

Mixed solvents: a key in solvothermal synthesis of KTaO_3

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Abstract

Perovskite and pyrochlore KTaO_3 were selectively synthesized in mixed solvents (water–ethanol and water–hexane systems) by solvothermal reaction with KOH, whose concentration was one order of magnitude lower than that in traditional methods. The samples were characterized by X-ray diffraction and transmission electron microscopy. Results show that the ratio of inert solvents (ethanol or hexane) to active solvent (water) played a significant role in the manipulation of the crystalline behavior of KTaO_3 to the form pyrochlore or perovskite nanocrystals. The possible mechanisms of the reactions are also discussed.

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1. Introduction

The choice of solvents is very important for the synthesis of target compounds. It can help transfer reactants and also change the reactivity of the reactants as well. A different choice of solvents always leads to different results. Mixed solvents are more complex systems than simple solvents. Some studies have shown that products with special morphology or special properties could be obtained in the mixed solvents reaction. Here, we report a new way of synthesizing perovskite and pyrochlore potassium tantalate selectively by easily changing the ratio of the mixed solvents.

Potassium tantalate, KTaO_3 , with perovskite structure, has attracted special attention because of its outstanding dielectric nonlinearity performance at low temperature near the transition temperature of high- T_c superconductors. As such, it has been extensively investigated by a variety of techniques over a wide range of conditions [1–3]. Recently, a series of tantalates, including the KTaO_3 , have been used as photo-

catalysts for overall water splitting, and showed rather excellent photocatalytic activity [4–7].

The conventional techniques for synthesizing KTaO_3 powder are based on the solid-state reaction, which requires long periods of heating above 1000°C [8]. Alternatively, when using precursors such as alkoxides, a defective pyrochlore phase, $\text{K}_2\text{Ta}_2\text{O}_6$ crystallizes at 650°C; the perovskite phase is obtained only after heating to 850°C [9]. The hydrothermal method has also been introduced into the synthesis of potassium tantalate thin films [10,11] and powders [12,13]. However, this phase of pyrochlore often appeared in the products of hydrothermal synthesis in a wide range of KOH concentrations [11,12]. The presence of pyrochlore phase can significantly reduce the relative permittivity of the ferroelectric films of some perovskite substances and, thus, pyrochlore should be avoided in the synthesis [14]. In order to obtain pure potassium tantalate perovskite in hydrothermal synthesis, a rather high concentration of KOH (15 mol/L) was employed [11,12]. This paper details a new attempt at the solvothermal synthesis of KTaO_3 powders with perovskite structure, using water–ethanol and water–hexane as solvents, at low KOH concentration. Different morphologies of the products were also obtained.

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2. Experimental section

The starting materials for the synthesis of KTaO_3 were Ta_2O_5 (A.R) and KOH (A.R). In a typical synthesis procedure, 1.68 g KOH (30 mmol) and 0.442 g Ta_2O_5 (1 mmol) were added into a Teflon-lined autoclave with a capacity of 40 mL, and different solvents, such as water, ethanol, hexane, and so on, were added up to 75% (30 mL) of the total volume separately, making the KOH concentration of the solution 1 mol/L. The autoclave was sealed and maintained at 160°C for 24 h without staking or stirring and allowed to cool to room temperature naturally. The crystalline powder product was filtered off, washed with deionized water and dried in air at 60°C .

The product was characterized by powder X-ray diffraction (XRD) on a D8 Advance Bruker X-ray diffractometer with monochromatized $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) incident radiation. XRD patterns were recorded from 10° to 70° (2θ) with a scanning step of 0.01° . The average crystal size was determined from the XRD pattern parameters according to the Scherrer equation: $D_c = K\lambda/\beta \cos \theta$. D_c is the average crystal size, K is the Scherrer constant equal to 0.89, β is the full-width at half-maximum (FWHM) and θ is the diffraction angle. The peak at 31.7° was used for the calculation of the crystal size of perovskite KTaO_3 , because it showed great disparity in intensity. The morphology of the products was examined with transmission electron microscopy (TEM) on an H-800 transmission electron microscope operated at 200 kV.

