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NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Hydrothermal epitaxy of $KTaO_3$ thin films under supercritical water conditions

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Abstract Potassium tantalate powders were hydrothermally synthesized at 400 °C using Ta_2O_5 and KOH as starting materials with various KOH concentrations (0.1–1.0 M) and heating durations (2–48 h). A defect pyrochlore phase of $KTa_2O_5(OH)\cdot nH_2O$, was obtained at low KOH concentration and short reaction time. The perovskite phase of $KTaO_3$ predominated as the heating duration and the KOH concentration increased. Pure $KTaO_3$ was obtained in 0.5–1.0 M KOH aqueous solutions and reaction times of 8–48 h. Heteroepitaxitial $KTaO_3$ thin films were achieved on the (100) $SrTiO_3$ substrate in 0.5 M KOH solution under supercritical water conditions. Based on the XRD, SEM-EDX and EBSP (Electron BackScatter Pattern) results, epitaxial $KTaO_3$ crystals were grown on the (100) oriented single-crystal $SrTiO_3$ substrate. Synthesis of perovskite $KTaO_3$ crystals in supercritical water employed significantly low KOH concentrations (<0.5 M), which was far less than the very high concentrations (>7 M) required for conventional hydrothermal method.

Introduction

$KTaO_3$ with perovskite structure is an incipient ferroelectric material that has promising applications in electromechanical [1–3], and photocatalytical [4–8] fields and thus has attracted considerable interest among material scientists. The $KTaO_3$ powders are commonly synthesized by homogeneous precipitation method and solid-state methods in which the mixture of reactants is heated under high temperature. Additionally, hydrothermal synthesis method has been successfully applied to prepare $KTaO_3$ powders over the past decade [9–13]. Compared with solid-state preparation, the hydrothermal method has unique merits including mild experimental conditions and homogeneity of the final products.

In conventional hydrothermal method, the starting materials for hydrothermal synthesis of $KTaO_3$ are tantalum pentoxide (Ta_2O_5) and the aqueous solution of potassium hydroxide (KOH) at high concentrations. Goh et al. reported that a defect pyrochlore phase of $KTa_2O_5(OH)$ formed at low concentrations of KOH (<4 M), and only when the alkaline concentration was above 7 M, perovskite phase of $KTaO_3$ could be obtained [13]. 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. He et al have reported the successful solvothermal preparation of $KTaO_3$ particles using 1.0 M KOH in water–ethanol mixed solvents [14, 15]. Reactions under solvothermal conditions could happen easier than those under conventional hydrothermal conditions because of the low dielectric constant. Although the required concentration of KOH was reduced, the organic solvents are flammable, and toxic.

In addition, the temperature also plays a pivotal role in the hydrothermal synthesis of $KTaO_3$. The hydrothermal temperatures so far reported for synthesizing $KTaO_3$ powders were in the range of 150–200 °C. Supercritical water has been proved to be an environmentally benign and ideal reaction medium in the material synthesis [16–19]. When the temperature and pressure of solvent, such as water, is above its critical point (for water, $T_C = 374$ °C,

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P_C = 22.1 MPa), the properties, such as dielectric constant and solubility for many compounds, will change dramatically. We have demonstrated that hydrothermal synthesis of $KNbO_3$ powders could be achieved in supercritical water at low alkalinity [20, 21]. Under supercritical water conditions, the KOH concentration needed in the preparation is far lower than that previously reported for conventional hydrothermal methods. Accordingly, the synthesis of certain materials, such as $KTaO_3$ powders, in supercritical water should have many advantages over those synthesized by the conventional hydrothermal or solvothermal methods. Therefore, it is a great challenge to explore an alternative method adopting supercritical water condition to synthesize $KTaO_3$.

Since hydrothermal epitaxy of $KTaO_3$ film was required high KOH concentration (>7 M) under the conventional hydrothermal conditions, in the present paper, we have demonstrated that $KTaO_3$ epitaxy is prepared on the (100) $SrTiO_3$ substrate in supercritical water with relatively low alkaline KOH solutions. The one-step hydrothermal synthesis of $KTaO_3$ thin films which are commonly synthesized with highly alkaline KOH solutions is successfully achieved in this work. The obtained $KTaO_3$ crystals have very crystalline, regular shape of rectangle and aligned in the substrate plane, which should play an important role in its incipient ferroelectric properties.

