Low-temperature synthesis of K_2NbO_3F powders by an alternative approach of solid-state reaction

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ABSTRACT

K_2NbO_3F powders were directly synthesized by an alternative solid-state method at low temperature. Stoichiometric ammonium niobium oxalate, $K_2C_2O_4$ and KF were mixed with small amounts of water and then dried at room temperature. X-ray diffraction results show that layered perovskite K_2NbO_3F powders can be obtained by calcining the mixture in temperature range from 550 to 700 °C for 3 h. The elemental composition, powder morphology and particle size of calcination products were analyzed by scanning electron microscope–energy dispersive spectroscopy (SEM/EDS). The SEM images suggest that the particles of the powders obtained at 550 °C are irregular platelets with a diameter of 0.5–1 μm and a thickness of 100–200 nm. The platelets are 3–5 μm in diameter and 1–2 μm in thickness when the calcination temperature reaches 700 °C. K_2NbO_3F decomposes to $K_5(NbO_3)_4F$ and KF when the temperature reaches 800 °C.

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1. Introduction

K_2NbO_3F (KNF) is a ferroelectric material with K_2NiF_4-type structure. A distinctive feature of this compound is its unique layered perovskite structure, which includes an ordered KF block and a KO block between layers [1]. The interlayer ions including alkali metals with lower valence are readily exchangeable with other ions. These structures are useful in the formation of photocatalysts, phosphors, ionic conductors and superconducting materials [2]. Potassium ions and fluorine ions are easily eliminated from KNF by stirring in water [2–4]. Therefore, KNF has always been used to produce $KNbO_3$ crystal and other Nb-containing mesoporous materials in aqueous solution [2,4–8].

The synthesis of KNF was first reported by Galasso and Darby in 1962 [9]. To the best of our knowledge, almost all KNF powders are prepared by a conventional solid-state method, in which high-purity K_2CO_3, Nb_2O_5 and KF powders are used as raw materials. The powders of K_2CO_3 and Nb_2O_5 were mixed in 1:1 molar ratio and then a large excess of KF was added to compensate for loss due to volatilization. The mixture was calcined above 750 °C for several hours followed by slow cooling [4–6,8–11]. After the reaction, the excess potassium fluoride was removed by washing the product with distilled water. Komatsu et al. [12] have prepared KNF ceramics by heating the mixture of K_2CO_3 and Nb_2O_5 in 1:1 molar ratio at 1000 °C for 15 h to obtain $KNbO_3$. Next, the prepared $KNbO_3$ was mixed with pure KF with the molar ratio of 1:1 and then the mixture was heated at 680–730 °C in air for 10 h.

The main disadvantages involved in conventional solid-state reaction are time-consuming ball milling process, inhomogeneous mixing, and high calcination temperature (above 730 °C). To decrease the calcination temperature, a simple combustion method [13,14] has been used to synthesize alkali niobate at 550 °C, in which metal oxides are used as raw materials and urea as fuel. In our previous work [15], we have also prepared pure $KNbO_3$ powders at low temperature (500 °C) by an alternative solid-state reaction. In this work, the synthesis of KNF was performed using ammonium niobium oxalate (ANO) as Nb-source by an alternative solid-state method. ANO can decompose to niobic acid, which is more active than Nb_2O_5, at about 330 °C [16]. Its main advantage lies in the possibility of preparing KNF powders at low temperature by a simple, rapid and cost-effective method, without addition of any fuel.

2. Results and discussion

Fig. 1 shows the TG curve of the precursor compound. The weight loss is about 55.7% in the temperature range from 30 to 530 °C, which results from the production of KNF powders (it can be confirmed later by XRD analysis). A further increase in temperature, to 650–800 °C, leads to another 1.5% weight loss. The little weight loss is due to the decomposition of small amount of CO_3^{2-} and $C_2O_4^{2-}$ (it can be confirmed later by XRD analysis).