3. Results and discussions

3.1. Solvothermal synthesis of KTaO_3 with water–ethanol solvent

The XRD spectra in Fig. 1 show the synthesis with pure water (a) and ethanol (b) as solvents separately. In spectrum (a), all the reflections can be readily indexed as pyrochlore KTaO_3 [space group: 227], identical to the reported data in the JCPDS cards (35-1464), which is consistent with the data reported before [11,12]. Spectrum (b) shows the product in ethanol is perovskite KTaO_3 [space group: 221], identical to the JCPDS cards (77-0918). In this case, the concentration of KOH is about 1 mol/L, far below 15 mol/L (25.2 g KOH was dissolved in about 30 mL solvent) which was mentioned in Ref. [12].

In the hydrothermal process, the hydroxyl ion activity was the critical effect promoting the formation of the perovskite phase [12]. Therefore, it is important to improve the degree of the hydroxyl ion activity of the solution in order to obtain perovskite. Because the effect of the solvent can exert considerable influence on acid

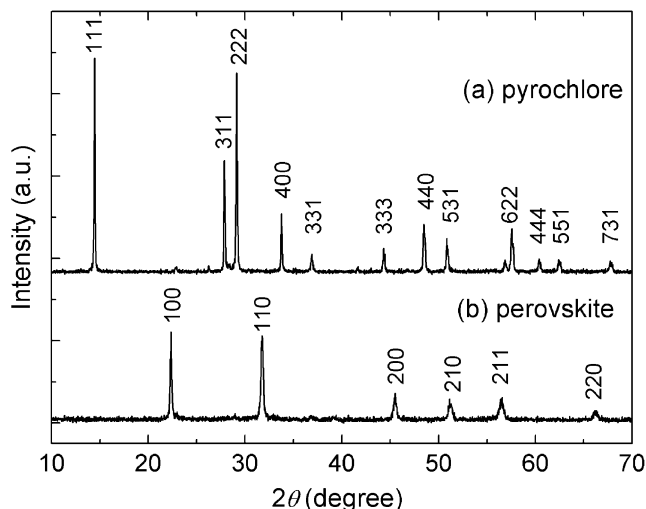


Fig. 1. XRD patterns of powders synthesized in water (a), and ethanol (b) with solvothermal method.

and base activity by differential solvation [15,16], it was attempted to use ethanol as the solvent instead of water. As we all know, water and ethanol are both protic solvents, with high solubility of KOH (37.0 g in ethanol and 54.3 g in water at room-temperature [17]). One mol/L KOH can be dissolved and ionized completely in both water and ethanol. But water is the solvent which has strong solvation by forming hydrogen bonds with ions. The molecule of H_2O is rather small and can be polarized easily, which can stabilize the anions and cations in the solution effectively, especially the anions, because it can form hydrogen-bond type solvation with anions [18]. So the hydroxyl ion in the KOH solution can be partly shielded by the H_2O molecules and make hydroxyl ion activity decrease. Compared with water, ethanol has relatively bigger molecules and weaker solvation. As a result, hydroxyl ion activity of ethanol solution is much greater than in water solution, with the same KOH concentration in each. The reactivity of the KOH ethanol solution is higher in the same way. Actually, this concept has already been used in organic reactions. Dimethyl sulfoxide (DMSO) is an important dipolar aprotic solvent with high dielectric constant and weak solvation. In DMSO, nucleophilic groups, such as hydroxyl and alkoxy ions are almost nude and have extremely strong activity compared to that in water. So many nucleophilic reactions are carried out in DMSO. In our case, ethanol plays a similar role and enhances the reactivity of KOH .

