



# An alternative solid-state method to prepare pyrochlore-free $\text{KTaO}_3$ at low temperature

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## ABSTRACT

Perovskite-type  $\text{KTaO}_3$  powder was synthesized by an alternative solid-state method at low temperature. Stoichiometric ammonium tantalum hydroxide,  $\text{K}_2\text{C}_2\text{O}_4$  and KF were mixed in water and then dried at room temperature. The crude product was formed by calcining the dried mixture at different temperatures. Pyrochlore-free  $\text{KTaO}_3$  powder was successfully synthesized after treating the crude product with water. KF plays an important role to inhibit the formation of pyrochlore  $\text{K}_2\text{Ta}_2\text{O}_6$  during the calcination process of ammonium tantalum hydroxide/ $\text{K}_2\text{C}_2\text{O}_4$ /KF mixture. X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) spectroscopy, UV–vis diffuse reflectance (UV–vis) spectroscopy and thermogravimetric (TG) analysis were used to characterize the precursor compound and as-prepared samples. XRD results show that pyrochlore-free  $\text{KTaO}_3$  powder can be obtained at 600 °C. SEM results reveal that the as-prepared products are agglomerated and each of the agglomerations consists of many small grains with 10–30 nm in diameter.

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## 1. Introduction

Potassium tantalate has perovskite and pyrochlore structures. Generally, the pyrochlore-type potassium tantalate ( $\text{K}_2\text{Ta}_2\text{O}_6$ ) is formed at low temperature and the perovskite-type ( $\text{KTaO}_3$ ) is formed at high temperature (above 800 °C) [1]. Potassium tantalate with perovskite structure is an incipient ferroelectric material having a variety of unique electronic, magnetic, optical, dielectric, photocatalytic properties, etc. [1–14]. In general, perovskite  $\text{KTaO}_3$  and pyrochlore  $\text{K}_2\text{Ta}_2\text{O}_6$  always coexist in the preparation of potassium tantalate powders and films [1,12,15–18]. The presence of pyrochlore phase can significantly reduce the relative permittivity of the ferroelectric films of some perovskite substances and, thus, how to synthesize pyrochlore-free  $\text{KTaO}_3$  is worth investigating.

Problems related to pyrochlore–perovskite phases control and to stoichiometric deviation (due to K losses) are frequently reported. Several approaches have been proposed to avoid these problems with more or less efficiency [1,12,15–20]. The conventional technique for synthesizing perovskite  $\text{KTaO}_3$  powder is based on solid-state reaction, which requires calcining the mixture of  $\text{Ta}_2\text{O}_5$  and  $\text{K}_2\text{CO}_3$  above 750 °C [6–8,10–13,21,22]. However, one of the difficulties encountered in the preparation of both single crystal as well as polycrystalline potassium tantalate was the loss of  $\text{K}_2\text{O}$  at

elevated calcining temperature, resulting in the formation of an undesirable secondary phase. Alternatively, pyrochlore  $\text{K}_2\text{Ta}_2\text{O}_6$  can be prepared at 650 °C when using alkoxides as precursors. However, the pyrochlore-free phase is obtained only after heating at 800 °C by this method [1,12]. Pyrochlore-free  $\text{KTaO}_3$  powder is also prepared at 650 °C by polymeric precursor method. Nevertheless, it has been verified that a small amount of secondary phases is formed at that temperature [17]. With the goal of reducing the forming temperature of pyrochlore-free  $\text{KTaO}_3$  powder, hydrothermal method and solvothermal method have been reported, which uses  $\text{Ta}_2\text{O}_5$  and KOH solution (or mixed solvents) as raw materials [9,15,20,23]. However, it must be achieved on the basis of long reaction time or high KOH concentration.

