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Low-temperature synthesis of $K_2Ta_2O_3F_6$

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ABSTRACT

New method for obtaining pure powdered $K_2Ta_2O_3F_6$ was suggested through fluorination of ammonium tantalum hydroxide with NH_4HF_2/KF at room temperature. The main reaction product $(NH_4)_2KTaOF_6$ was assumed to be a precursor. $K_2Ta_2O_3F_6$ can be obtained by calcining the precursor at 300 °C. The reaction of $(NH_4)_2KTaOF_6$ with NH_4HF_2 may take place at 200–250 °C, resulting the formation of NH_4KTaF_7. The thermal decomposition of NH_4KTaF_7 resulted in $KTaF_6$ at 300 °C for 1 h. Hydrolysis of $KTaF_6$ produces $K_2Ta_2O_3F_6$ at 300 °C for 2–3 h.

1. Introduction

Marignac's salt was prepared by boiling an aqueous solution of K_2TaF_7. For a long time it was believed that the formula of Marignac's salt is $K_4Ta_4O_5F_{14}$. Rogachev et al. studied the structures of Marignac's salt in detail [1]. Almost at the same year in 1976, Vlasse et al. established the formula $K_2Ta_2O_3F_6$ for Marignac's salt [2,3]. The crystals of Marignac's salt are orthorhombic, $a = 10.212$, $b = 5.581$, $c = 14.499$, space group Pnma (No. 62). Up to the present time, only limited work focused on the synthesis and structure of $K_2Ta_2O_3F_6$. Rogachev et al. synthesized $K_2Ta_2O_3F_6$ by slowly cooling a melt of K_2TaF_7 and Ta_2O_5 in the molar ratio 3:1 from 700 °C to room temperature in an atmosphere of argon. However, the chemiometric ratio of K:Ta:F is unreasonable, which may lead to the problem of purity of the product. Zhao et al. synthesized the microsized ellipsoidal $K_2Ta_2O_3F_6$ by using tantalum foil anodization in saturated solutions of KCl containing 5 wt.% HF [4].

$KTaO_3$ presents two possible forms which are the pyrochlore $K_2Ta_2O_6$ phase and the perovskite $KTaO_3$ phase [5–12]. $K_2Ta_2O_3F_6$ may be regarded as that three of the oxygen ions in pyrochlore $K_2Ta_2O_6$ are substituted by six fluorine ions. Recently we found that pyrochlore-free $KTaO_3$ can be formed by calcination of ammonium tantalum hydroxide/$K_2C_2O_4$/KF mixture at 600 °C, KF plays an important role to inhibit the formation of pyrochlore $K_2Ta_2O_6$ during the calcination process [9]. Agylyansky et al. reported the synthesis of KTF_6 and K_2TaF_7 by heating the initial mixtures of Ta_2O_5-2KF-10NH_4HF_2 and Ta_2O_5-4KF-10NH_4HF_2 at 400 °C and 450 °C, respectively [13]. Since the reactivity of ammonium tantalum hydroxide is higher than that of Ta_2O_5, it might be reasonable to prepare fluorotantalates directly by thermal decomposition of ammonium tantalum hydroxide/NH_4HF_2/KF mixture at even low temperature (200–300 °C). The method described can be easily modified to yield $K_2Ta_2O_3F_6$.

2. Results and discussion

2.1. Analysis of ammonium tantalum hydroxide

TG–DTG curves of ammonium tantalum hydroxide and XRD patterns of the product obtained by calcining ammonium tantalum hydroxide for 3 h at 800 °C are given in Fig. 1. It can be seen in Fig. 1(a) that the weight loss starts at 30 °C, weight loss finishes at 800 °C with 82.30% remaining weight. Fig. 1(b) shows that single phase Ta_2O_5 can be obtained by calcining ammonium tantalum hydroxide for 3 h at 800 °C. All the diffraction peaks of calcining product can be indexed to standard Ta_2O_5 (Pdf Card No. 19-1299) and the peak width is broadened, indicating the smaller particle size of Ta_2O_5.