Further investigations have been conducted with different amounts of water introduced into ethanol before the same solvothermal process. When diluted with water, the solvent will have a stronger solvation while hydroxyl ion activity of the KOH solution will decrease. Fig. 2 shows the XRD spectra for the KTaO_3

products synthesized with different amounts of water in the solutions. When the volume of additive water is equal to or less than 5 mL, the products prove to be pure perovskite KTaO_3 . If the volume of water is 7 mL, the products are a mixture of perovskite and pyrochlore

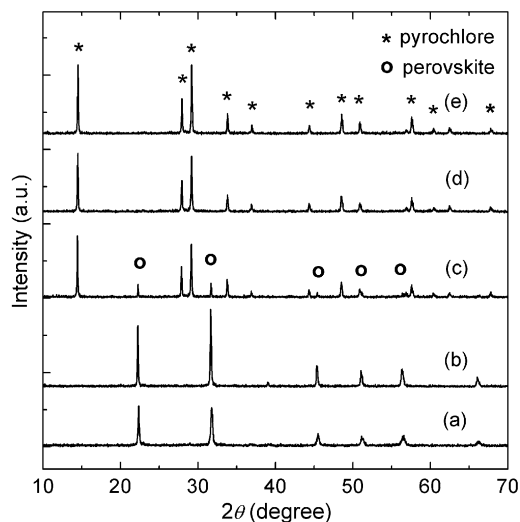


Fig. 2. XRD patterns of KTaO_3 powders synthesized in ethanol with additional water being (a) 0.5 mL, (b) 5 mL, (c) 7 mL, (d) 9 mL, and (e) 15 mL (the total volume of the solution is 30 mL).

KTaO_3 . Finally, increase in the volume of water above 9 mL causes the products to gradually turn to pure pyrochlore KTaO_3 . Hereby, it is an easy way to control the crystal phase of the KTaO_3 products by only adjusting the ratio of the solvent mixture.

Fig. 3 shows typical TEM images of KTaO_3 products obtained with different ratios of solvents. All the perovskite KTaO_3 , which are shown in (a) and (b), are of cubic morphology with the average size of 60–100 nm. In the pyrochlore products the size of which is almost 150–200 nm, some parallelepiped as well as cubic morphology is found. The different grain size and morphology of pyrochlore and perovskite KTaO_3 cannot be related to a precipitation by heterogeneous nucleation but are instead consistent with a precipitation process by dissolution precipitation, as previously observed in the synthesis of BaTiO_3 [19]. Energy dispersive X-ray analysis (EDXA) has also been conducted and the results show that the K/Ta ratio of all the pyrochlore phase obtained in our cases is ≈ 0.5 while the K/Ta ratio of all the perovskite phase is ≈ 1 . The possible reactions may be formulated as

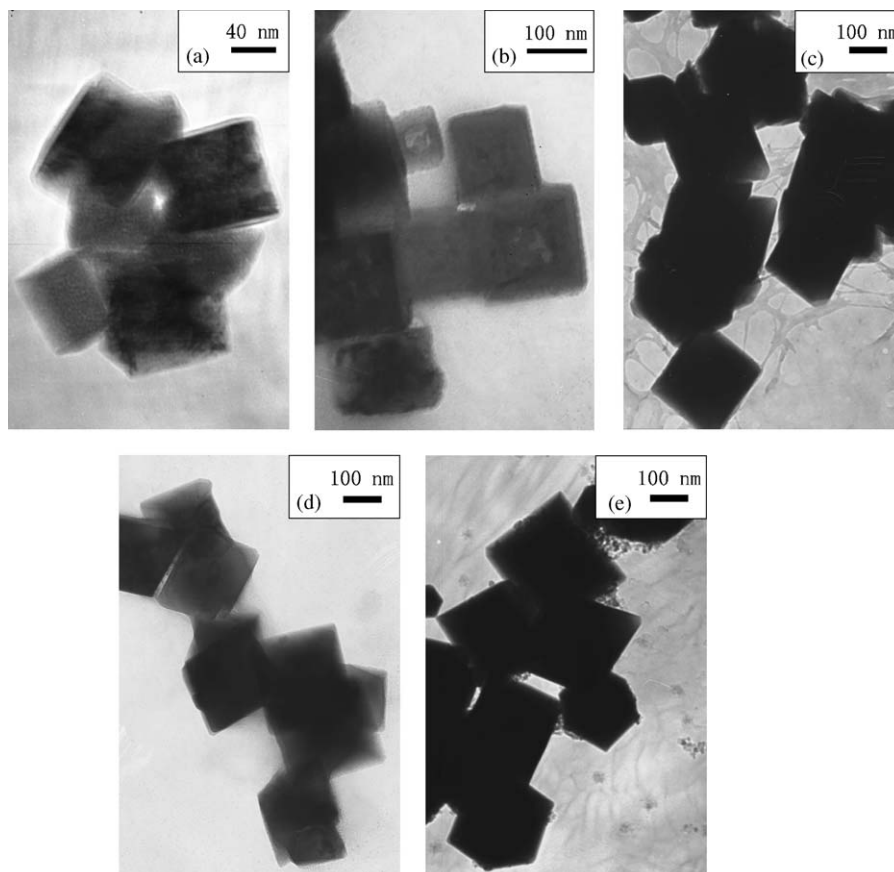
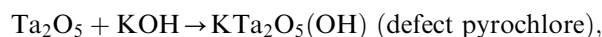
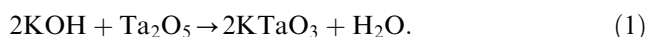