Materials and methods

Preparation

The starting reagents used in the hydrothermal preparation were Ta_2O_5 powder (99.99%, Nakarai Chemical Co., Ltd) and potassium hydroxide (85%, Wako Pure Chemical Industries, Ltd) aqueous solution. A 5 g of Ta_2O_5, and 250 cm^3 of 0.11–1.0 M KOH aqueous solution were mixed together and stirred for 4 h to become white slurry. Then the slurry was put into a gold tube in the autoclave. The autoclave in this work is made of incorruptible nickel alloy (Inconel 625) with cylindrical shape (500 cm^3 capacity). Thin films were synthesized on (100) oriented $SrTiO_3$ single-crystal substrates (Dalian Danning Opto-electronics Technology Co, China) that had one side polished. The substrate was fixed in a Stainless holder with the polished side facing up and held approximately 20 mm above the solution. The hydrothermal reaction was carried out at 400 °C with autogenous pressure inside the autoclave. The pressure inside the autoclave is measured by using a pressure transducer connected with electrical displaying system. The value is 25 MPa as the temperature is 400 °C. Upon completion of the reaction, the gold tube with product in it was taken out. The white powders were filtrated and washed with distilled water, then dried at 60 °C. The films were rinsed repeatedly with de-ionized water and dried at 60 °C. Synthesis by solid-state reaction was also carried out for comparison using K_2CO_3 and Ta_2O_5 in a K:Ta molar ratio of 1.1:1 and heating at 900 °C for 10 h with a heating rate of 15 °C min^{-1}.

Characterization

Crystal structures of resulting powders and thin films were determined by the X-ray powder diffraction (XRD), performed on a Rigaku RINT 2200 diffractometer using CuK_α radiation (40 kV and 20 mA) and a scan speed of 2 min^{-1} in 2θ. The morphology and elementary analysis (K/Ta atomic ratio) of the prepared potassium tantalate crystals was performed by using JEOL JSM-5600 scanning electron microscope equipped with an energy disperse spectroscopy (SEM-EDS), operating at 15 kV. Elemental mapping on the $SrTiO_3$ substrate was performed for K, Ta and Ti. Electron BackScatter Patterns (EBSP) for the thin film was carried out using Hitachi S-4300SE FE-SEM equipped with EBSP detector (TSL OIM4.6), operating at 20 kV. EBSP data were collected for 15 points of $KTaO_3$ crystals and 4 points on the $SrTiO_3$ substrate and analyzed the orientation of the crystal.

Results and discussion

Phase composition

At first, to determine the synthetic conditions for single phase of perovskite type potassium tantalate, KOH concentration and reaction time were varied at 400 °C. Synthetic conditions, crystal phases and K/Ta atomic ratio of the products are summarized in Table 1. In the case of KOH concentration of 0.11 M, the starting material, Ta_2O_5 (JCPDS 79-1375) was remained, indicating that tantalum oxide did not readily transform to potassium tantalate at the initial K/Ta molar ratio of unity. The profiles for the products hydrothermally synthesized in KOH concentration of 0.18 can be assigned to $K_2Ta_2O_6$ (JCPDS 35-1464). It was reported that a potassium-deficient defect pyrochlore incorporating protons with a chemical formula of $KTa_2O_5(OH)\cdot nH_2O$ and not $K_2Ta_2O_6$ was produced under conventional hydrothermal conditions[1]. In the profiles for the products in KOH concentration of 0.34 M or higher, the perovskite phase for $KTaO_3$ (JCPDS 77-918) was formed. According to the previous results, high concentration of KOH was found to be a critical requisite for the formation of $KTaO_3$ at 200 °C and an intermediate pyrochlore potassium tantalate species formed first before

Table 1 Experimental conditions and results

Run no.	Reaction time/h	KOH concentration (K/Ta molar ratio)	Crystal phase	K/Ta atomic ratio
1	4	0.11 M (1)	$H_2Ta_2O_6$, (Ta_2O_5)	0.42
2	4	0.18 M (2)	$K_2Ta_2O_6$	0.45
3	4	0.37 M (4)	$K_2Ta_2O_6$, ($KTaO_3$)	0.53
4	2	0.34 M (4)	$K_2Ta_2O_6$, ($KTaO_3$)	0.54
5	8	0.34 M (4)	$K_2Ta_2O_6$, ($KTaO_3$)	0.65
6	24	0.34 M (4)	$KTaO_3$, ($K_2Ta_2O_6$)	0.89
7	8	0.5 M (4)	$KTaO_3$, ($K_2Ta_2O_6$)	0.76
8	24	0.5 M (4)	$KTaO_3$, ($K_2Ta_2O_6$)	0.82
9	48	0.5 M (4)	$KTaO_3$	1.00
10	8	1.0 M (8)	$KTaO_3$	1.00
11	10 (SS-900 °C)	(1.1)	$KTaO_3$	1.00