According to our previous works [14], ammonia is strongly absorbed on tantalum hydroxide prepared by ammonia neutralization of TaF_7^{2-} or TaF_6^{-} complexes. Therefore, the formula of tantalum hydroxide prepared by this method cannot be expressed by $Ta(OH)_5$. Since the ammonium can be released by reacting ammonium tantalum hydroxide with concentrated KOH solution, the NH_3 content is determined by titration the distillate from the

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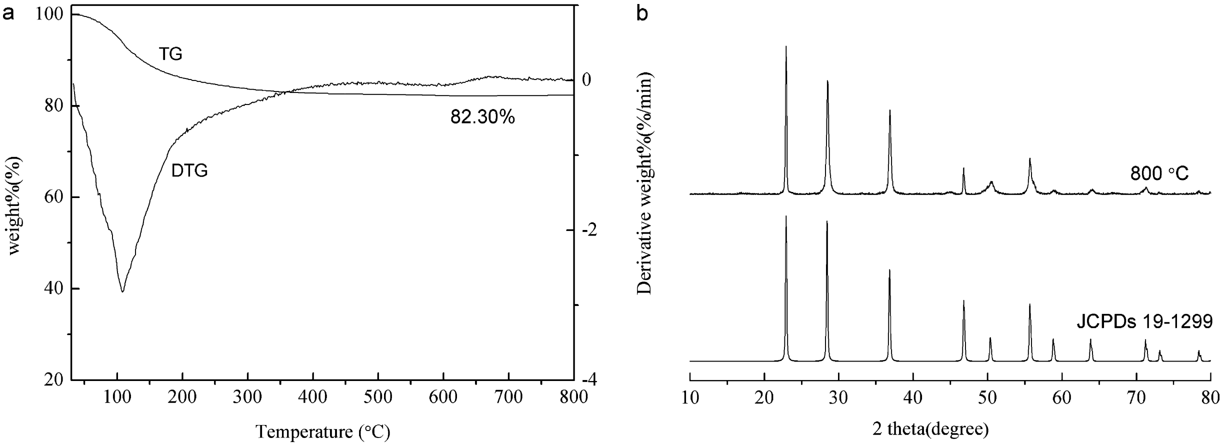

Fig. 1. TG–DTG curves of ammonium tantalum hydroxide (a) and XRD patterns of the product obtained by calcining ammonium tantalum hydroxide for 3 h at 800 °C (b).

mixture of 10 g sample, 20 g KOH and 180 mL water. The result of titration shows that the NH_3 content in the sample is 2.83 ± 0.05 mass% and the formula of ammonium tantalum hydroxide can be written as $(NH_4)_{0.4}TaO_{2.7}\cdot 2H_2O$.

2.2. Analysis of the precursor

Fluorination reactions with hydrogen fluorides proceed often at room temperature (RT) under the grinding initial components [15]. This fluorination stage is often overlooked in the literature. In the case of precursor obtained by grinding the initial components of ammonium tantalum hydroxide, NH_4HF_2 and KF at room temperature, the XRD patterns (Fig. 2 a) of the precursor clearly show that the characteristic peaks of NH_4HF_2 and KF disappear and a new crystalline phase is formed. Since the initial component of ammonium tantalum hydroxide is amorphous, some reactions must occur at room temperature based on the analysis of XRD patterns of the precursor. The diffraction peaks in Fig. 2(a) can be indexed to $(NH_4)_3NbOF_6$ with a cubic structure, similar with the reported data in the JCPDS card 14-529. The diffractogram is also very similar to that of typical cubic fluoroelpasolites, their structure was recently refined by Udovenko and Laptash [16]. Therefore, it is reasonable to infer that the new crystalline phase might be $(NH_4)_2KTaOF_6$. FTIR spectra (Fig. 2 b) again demonstrate that the reaction of the initial components grinded at RT. The IR spectra of the product at RT did not show the presence of strong peaks at 1229 cm^{-1} of NH_4HF_2 and new peak at 880 cm^{-1} is observed, including reaction without heating. The IR band at 880 cm^{-1} should be assigned to Ta–O terminal bond which has a triple character (one σ and two π bonds) in seven-coordinated $TaOF_6^{3-}$ [17].