In our previous works [24–26], we have prepared  $\text{MnNbO}_3$  (M: Li, Na and K) powder at 500 °C using different M-source and ammonium niobium oxalate as raw materials by an alternative solid-state reaction. It has been demonstrated that the activity of organic salts is higher than that of inorganic salts in our previous works. Furthermore,  $\text{Ta}_2\text{O}_5$ , usually used as Ta source to prepare potassium tantalate, is more stable compared to ammonium tantalum hydroxide. Therefore, in this work ammonium tantalum hydroxide, potassium oxalate ( $\text{K}_2\text{C}_2\text{O}_4$ ) and potassium fluoride (KF) were used as raw materials. The addition of KF can inhibit the formation of pyrochlore  $\text{K}_2\text{Ta}_2\text{O}_6$ . The aim of the present study is to prepare pyrochlore-free  $\text{KTaO}_3$  powder at low temperature using a facile, rapid and cost-effective route. It may be used as photocatalyst because low temperature synthesized perovskite-type  $\text{KTaO}_3$  has smaller granular size and higher specific area.

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## 2. Experimental section

All chemicals were analytical reagent and used without further purification. Ammonium tantalum hydroxide, potassium oxalate, potassium fluoride and tantalum pentoxide were used as raw materials in this study. Ammonium tantalum hydroxide was synthesized by a hydrofluoric acid method and its molecular formula was determined as  $TaO_x(OH)_{5-x}(NH_4)_x$  [27].  $NH_3$  content is about 15% by titration method. The water content of the raw materials was measured by thermogravimetric (TG) analysis before use.

### 2.1. Controlled experiments

Two controlled experiments were carried out according to the succedent steps. A stoichiometric potassium oxalate ( $K_2C_2O_4 \cdot H_2O$ , 4.98 g) and  $TaO_x(OH)_{5-x}(NH_4)_x$  (15.48 g,  $Ta_2O_5$  content is 77.15% by TG analysis) with 1:1 molar ratio of K:Ta were ground in an agate mortar and pestled in 10 mL water. The mixed slurry was ground for 2–3 h under IR lamp till water was vaporized. Small amounts of  $NH_3$  were released simultaneously during the grinding process. The mixture was calcined at 600, 700 and 800 °C for 3 h, thus the obtained samples were referred to as KTH600, KTH700 and KTH800, respectively. Mix the stoichiometric raw materials of potassium oxalate (5.02 g) and tantalum pentoxide ( $Ta_2O_5$ , 12.02 g) with 7 mL water. Heat the dried mixture at 600, 700 and 800 °C for 3 h, thus the obtained samples were referred to as KTO600, KTO700 and KTO800, respectively.

### 2.2. Formation process of crude product

Stoichiometric amounts of  $TaO_x(OH)_{5-x}(NH_4)_x$  (15.57 g), potassium oxalate (5.01 g) and potassium fluoride ( $KF \cdot 2 \cdot 12H_2O$ , 5.24 g) were pestled in 6.0 mL water. The mixed slurry was ground for 2–3 h till water was vaporized. Small amounts of  $NH_3$  were released simultaneously during the grinding process. The mixture was heated at 550, 600, 700 and 800 °C for 3 h, thus these obtained samples were referred to as KTF550, KTF600, KTF700 and KTF800, respectively.

### 2.3. Purification of $KTaO_3$

KTF series sample (1.5 g for each) was put into a PTFE crucible with 40 mL water. The crucibles were heated in oven at 80 °C for

24 h. The products were filtrated and washed with water, and then dried at 80 °C for several hours. The dried samples were referred to as KT550, KT600, KT700 and KT800, respectively.