Fig. 3. TEM images of KTaO_3 synthesized in ethanol with the additional water being (a) none; (b) 2 mL, (c) 7 mL, (d) 15 mL, and (e) 30 mL.

This result is consistent with Ref. [12], which showed the hydrothermal synthesis of pyrochlore and perovskite KTaO_3 with different concentrations of KOH.

3.2. Solvothermal synthesis of KTaO_3 with hexane–water solvent

In a typical hydrothermal reaction, KOH could be soluble in water and the KOH solution reacts with the Ta_2O_5 , just as Eq. (1) shows:



And if pure hexane is used as the solvent, both KOH and Ta_2O_5 cannot be resolved in it and they cannot contact each other sufficiently. As a result, reaction (1) will probably cease. Now suppose the mixture of water and hexane was used as the solvent in the reaction. As known, hexane is insoluble in water. If hexane and water are put together as solvents of the solvothermal reaction, they would form some kind of emulsion under high temperature and pressure. This is to say, there are two phases in the solvent, water and oil. KOH will be resolved in water phase and the droplets of water could be tiny reactors. Also, even if the total KOH concentration is invariable, the concentration of KOH in the water droplet can be easily adjusted by changing the ratio of volume of water and hexane solvent. So we could theoretically easily control the crystal phase of KTaO_3 products in this way.

Fig. 4 shows the XRD spectra for the KTaO_3 products synthesized with the different amounts of water in hexane. The results confirmed our assumption satisfactorily. If pure hexane was used as solvent, the products are almost amorphous. Only some weak peaks belonging to perovskite KTaO_3 could be seen, which were probably because of the trace impurity of water in the reaction system. When water (less than 2 mL) was introduced into the reaction, pure perovskite KTaO_3 was obtained. However, if additional water is equal to or more than 5 mL, this perovskite was gradually replaced by pyrochlore. A total of 30 mmol KOH used in each reaction. So if 2 mL H_2O was added up, the KOH concentration of the water droplets in the solvothermal reaction system was approximately 15 mol/L, same as mentioned in Ref. [12]. The results also show that the KOH concentration is a key factor in obtaining perovskite KTaO_3 in hydrothermal reaction.

In addition, the FWHM changed much and intensity increased greatly from samples (b) to (d). The average crystal size of the three samples was calculated to be 17.1, 30.6 and 79.7 nm, respectively, indicating that the amount of additional water also had a strong effect on the average crystal size of the products. TEM observation was made to make further investigation. Fig. 5 shows the morphology of the KTaO_3 powders synthe-