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Fig. 1. TG curve of the precursor compound.
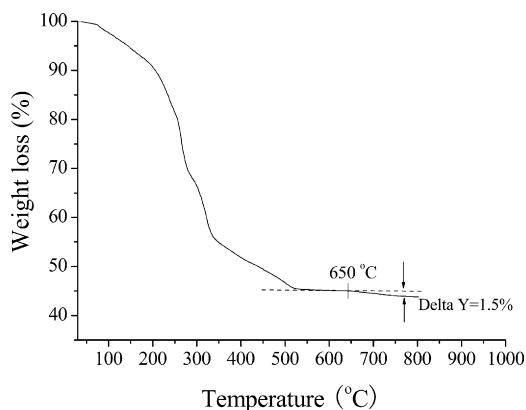
Table 1
XRD results of the experimental products.

Starting materials	Calcination temp.	Calcination product	Matching JCPDS no.
$K_2C_2O_4$ + KF + ANO	500 °C	$KNbO_3$	71-0947
	550 °C	KNF	72-0364
	600 °C	KNF	72-0364
	700 °C	KNF	72-0364
	800 °C	KNF + $K_5(NbO_3)_4F^a$	72-0364 + 83-2383
$K_2C_2O_4$ + KF + Nb_2O_5	500 °C	Amorphous and $KNbO_3$	71-0947
	550 °C	Amorphous and KNF + $KNbO_3{}^a$	72-0364 + 71-0947
	600 °C	Amorphous and KNF + $KNbO_3{}^a$	72-0364 + 71-0947
	700 °C	KNF + $KNbO_3{}^b$	72-0364 + 71-0947
	800 °C	$K_5(NbO_3)_4F$ + KNF^a	83-2383 + 72-0364

[a] Small.
[b] Trace.

Actually, KNF is unstable and can be decomposed at relatively high temperatures, as shown in Eq. (1) [17]:

$$4K_2NbO_3F \rightarrow KF \cdot 4KNbO_3 + 3KF \tag{1}$$

The high stability of $KF \cdot 4KNbO_3$ is related to the steric similarity between potassium and fluorine ions, which is hardly the case with other alkali metals [17].

The precursor compound was calcined in the temperature range from 500 to 800 °C for 3 h based on the TG curve. The XRD patterns of KNF500–700 samples are shown in Fig. 2(a). The powders calcined at 500 °C exhibit the characteristic diffraction peaks of $KNbO_3$ crystal. The peaks of $KNbO_3$ disappear and a pure KNF phase, which belongs to tetragonal symmetry (JCPDS no. 72-0364), is obtained when the calcination temperature reaches 550 °C. The similar results can be observed below 700 °C. However, the impure peaks at 10.6°, 15.0°, 27.8° and 28.7° appear when the temperature increases to 800 °C as shown in Fig. 2(b). It indicates that a small amount of $K_5(NbO_3)_4F$ is produced in the as-prepared powders at 800 °C. The corresponding results are listed in Table 1. It is concluded that the precursor mixture is first turned into active $KNbO_3$ phase, and then it reacts with KF to form pure KNF phase between 550 and 700 °C.

The controlled experiments were performed to investigate the effect of different niobium sources on product compositions. Table 1 lists the XRD results of experimental products. If Nb_2O_5 reagent is directly employed as raw material, pure KNF powders cannot be obtained even at approximately 700 °C and large amounts of

$K_5(NbO_3)_4F$ can be found at 800 °C. ANO and $K_2C_2O_4$ decompose to niobic acid and K_2CO_3 at about 330 °C and 500 °C, respectively. It makes the raw materials react easily to produce KNF crystalline. Therefore, it can be concluded that the reactive activity of ANO is much higher than that of Nb_2O_5. The addition of ANO promotes the nucleation of KNF at low temperature and improves the stability of KNF.

Fig. 3 and Table 2 show the phase composition of the powders obtained at 550 °C for 3 h. Fig. 3(b) shows the EDS profile of plot 3 in Fig. 3(a). K, Nb, O and F peaks are observed in the EDS profile. It indicates that the as-prepared product is composed of K, Nb, O and F element. Table 2 shows the weight percent of K, Nb, O and F in KNF550 powders with use of five measurement data. These values relatively accord with the composition of KNF as taking account of measurement error. Actually, EDS is a relative rather than absolute quantitative technique. The quantitative analyses of elemental compositions are with big error due to the lack of well-characterized reference samples [18].