Reaction temperature: 400 °C. Bracked phase in the crystal phase column indicates the minor phase

eventually converting to the perovskite phase of $KTaO_3$. Under conventional hydrothermal conditions, the formation of potassium tantalate can be described as follows [13]:

$$Ta_2O_5 + KOH \rightarrow KTa_2O_5(OH) \text{ (defect pyrochlore)} \quad (1)$$

which then further reacts at high OH^- concentrations to form the pervskite phase

$$KTa_2O_5(OH) + KOH \rightarrow 2KTaO_3 \text{ (perovskite)} + H_2O \quad (2)$$

In general, the particles of $KTaO_3$ might form in dissolution of pyrochlore and recrystallization as $KTaO_3$ followed by the crystal growing during the hydrothermal reaction with KOH. A mixed phases of perovskite/pyrochlore was confirmed from K/Ta atomic ratio determined by EDS as shown in Table 1. The K/Ta atomic ratio for the potassium tantalate hydrothermally synthesized varied from 0.42 to 1.0 as the heating duration and the KOH concentration increased, corresponding to the K/Ta atomic ratio from $KTa_2O_5(OH)$ to $KTaO_3$. It is noteworthy that the appearance of perovskite phase rather than pyrochlore phase even at low OH^- concentration under supercritical water conditions. This is because hydrothermal reaction in supercritical water is similar to the solvothermal reaction in nonpolar solvents. Low dielectric constant of supercritical water contributes to enhance the reaction kinetics [22]. In addition, the properties of supercritical water greatly affected the dissolution of KOH. The solubility of KOH is much lower than the initial KOH concentration under normal temperature and pressure [23, 24]. Accordingly, the concentration of KOH within the local area is high enough to react with $KTa_2O_5(OH)$. As a result, highly KOH concentration is not required to form perovskite phase under supercritical water conditions.

The effect of the reaction time on the crystalline structure of final product was examined under 0.5 and 1.0 M KOH concentrations. Here, the reaction time was 8 h. As 0.5 M KOH aqueous solution is employed in the reaction, the obtained powder was characterized to be perovskite phase $KTaO_3$ whereas the defect pyrocholore phase of $KTa_2O_5(OH)$ was coexisted. When the hydrothermal reaction is carried out at 400 °C in 1.0 M KOH solution with reaction time of 8 h, only $KTaO_3$ phase displaying strong and sharp diffraction peaks in XRD patterns could be obtained. Transformation from the pyrochlore phase to the perovskite phase is accelerated in the higher concentrated alkaline media, complete conversion (K/Ta = 1.0) was achieved by the increase in the KOH concentration from 0.5 to 1.0 M.

Figure 1 shows XRD patterns of the hydrothermally synthesized in KOH concentration of 0.34 M at various reaction times. Perovskite phase predominated with an

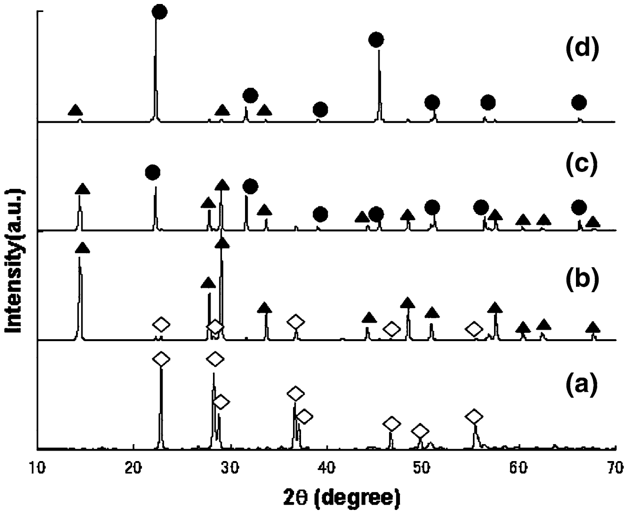


Fig. 1 XRD patterns of Ta_2O_5 (a) and potassium tantalate powders hydrothermally synthesized at 400 °C after 2 h (b), 8 h (c) and 24 h (d). ◇, Ta_2O_5 (JCPDS79-1375); ▲, pyrochlore (JCPDS35-1464); ●, perovskite (JCPDS77-918)

