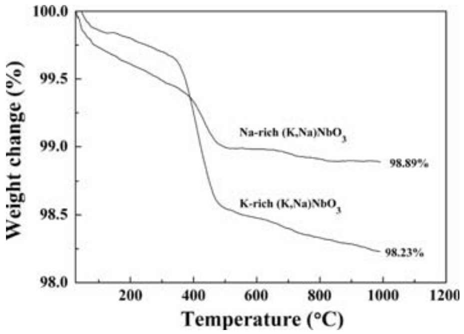


Fig. 6 TG curves of KNN09 (Na-rich KNN phase) and KNN11 (K-rich KNN phase)

preparing complete (K, Na)NbO_3 solid solution, the effects of (K + Na)/Nb molar ratio were investigated. Figure 4 shows that the phases of the as-prepared particles shift from a mixture of Na-rich (K, Na)NbO_3 solid solution and K-rich (K, Na)NbO_3 solid solution to complete (K, Na)NbO_3 solid solution gradually with the (K + Na)/Nb molar ratio increasing from 5:1 to 30:1. By increasing the (K + Na)/Nb molar ratio in the starting suspensions, the problem of that $NaNbO_3$ and $KNbO_3$ phases formed, respectively, in the samples is solved successfully. The results show that (K + Na)/Nb molar ratio is the key point for the formation of complete (K, Na)NbO_3 solid solutions. That may be explained that when (K + Na)/Nb molar ratio increases, the K also can react readily with Nb in the reaction solution with higher concentration of K. Thus, the higher reaction activity of Na than K is no longer remarkable. Therefore, K and Na react with Nb equally and the two elements dissolve into the crystal lattice at the same time to form complete (K, Na)NbO_3 solid solutions.

In order to obtain complete (K, Na)NbO_3 solid solutions with the accurate composition of $K_{0.5}Na_{0.5}NbO_3$, K/(K + Na) molar ratio was adjusted while the (K + Na)/Nb molar ratio was fixed to be 30:1. The samples' patterns are shown in Fig. 5. Single-phase (K, Na)NbO_3 particles with orthorhombic symmetry are obtained in the samples of KNN09, KNN10, and KNN11. Moreover, the KNN09 and KNN10 samples are Na-rich (K, Na)NbO_3 solid solutions, while the KNN11 sample is K-rich (K, Na)NbO_3 solid solution. Therefore, $K_{0.5}Na_{0.5}NbO_3$ could be synthesized when K/(K + Na) molar ratio is between 0.80 and 0.85 while the (K + Na)/Nb molar ratio is 30:1.

The compositions of the samples KNN09, KNN10, and KNN11 are also listed in Table 2. The K/Na molar ratio in the as-synthesized samples KNN09 and KNN10 are similar with each other. However, there is a big jump from KNN10 (K/Na = 14:86) to KNN11 (K/Na = 72:28). Therefore, the peak shift is large between the samples KNN10 and KNN11 as shown in Fig. 5b, c, and the peak shift is small between the samples KNN09 and KNN10 as shown in Fig. 5a, b.

Figure 6 shows the TG curves of as-synthesized samples KNN09 and KNN11, which represent the Na-rich and K-rich (K, Na)NbO_3 phase, respectively. The similar profiles were also found in the $KNbO_3$ powders synthesized by hydrothermal method [13]. In present work as shown in Fig. 6, the weight losses of (K, Na)NbO_3 solid solutions in the temperature range 20–350 °C are attributable to the physically adsorbed water. However, the weight losses in the temperature range 350–550 °C could be assigned to the dehydration of chemically adsorbed water. After the samples were heated to 1,000 °C, the residual weight relative to the starting weight of the Na-rich and K-rich (K, Na)NbO_3 samples are 98.89 and 98.23%, respectively. That means the weight loss of K-rich (K, Na)NbO_3 phase is higher than that of Na-rich phase. Goh et al. [13] have reported that protons may be present in the perovskite lattice either in the form of hydroxyl ions or as H_2O molecules. Hydroxyl ions reside on oxygen sites and H_2O molecules reside on vacant potassium sites for the

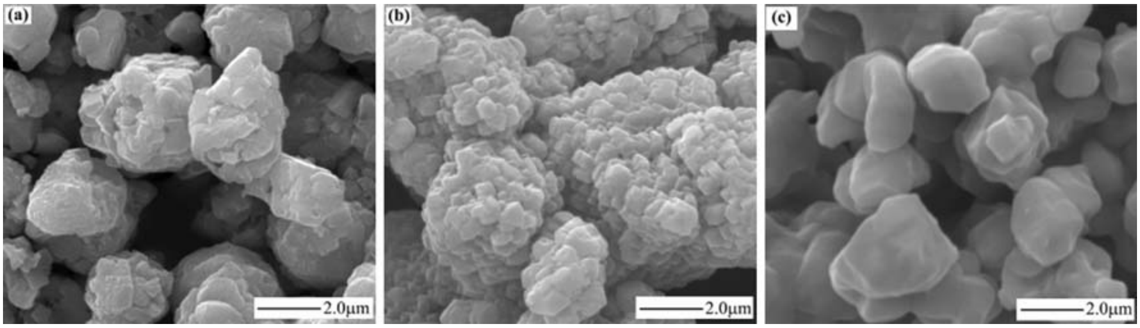


Fig. 7 SEM images of the particles prepared from the starting suspensions with the different (K + Na)/Nb molar ratios: **a** 5:1, **b** 30:1 when K/(K + Na) molar ratio is 0.8, and **c** the (a) sample annealed at 900 °C