Fig. 4 is the SEM images of KNF550, KNF600 and KNF700 samples. It can be observed from Fig. 4(a) that the particles are irregular platelets with a diameter of 0.5–1 μm and a thickness of 100–200 nm. It has no obvious increase in grain size when the temperature reaches 600 °C. The particle growth is mainly controlled by the diffusion rate of K^+ ion [19]. K^+ ion has a high

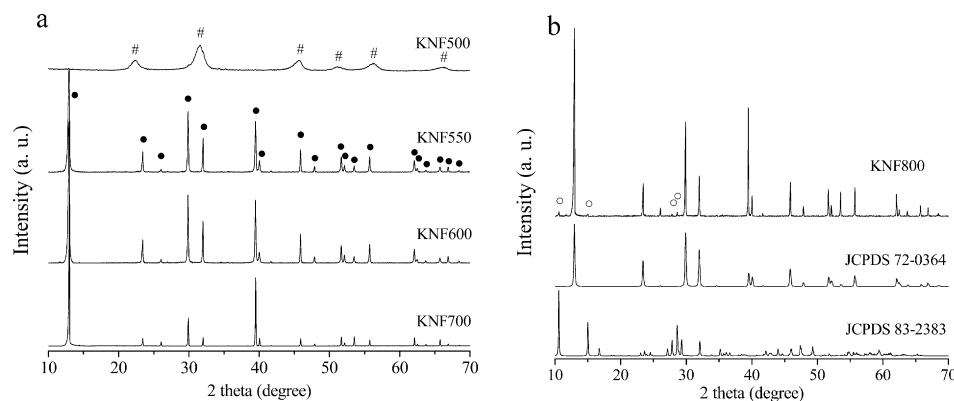**Fig. 2.** (a) XRD patterns of KNF500–700 samples. (b) XRD pattern of KNF800 and the standard XRD patterns of KNF (JCPDS no. 72-0364) and $K_5(NbO_3)_4F$ (JCPDS no. 83-2383). Peaks with a closed circle (●) are associated with KNF phase, peaks with a pound sign (#) are with $KNbO_3$ phase, and peaks with an opened circle (○) are with $K_5(NbO_3)_4F$ phase.
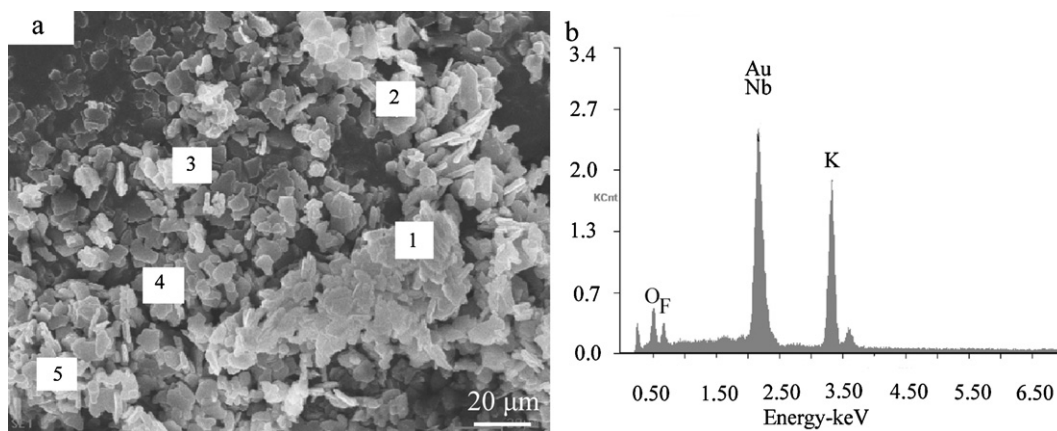
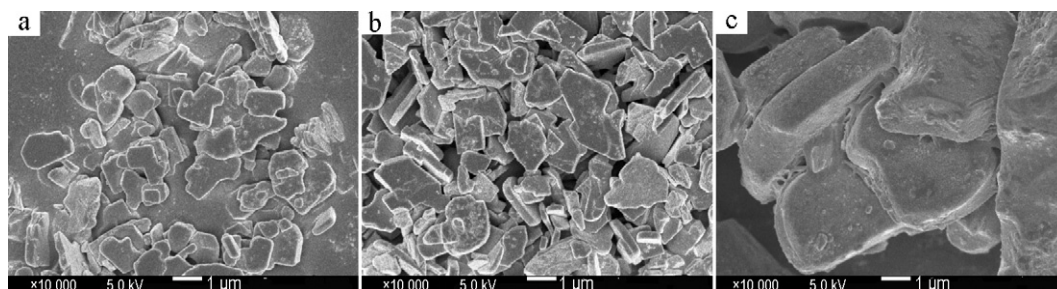Fig. 3. (a) SEM micrograph and (b) EDS profile (plot 3) of KNF550 powders.