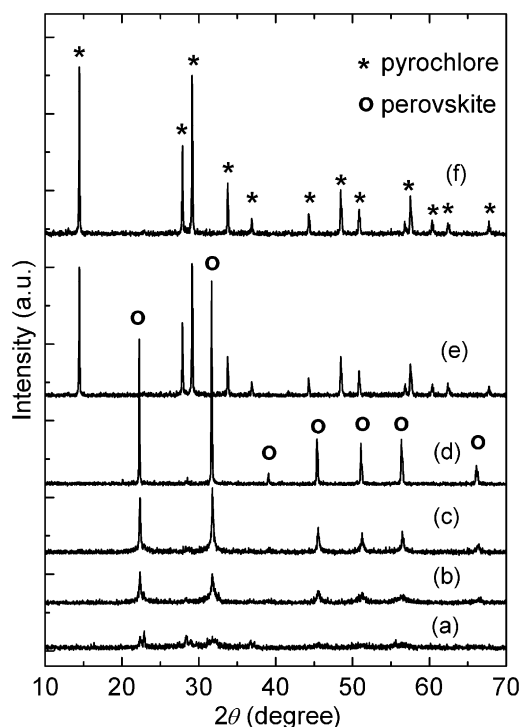


Fig. 4. XRD patterns of KTaO_3 powders synthesized in hexane with the additional water being (a) 0 mL, (b) 0.05 mL, (c) 0.5 mL, (d) 2 mL, (e) 5 mL, and (f) 15 mL (the total volume of the solution is 30 mL).

sized by solvothermal reaction when the additional water being (a) none, (b) 0.05 mL, (c) 0.2 mL, (d) 0.5 mL, (e) 2 mL, (f) 5 mL, and (g) 15 mL. If no water was added in the reaction, the product would be poorly crystallized, which was consistent with the XRD result. And when 0.05 mL H_2O was added, many square nanoflakes with an average length of about 100 nm were obtained. This is the first time perovskite KTaO_3 nanoflakes are synthesized. The specific morphology of KTaO_3 will probably bring in some novel properties as a result, such as larger surface area, which is good for its photocatalytic activity. The study of its performance is still in progress. The nanoflake morphology disappeared with the increase of the additional water. Some kind of short bundles of nanorods turned up when the additional water was 0.2 mL. The bundles then aggregated each other and formed with an approximately cubic morphology with additional water increasing to 0.5 mL. The cubic morphology became more and more perfect. If 2 mL water was added, the products completely exhibited perfect cubic morphology with the average size of 150 nm; (f) and (g) show the TEM images of pyrochlore KTaO_3 synthesized with 5 and 15 mL additional water. Both the morphology and size of the two powders are similar. Also some parallelepipeds are found in the images, which are consistent with the ethanol–water reaction system.