similarity in size of K and H_2O. In the K-rich (K, Na)NbO_3 phase, the size of the vacant A sites should be larger as the radius of K is larger than that of Na. This could be beneficial to adsorbing more H_2O molecules. Therefore, the higher weight loss of K-rich (K, Na)NbO_3 phase occurs in the TG curves.

Figure 7a, b shows the SEM photographs of KNN04 and KNN10 samples synthesized from the starting solutions with different (K + Na)/Nb molar ratio. Both of them are aggregation with small grains. As the (K + Na)/Nb molar ratio increases, the shape of the small grains shifts from irregular shape as shown in Fig. 7a to cubic shape as shown in Fig. 7b. This corresponds to the results that two phases coexisted in the KNN04 sample and KNN10 sample is single-phase.

Effects of annealing temperature

The phase evolution of the KNN04 sample before and after annealing at different temperatures is shown in Fig. 8. With the increase in annealing temperature, the crystallinity of the $NaNbO_3$ and $KNbO_3$ phases in the KNN04 sample decrease, and then change into (K, Na)NbO_3 solid solutions above 900 °C. That means $NaNbO_3$ reacts with $KNbO_3$ to form (K, Na)NbO_3 solid solutions by solid-state reaction when the as-prepared particles are annealed at high temperatures. As a result, the sample annealed at 900 °C changes to a single-phase (K, Na)NbO_3 solid solution. The possible formula is $K_{0.60}Na_{0.40}NbO_3$ based on the results of compositional analysis. It is indexed in orthorhombic symmetry (space group *Bmm2*) as shown in Fig. 8d. The lattice parameters of $K_{0.60}Na_{0.40}NbO_3$ are calculated by Jade software and the details are listed in Table 3.

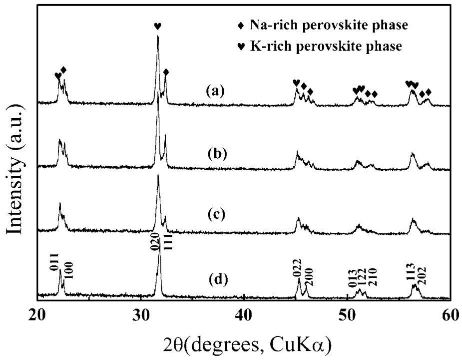


Fig. 8 XRD patterns of *a* the KNN04 sample and annealed at different temperatures: *b* 500 °C, *c* 700 °C, *d* 900 °C

Table 3 The crystallographic study of the sample KNN04 annealed at 900 °C for 2 h

Formula	Symmetry	Lattice parameters[a]		
		a (Å)	*b* (Å)	*c* (Å)
$K_{0.60}Na_{0.40}NbO_3$	Orthorhombic	3.941(1)	5.645(3)	5.669(2)

[a] Lattice parameters were calculated by Jade software

Figure 7c shows SEM photographs of the KNN04 sample after annealing at 900 °C. The morphology is inherited and spherical particle is obtained due to the atomic diffusion at high temperature.

Conclusions

The (K, Na)NbO_3 solid solutions were successfully synthesized via isopropanol-assisted hydrothermal method through adjusting the K/(K + Na) molar ratio and (K + Na)/Nb molar ratio in the starting suspensions. The results indicate that with the addition of isopropanol, the required alkaline concentration was reduced to 2 mol/L. The (K + Na)/Nb molar ratio is the key point for the formation of complete (K, Na)NbO_3 solid solutions, and the K/(K + Na) molar ratio also plays an important role on the phase evolution and composition of the product. When the (K + Na)/Nb molar ratio in the starting suspensions is 5:1, Na-rich (K,Na)NbO_3 solid solution and K-rich (K,Na)NbO_3 solid solution are obtained when the K/(K + Na) molar ratio is less than 0.70

and more than 0.85, respectively. On the contrary, the two phases coexisted when the K/(K + Na) molar ratio is between 0.75 and 0.8. After annealing at 900 °C for 4 h, the two phases disappear, and form a complete (K, Na)NbO_3 solid solution because of the atomic diffusion. However, when the (K + Na)/Nb molar ratio is 30:1, a complete (K, Na)NbO_3 solid solution can be synthesized under hydrothermal condition as the K/(K + Na) molar ratio is 0.75, 0.80, and 0.85. The change of morphology is in agreement with the phase evolution.

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