Fig. 4. SEM images of (a) KNF550, (b) KNF600 and (c) KNF700.

diffusion rate at high temperature and hence the particles can grow up. The platelets are 3–5 μm in diameter and 1–2 μm in thickness when the calcination temperature reaches 700 °C (as shown in Fig. 4(c)).

FTIR technology was employed to characterize the quality of the as-synthesized products and the results were shown in Fig. 5. As shown in Fig. 5, bands due to carboxylate disappear when the precursor is calcined above 550 °C. Peak at 1635 cm^{-1} is due to OH vibration. Peaks at 1550–1260 cm^{-1} and 880 cm^{-1} are attributed to the vibration of CO_3^{2-}. While peak at 780 cm^{-1} results from δ_{COO^-}. Peak at about 550 cm^{-1} is due to Nb–O. 1600, 1407 and 780 cm^{-1} bands are attributed to the vibration of –COO^- in the IR spectrum of $K_2C_2O_4$. 1315 and 575 cm^{-1} bands are the result of C–C vibration. It established that there have small amounts of CO_3^{2-} and $C_2O_4^{2-}$ in the final product. When the calcination temperature reaches 700 °C, part of $C_2O_4^{2-}$ decomposed, which can be confirmed by above TG analysis (Fig. 1). Although small amount of anions CO_3^{2-} and $C_2O_4^{2-}$ exists in the KNF powders, it can be eliminated by washing with water.

The UV–vis diffuse reflectance spectra of KNF550, KNF600 and KNF700 samples are as shown in Fig. 6. The band gap absorption edge of KNF550, KNF600 and KNF700 samples is estimated as 407,
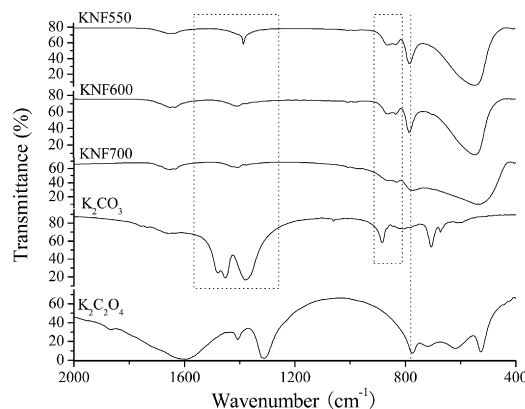

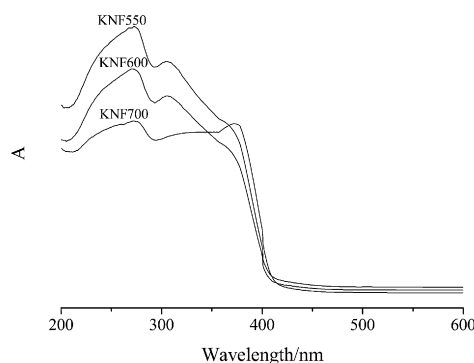Fig. 5. FTIR spectra of KNF550, KNF600, KNF700, K_2CO_3 and $K_2C_2O_4$.

Table 2
Elemental composition of the KNF550 powders determined by EDS analysis.

	Wt.%				
	K	Nb	O	F	Total
Nominal composition	32.8	39.0	20.2	8.0	100.0
1	37.8	29.0	23.7	9.5	100.0
2	30.1	27.6	30.0	12.3	100.0
3	34.9	31.8	24.0	9.3	100.0
4	36.1	32.4	22.3	9.2	100.0
5	37.9	35.6	18.6	7.9	100.0
Average	35.4	31.3	23.7	9.6	100.0

Fig. 6. UV–vis diffuse reflectance spectra of KNF550, KNF600 and KNF700 samples.