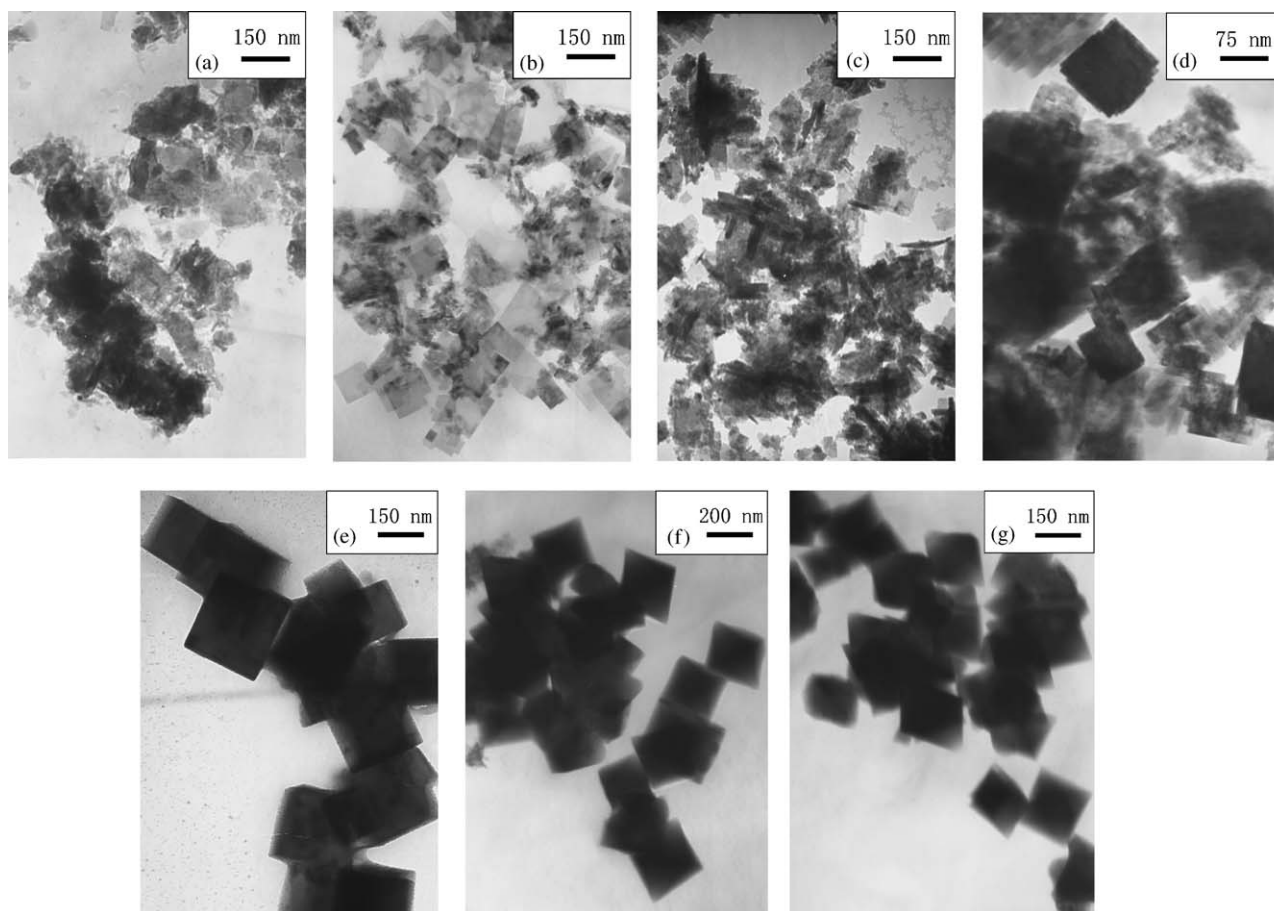


Fig. 5. TEM images of KTaO_3 synthesized in hexane with the additional water being (a) none, (b) 0.05 mL, (c) 0.2 mL, (d) 0.5 mL, (e) 2 mL, (f) 5 mL, and (g) 15 mL.

EDXA also indicates that the K/Ta ratios of all the pyrochlore phases are ≈ 0.5 while the K/Ta ratio of all the perovskite phases are ≈ 1 , same as the one of the ethanol–water system.

The reason why nanoflakes and short bundles of nanorods turned up in the hexane–water reaction system was probably because water has a weak solubility in hexane. Though water and hexane are insoluble in each other at room temperature, traces of water will still be resolved in hexane and form an extremely diluted homogeneous solution. With the temperature and pressure increasing, the solubility of water will increase. As a result, if a little water was added to hexane, a homogeneous water–hexane solution would probably be formed in the solvothermal condition. This would help synthesize the uniform nanoflake products. Adding water continually, the excess water will separate out from hexane and become tiny droplets. Consequently, nanoflake structure will be destroyed and typical cubic morphology will appear. Though the detailed mechanism of the formation of nanoflake is still unclear, it is a novel way to synthesize such kind of nanostructure materials in extremely diluted water–oil solution by solvothermal reaction.

4. Conclusion

We have exploited two novel solvothermal methods to synthesize perovskite and pyrochlore KTaO_3 selectively in mixed solvents even with low KOH concentration. Though the reaction mechanisms in the water–hexane and water–ethanol systems are different, controlling the crystal phase of KTaO_3 product can be easily realized. In addition, perovskite KTaO_3 with nanoflake structure was also successfully synthesized in the water–hexane system. We believe that these two solution synthetic routes with mixed solvents, requiring no high temperature or high KOH concentration, and ensuring higher purity and uniformity of the products, will greatly reduce the production cost and offer great opportunity for synthesis of some other important substances, such as niobates [20], and titanates [21,22], in a more controllable way.

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