### 2.4. Characterization

The structures of as-synthesized materials were confirmed by powder X-ray diffraction (XRD) using a D/MAX-RB X-ray diffractometer (XRD, Rigaku, Japan) with graphite monochromater and  $CuK\alpha$  radiation (40 kV, 100 mA). The step scan mode was performed with a step width of 0.02°, at a rate of 4° ( $2\theta$ ) per min. The phase indexing was performed by MDI Jade 5.0 software. The morphologies were observed using a scanning electron microscope (SEM) (JSM-7500 F-EDS). UV–vis diffuse reflectance (UV–vis) spectra were recorded with a Lamda 900 UV–vis-NIR spectrophotometer. The PELA-1020 Sphere Accessory is equipped with a 60 mm Spectralon® integrating sphere, transfer optics, a thermostat-regulated lead sulfide detector, and an extended range photomultiplier tube. TG analysis was carried out on a Perkin–Elmer Pyris 1 TGA. The atmosphere was air with a flow rate of 20 mL  $min^{-1}$ . The samples were heated in the range from 30 to 800 °C at 20 K  $min^{-1}$ . Fourier transform infrared (FTIR) spectra were obtained in KBr discs on a Perkin–Elmer Spectrum GX. Sixteen scans were co-added with a resolution of 4  $cm^{-1}$ , in the range of 4000–400  $cm^{-1}$ .

## 3. Results and discussion

### 3.1. Controlled experiments

Two controlled experiments were performed using  $K_2C_2O_4/TaO_x(OH)_{5-x}(NH_4)_x$  and  $K_2C_2O_4/Ta_2O_5$  as raw materials, respectively. The XRD results of KTH600–800 and KTO600–800 samples are shown in Fig. 1. It can be seen from Fig. 1a that KTH600–800 products are the mixture of pyrochlore-type  $K_2Ta_2O_6$  and perovskite  $KTaO_3$  with different ratio. The main phase of KTH600 is pyrochlore-type  $K_2Ta_2O_6$ , while most of them transformed into perovskite  $KTaO_3$  at 800 °C. KTH800 is determined as perovskite-type  $KTaO_3$  with a small quantity of the pyrochlore  $K_2Ta_2O_6$  by XRD analysis.  $K_2Ta_2O_6$ ,  $KTaO_3$  and  $Ta_2O_5$  phase coexist if  $Ta_2O_5$  and  $K_2C_2O_4$  are used as raw materials (see Fig. 1b). It can be concluded that the activity of ammonium tantalum hydroxide is higher than that of  $Ta_2O_5$  reagent.

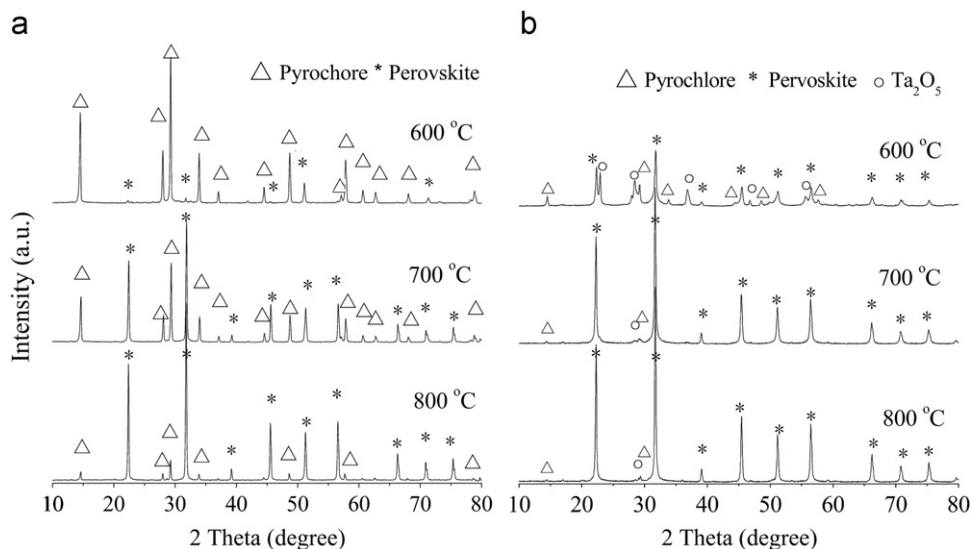


Fig. 1. XRD patterns of the precursor calcined at different temperatures for 3 h using  $K_2C_2O_4/TaO_x(OH)_{5-x}(NH_4)_x$  (a) and  $K_2C_2O_4/Ta_2O_5$  (b) as raw materials.