406, and 409 nm, respectively. The result shows that there is no correlation between absorption edge and calcination temperature. The average value of them is about 407.3 nm. The corresponding band gap energy is determined as 3.0 eV by the following Eq. (2) [20]:

$$\lambda \, (nm) = \frac{1240}{E_g} \, (eV) \qquad (2)$$

where E_g denotes the energy gap of semiconductor and λ denotes the band gap absorption edge.
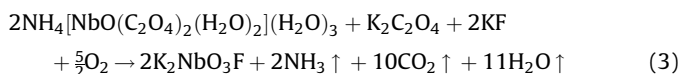
3. Conclusions

Crystalline powders of KNF were synthesized by an alternative solid-state reaction at low temperature, in which $K_2C_2O_4$, KF, and ANO were used as raw materials without addition of any organic fuel. The raw materials were adjusted to uniformly distributed slurry by adding small amounts of water instead of the ball milling process, which avoided the interfusion of contamination to KNF powders. KNF powders were successfully synthesized by simply calcining the dried mixture between 550 and 700 °C for 3 h. The particles of the product obtained at 550 °C are plate-like with a diameter of 0.5–1 μm and a thickness of 100–200 nm. The platelets are 3–5 μm in diameter and 1–2 μm in thickness when the calcination temperature is increased to 700 °C. This method is a simple, cost-effective and environmentally friendly way to prepare stoichiometic, homogeneous, and fine powders. It is found that typical environmental problems, as the use of toxic reagent, presence of chlorine ion, or polluted secondary products, have been successfully bypassed.

4. Experimental

4.1. Synthesis

$K_2C_2O_4$, KF, and Nb_2O_5 (AR) were used as raw materials in the synthesis of KNF powders. ANO was prepared according to US Patent 7 241 911 [21]. The molecular formula of the recrystallized ANO was established as $NH_4[NbO(C_2O_4)_2(H_2O)_2](H_2O)_3$ by X-ray diffraction (XRD) analysis. The XRD result was matched well with the standard data (JCPDS 83-1993). The water content of each reagent was measured by thermogravimetric (TG) analysis.

The starting materials were weighed according to the required stoichiometric ratio, as shown in Eq. (3):

$$2NH_4[NbO(C_2O_4)_2(H_2O)_2](H_2O)_3 + K_2C_2O_4 + 2KF$$
$$+ \tfrac{5}{2}O_2 \rightarrow 2K_2NbO_3F + 2NH_3\uparrow + 10CO_2\uparrow + 11H_2O\uparrow \qquad (3)$$

$K_2C_2O_4 \cdot xH_2O$ (7.33 g, x is 1.13 by TG analysis), ANO (32.33 g, Nb_2O_5 content is 32.3%) and $KF \cdot xH_2O$ (7.65 g, x is 2.18 by TG analysis) in 1:2:2 molar ratio were mixed with water (7 mL) to form a slurry. The slurry was ground for 1–2 h till water was vaporized. The reactants were heated under IR lamp at about 50–60 °C with continuously grounding. The dried mixture was calcined in the range from 500 to 800 °C for 3 h, respectively. These obtained samples were named as KNF500, KNF550, KNF600, KNF700 and KNF800, respectively. The controlled experiments were carried out by using $K_2C_2O_4$, KF and Nb_2O_5 as raw materials, which followed the same procedure as described for KNF samples.

4.2. Instrumentation

The structures of as-synthesized products were confirmed by powder XRD using a D/MAX-RB X-ray diffractometer (Rigaku, Japan) with graphite monochromater and CuKα radiation (40 kV, 100 mA). The step scan mode was performed with a step width of 0.02°, at a rate of 4° (2θ) per min. The phase indexing was performed by MDI Jade 5.0 software. Scanning electron microscope (SEM; JSM-7500 F, JEOL Co.) and energy dispersive spectroscopy (EDS; Genesis XM, EDAX Co.) were coupled to determine the morphology and elemental composition of as-prepared products. SEM/EDS experiment was operated under high vacuum (10^{-8} Pa) condition. The accelerating voltages were 5 and 10 kV for SEM and EDS analysis, respectively. TG analysis was carried out on a Perkin-Elmer Pyris 1 TGA. The atmosphere was air with a flow rate of 20 mL min^{-1} at 20 K min^{-1} in the range from 30 to 800 °C.

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