2.3. XRD patterns analysis of the products

X-ray diffraction patterns of the products calcining at different temperatures for 3 h, the standard potassium tantalum oxyfluoride ($K_2Ta_2O_3F_6$ Pdf Card No. 72-494) and the potassium heptafluorotantalate (K_2TaF_7, Pdf Card No. 44-1039) are given in Fig. 3.

It can be seen in Fig. 3 that single phase $K_2Ta_2O_3F_6$ can be obtained at 300 °C, all the diffraction peaks can be indexed to orthorhombic phase of $K_2Ta_2O_3F_6$ (Pdf Card No. 72-494), however, single phase $K_2Ta_2O_3F_6$ could not be obtained at 200 and 250 °C, the product contains K_2TaF_7 (Pdf Card No. 44-1039). Most likely, NH_4KTaF_7 is isostructural with K_2TaF_7. Since the excess of NH_4HF_2 (3.5 mol) was taken, the reaction of $(NH_4)_2KTaOF_6$ with NH_4HF_2 may take place at 200–250 °C, resulting the formation of NH_4KTaF_7. FTIR analysis show that there is a strong peak at

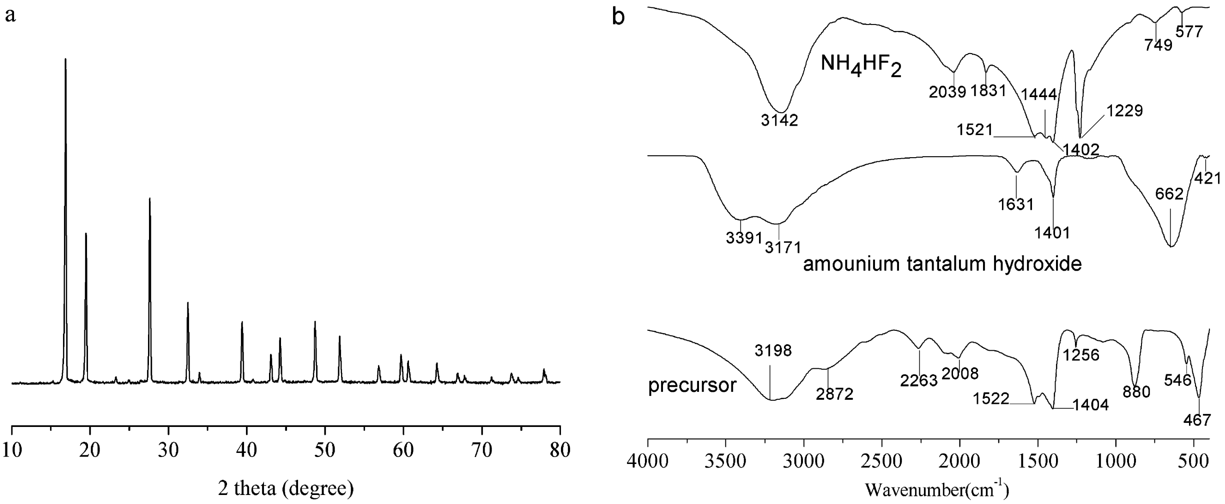

Fig. 2. XRD pattern and FT-IR spectra of the precursor.

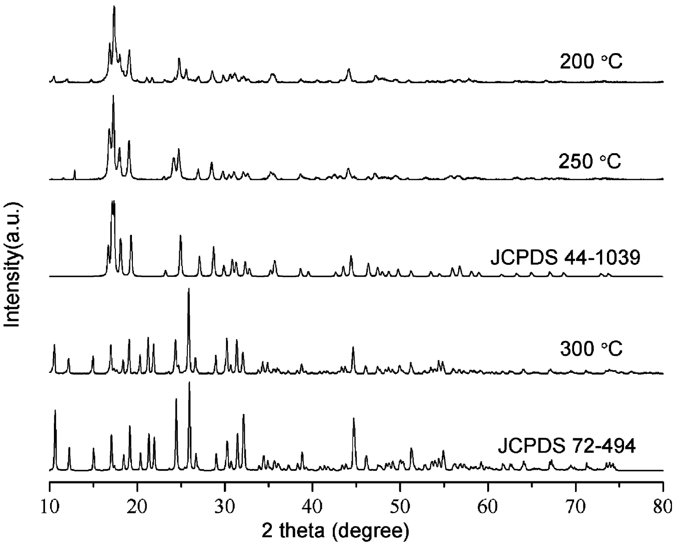

Fig. 3. XRD patterns of $K_2Ta_2O_3F_6$ and K_2TaF_7 at different calcination temperatures for 3 h.