K-Ta mixed oxides with two different crystal structures, i.e.  $\text{KTaO}_3$  and  $\text{K}_2\text{Ta}_2\text{O}_6$ , have been prepared by alkoxide and solid-state reaction routes [12].  $\text{K}_2\text{Ta}_2\text{O}_6$  single phase with pyrochlore structure can be obtained by alkoxide method, however, this phase cannot be obtained by conventional solid-state reaction [12,19]. In this study  $\text{K}_2\text{Ta}_2\text{O}_6$  has been prepared at 600 °C using an alternative solid-state method, as shown in Fig. 1a and b.

### 3.2. Formation process of crude product

$\text{TaO}_x(\text{OH})_{5-x}(\text{NH}_4)_x$ ,  $\text{K}_2\text{C}_2\text{O}_4$  and KF were mixed with water and then dried at room temperature. The thermal behavior of the above precursor was investigated by TG/DTG analysis as shown in Fig. 2. The first weight loss below 180 °C is due to the water evaporation of precursor. TG curve shows a 10.1% weight loss from 450 to 600 °C, which results from the formation of  $\text{KTaO}_3$  powder (it can be confirmed later by XRD analysis). The precursor powder was calcined at temperature range from 550 to 800 °C (referred to as KTF550–800) based on the TG/DTG curves.

Fig. 3 shows the XRD patterns of KTF550, KTF600, KTF700 and KTF800 samples. Compared with Fig. 1a, the formation of the

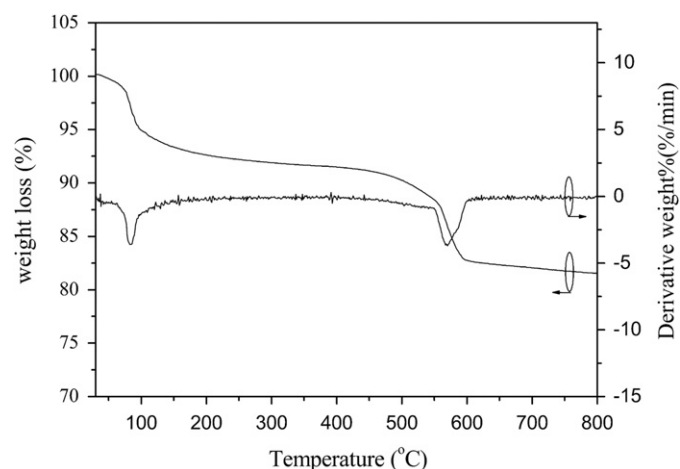


Fig. 2. TG/DTG curves of the precursor compound for the formation process of crude product.

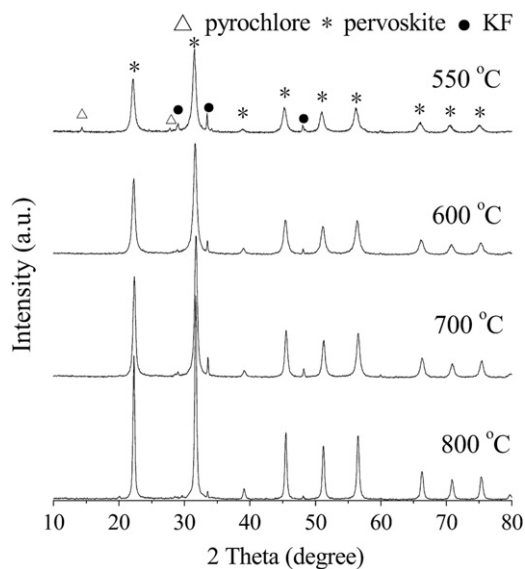


Fig. 3. XRD patterns of KTF550, KTF600, KTF700 and KTF800 obtained by calcining the precursor at 550, 600, 700 and 800 °C, respectively, for 3 h.

pyrochlore phase ( $\text{K}_2\text{Ta}_2\text{O}_6$ ) is inhibited significantly in the presence KF. It can be seen from Fig. 3 that only trace amount of  $\text{K}_2\text{Ta}_2\text{O}_6$  can be observed when the calcination temperature is 550 °C. However, pure perovskite phase  $\text{KTaO}_3$  is observed when the calcination temperatures are 600–800 °C. These results demonstrate that the pyrochlore phase is completely transformed into the perovskite phase at about 600 °C. The synthetic temperature is much lower than the other hard chemistry methods [6–8,10–13,21,22]. Although the pyrochlore-free  $\text{KTaO}_3$  has been synthesized, the XRD patterns attributed to KF can be observed at different calcination temperatures.