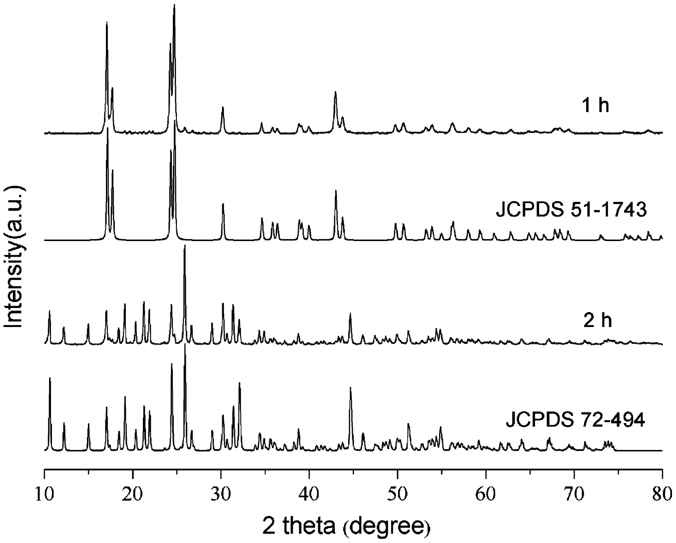

Fig. 4. XRD patterns of $K_2Ta_2O_3F_6$ and $KTaF_6$ at 300 °C with different calcination times.

1432 cm^{-1}, which is characteristic peak of NH_4^+ group, indicating the formation of NH_4KTaF_7 when the precursor was calcinated at 200–250 °C.

Fig. 4 shows the X-ray diffraction patterns of the products calcinated at 300 °C for different times, the standard potassium tantalum oxyfluoride ($K_2Ta_2O_3F_6$ Pdf Card No. 72-494) and the potassium hexafluorotantalate ($KTaF_6$ Pdf Card No. 51-1743). As can be seen from Fig. 4, single phase $K_2Ta_2O_3F_6$ can be obtained by calcining for 2 h, all the diffraction peaks can be indexed to orthorhombic phase of $K_2Ta_2O_3F_6$ (Pdf Card No. 72-494), however, single phase $K_2Ta_2O_3F_6$ cannot be obtained by calcining for 1 h, the product contains $KTaF_6$.

The XRD search results of the product calcinated at 300 °C for different times are listed in Table 1. It can be concluded that the product possesses orthorhombic syngony, with a space group of Pnma – D_{2h}^{16}, $Z = 4$. Cell parameters of the products are calculated by MDI Jade 5.0 software, the results are shown in Table 1. The corresponding cell parameters of the standard potassium tantalum oxyfluoride ($K_2Ta_2O_3F_6$ Pdf Card No. 30-0995) are: $a = 10.220$, $b = 5.570$, $c = 14.520$.

2.4. SEM micrographs

The SEM images of powders calcining at 300 °C for 2 h (a) and 3 h (b) are shown in Fig. 5. The as-prepared powders are agglomerated. The particles of the product are flake-like with the thickness of 200–400 nm.

2.5. FTIR analysis

FTIR spectra of the product obtained by calcining for different times at 300 °C are shown in Fig. 6. Peaks at 3435 and 1637 cm^{-1}

Table 1
XRD search results of $K_2Ta_2O_3F_6$ crystal.

Calcination time/h	Calcination product	Matching JCPDS no.	Cell parameters/nm (±0.002 nm)
1	$KTaF_6 + K_2Ta_2O_3F_6$	51-1743 + 30-0995	–
2	$K_2Ta_2O_3F_6$	30-0995	$a = 10.223$ $b = 5.585$ $c = 14.503$
3	$K_2Ta_2O_3F_6$	30-0995	$a = 10.222$ $b = 5.560$ $c = 14.501$

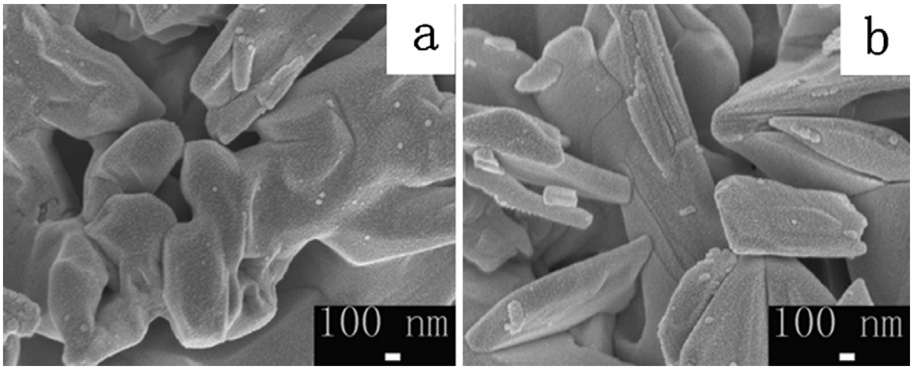

Fig. 5. SEM micrographs of $K_2Ta_2O_3F_6$ powders caclining for 2 h (a) and 3 h (b) at 300 °C.

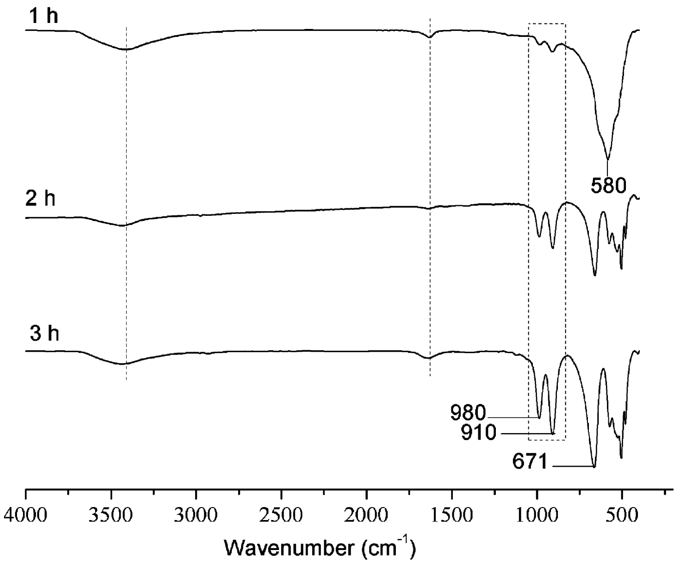

Fig. 6. FTIR spectra of the product obtained by calcining for different times at 300 °C.

are assigned to stretching and bending vibrations of H_2O, respectively, due to KBr disc's hygroscopicity. The characteristic absorption peaks of $K_2Ta_2O_3F_6$ are 988, 916, 668, 553, 508 and 495 cm^{-1}. The peak at 580 cm^{-1} is the characteristic absorption peak of $KTaF_6$ [14]. It can be seen from Fig. 6 that the product calcinated for 1 h has a strong peak at 580 cm^{-1} and two weak peaks at 980 cm^{-1} and 910 cm^{-1}. It indicates that the main product is $KTaF_6$. The peak at 580 cm^{-1} disappears and peaks at 980 cm^{-1} and 910 cm^{-1} become stronger when the precursor were calcinated for 2 and 3 h.

2.6. Reaction mechanism

The above results of XRD analysis show that the reaction may consist of four steps. The first step is that the reaction of $(NH_4)_{0.4}TaO_{2.7}{\cdot}2H_2O/NH_4HF_2/KF$ mixture yields $(NH_4)_2KTaOF_6$ at RT, as shown in Eq. (1).

$$(NH_4)_{0.4}TaO_{2.7}\cdot 2H_2O + 2.5NH_4HF_2 + KF \xrightarrow{RT} (NH_4)_2KTaOF_6 + 0.9NH_3 + 3.7H_2O \quad (1)$$

The second step is the reaction of $(NH_4)_2KTaOF_6$ with NH_4HF_2 may take place at 200–250 °C, resulting the formation of NH_4KTaF_7 (Eq. (2)).