### 3.3. Purification of $\text{KTaO}_3$

It is necessary to remove KF by treating with water because  $\text{KTaO}_3$  is insoluble in water while KF is easily soluble in water. KTF550, KTF600, KTF700 and KTF800 products were treated with water at 80 °C for 24 h and filtrated. KT series samples were obtained after drying the filter cake at 80 °C for several hours. The XRD patterns of KT550, KT600, KT700 and KT800 are shown in Fig. 4. The XRD diffraction peaks of KF disappear after the KT series samples were treated with water. The diffraction peaks of KT600, KT700 and KT800 can be indexed as cubic perovskite  $\text{KTaO}_3$  (JCPDS card 77-1133), and no characteristic peaks of the impurity can be detected. It indicates that pyrochlore-free  $\text{KTaO}_3$  phase can be obtained at 600 °C and the secondary phases (due to K losses) are not appeared. The intensity of diffraction peaks increases with increasing calcination temperature, which indicates the crystal growth and high crystallinity. Indeed, pure perovskite  $\text{KTaO}_3$  has been synthesized above 750 °C [6–8,10–13,16,20–22]. Weber et al. [17] prepared perovskite  $\text{KTaO}_3$  at moderate temperatures (650 °C) by polymeric precursor method. However, a small amount of K deficient phases have been formed between 650 and 850 °C. Compared with above methods, the synthetic temperature of pyrochlore-free  $\text{KTaO}_3$  powder is decreased in our study.

The SEM images of KT600, KT700 and KT800 samples are shown in Fig. 5. The as-prepared powders are agglomerated and irregular in shape. Each of the agglomerations consists of many small grains with 10–30 nm in diameter. The results have been confirmed by the XRD patterns, in which the peak width is not obviously difference for various samples.

To check out the quality of the as-synthesized samples by this method, FTIR technology was employed to characterize the

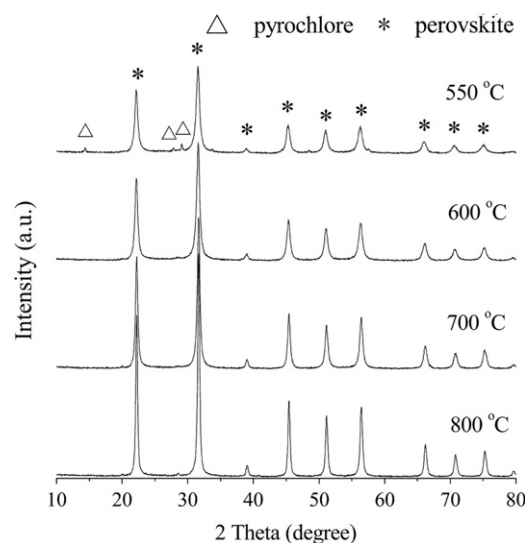


Fig. 4. XRD patterns of KT550, KT600, KT700 and KT800 samples.

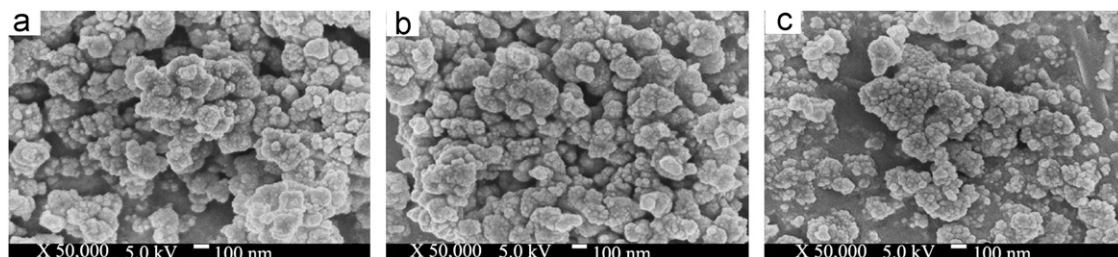


Fig. 5. SEM images of KT600 (a), KT700 (b) and KT800 (c) samples.