$$(NH_4)_4KTaOF_6 + 0.5NH_4HF_2 \xrightarrow[3\ h]{200-250\,^{\circ}C} NH_4KTaF_7 + 1.5NH_3 + H_2O \quad (2)$$

The third step is actually thermal decomposition of the above complexes with the formation of $KTaF_6$ at 300 °C (Eqs. (3) and (4)).

$$(NH_4)_2KTaOF_6 \xrightarrow[1\ h]{300\ ^{\circ}C} KTaF_6 + 2NH_3 + H_2O \quad (3)$$

$$NH_4KTaF_7 \xrightarrow[1\ h]{300\ ^{\circ}C} KTaF_6 + NH_3 + HF \quad (4)$$

$KTaF_6$ is sensitive to water or atmospheric moisture, especially when the temperature exceeds 160 °C [18,19]. Consequently, the forth step is the hydrolysis of $KTaF_6$, as shown in Eq. (5).

$$2KTaF_6 + 3H_2O \xrightarrow[2-3\ h]{300\ ^{\circ}C} K_2Ta_2O_3F_6 + 6HF \quad (5)$$

It is obvious that the reaction yields $K_2Ta_2O_3F_6$ and all volatile components will evaporate. The controlled experiment was done under argon atmosphere by calcining the mixture at 300 °C for 3 h. The results show that the product is mainly $KTaF_6$, only small amount of $K_2Ta_2O_3F_6$ was observed.

3. Conclusion

Crystalline powders of $K_2Ta_2O_3F_6$ were synthesized by calcining the mixture of ammonium tantalum hydroxide/NH_4HF_2/KF at 300 °C for 2–3 h. The intermediate of the reaction was $KTaF_6$ and then $K_2Ta_2O_3F_6$ was produced by the hydrolysis of $KTaF_6$. The calcination time and temperature play important roles for the formation of crystalline $K_2Ta_2O_3F_6$ powders. The product has higher degree of crystallinity with prolonging the calcination time. The particles of the product obtained at 300 °C for 2–3 h are flake-like with the thickness of 200–400 nm.

4. Experimental

4.1. Analysis of ammonium tantalum hydroxide

Ammonium tantalum hydroxide was prepared according to the literature [14] by neutralization of H_2TaF_7 with aqueous ammonia. The carefully washed filter cake was dried in an oven at 65 °C for 12 h, with periodical grinding with a mortar to achieve the purpose of uniform drying. The NH_3 content is determined by titration the distillate from the mixture of 10 g sample, 20 g KOH and 180 mL water. Ta_2O_5 content of ammonium tantalum hydroxide were analyzed by TG. Ammonium tantalum hydroxide was calcinated for 3 h at 800 °C and the calcination product was analyzed by X-ray powder diffraction.

4.2. Synthesis of $K_2Ta_2O_3F_6$

Ammonium tantalum hydroxide (7.97 g, equivalent to 29.8 mmol $(NH_4)_{0.4}TaO_{2.7}{\cdot}2H_2O$), NH_4HF_2 (5.56 g, 97.54 mmol) and $KF{\cdot}nH_2O$ (2.67 g, n is 2.12 by TG analysis, 27.73 mmol) were mixed with methanol (4 mL) in the PTFE mortar to form the slurry. The molar ratio of Ta: K: F is 1:1:8. The precursor was obtained by drying the slurry under the infrared lamp for about 4~5 h. The precursor was calcinated in a PTFE crucible at different temperatures for 3 h. The calcination procedure was performed in two steps: Firstly, the precursor was heated from room temperature to 50 °C with a heating rate of 5 K/min and then held 30 min at 50 °C. Secondly, heating from 50 °C to the target temperature (200 °C, 250 °C and 300 °C, respectively) with 10 K/min and then held 3 h. In addition, the precursor was calcinated at 300 °C for 1 h and 2 h, respectively. The relative humidity of the air was 55–65% during the calcination.

4.3. Characterization

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 raw materials were heated in the range from 30 °C to 800 °C at 20 °C min^{-1}. X-ray power diffraction patterns were obtained with a D/max-RB diffractometer in the 2θ range using graphitmonochromated 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 morphologies were observed using a scanning electron microscope (SEM) (JSM-7500F-EDS).

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