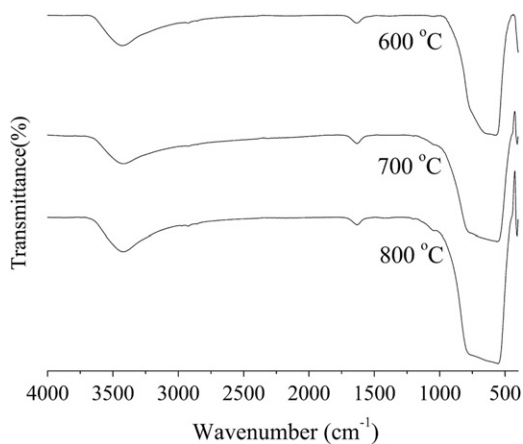


Fig. 6. FTIR spectra of KT600, KT700 and KT800 samples.

products and the results are shown in Fig. 6. As shown in Fig. 6, the bands of organic compound absent when the precursor is calcined above 600 °C and then treated with water. Only the broad Ta–O bands in the region from 790 to 550  $\text{cm}^{-1}$  are clearly visible. Peaks at 3430 and 1635  $\text{cm}^{-1}$  are attributed to OH vibration, which results from the KBr discs.

Fig. 7 shows UV–vis spectra of KT600 and KTH600 samples. The main phase is pyrochlore  $\text{K}_2\text{Ta}_2\text{O}_6$  for KTH600 sample, while KT600 sample consists of perovskite  $\text{KTaO}_3$ . It can be seen that the onset of KTH600 powder differs from that of KT600 sample. Absorption edges appear at about 270 and 340 nm wavelength for KTH600 and KT600, indicating optical band gap of 4.6 and 3.6 eV, respectively. The band gap was estimated by extrapolating the onset point of the UV spectrum to the abscissa at zero absorption [28]. The change of absorption edge is consistent with the phase transformation of pyrochlore into perovskite phase [1,9–13].

#### 4. Conclusions

Perovskite  $\text{KTaO}_3$  were synthesized by an alternative solid-state reaction at low temperature, in which  $\text{K}_2\text{C}_2\text{O}_4$ ,  $\text{TaO}_x(\text{OH})_{5-x}(\text{NH}_4)_x$ , and KF 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 products. Pyrochlore-free  $\text{KTaO}_3$  powder was successfully synthesized by simply calcining the raw mixtures at 600 °C for 3 h and treating the calcination product with water. The agglomerations of the products are irregular in shape and consist of small grains with 10–30 nm in diameter. This method is a simple, cost-effective and environmentally friendly way to prepare stoichiometric, homogeneous and fine powders.

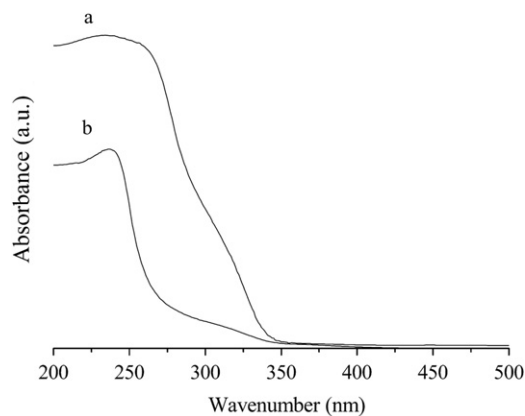


Fig. 7. UV–vis spectra of KT600 (a) and KTH600 (b) samples.

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