increase in the reaction time. Since the pyrochlore phase was formed even in 2 h at low KOH concentration, the dissolution rate of tantalum pentoxide is fast. Thus, the dissolution of pyrochlore phase is rate-limiting step. Figure 2 shows the SEM images of potassium tantalate particles synthesized at 400 °C in 0.34 M KOH solution with the various reaction times. Only fine particles were observed after 2 h hydrothermal reaction. In contrast, crystals having cubic shape in the range from 1 to 10 μm in diameter predominated as the reaction time increased. Large crystals can be attributed to the perovskite $KTaO_3$ and fine particles to be pyrochlore $KTa_2O_5(OH)$. Elemental analyses supported this. Potassium content in large crystals is higher than that in the fine particles region. Furthermore, morphology of the crystals hydrothermally synthesized for 48 h tends to a rectangular shape, which indicates specific surface of the crystals grows and morphology changes from cubic shape to rectangular shape with the size in the range from 10 to 100 μm.

Figure 3 presents the XRD patterns of the hydrothermally and solid-state synthesized $KTaO_3$ powders. In Fig. 3a, the intensity of (100) peak in the XRD pattern of the hydrothermally synthesized sample is relatively stronger in comparison with that of the solid-state synthesized sample and the JCPDS file data of $KTaO_3$, indicating that the preferred crystals growth takes place in the direction of (100) under supercritical water conditions.

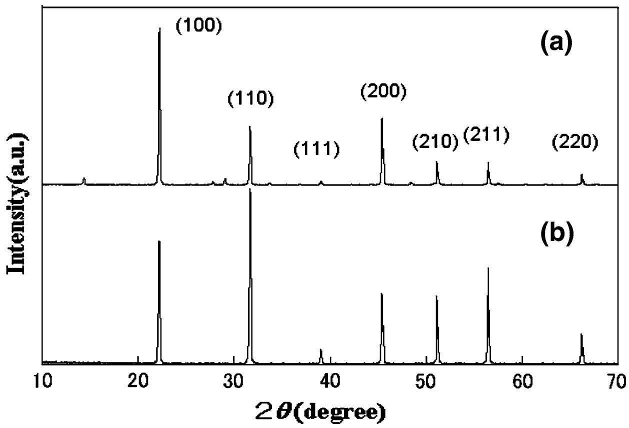


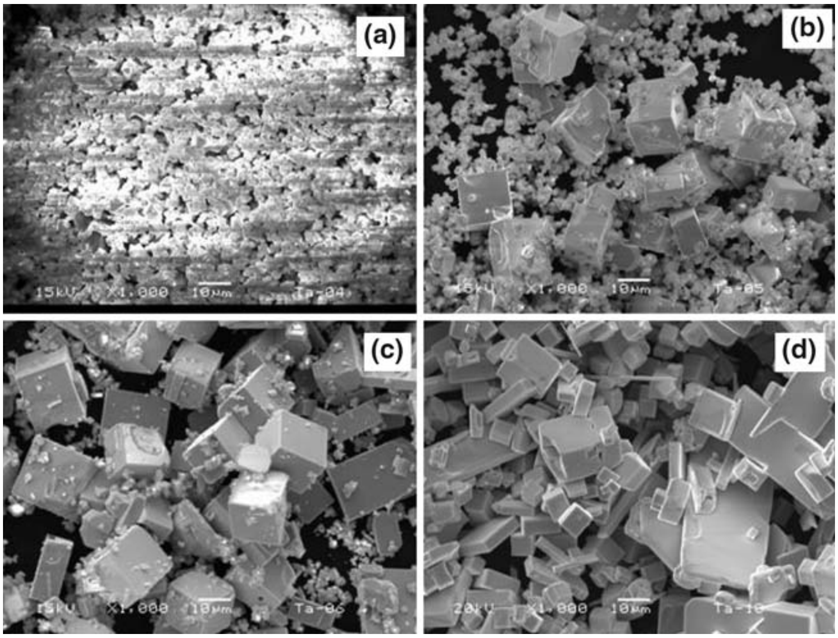
Fig. 3 XRD patterns of hydrothermally synthesized $KTaO_3$ (a) 400 °C after 24 h, and solid-state synthesized $KTaO_3$ (b) 900 °C after 10 h

$KTaO_3$ thin film formation on $SrTiO_3$ substrate

Figure 4 depicts the SEM images of $KTaO_3$ crystals observed on the $SrTiO_3$ (100) substrate. All the crystals are aligned in the surface of the substrate and the crystals enlarged in the lateral directions and each crystals united to thin film in some places. Elemental mapping (Fig. 5) reveals that crystals on the $SrTiO_3$ substrate are composed with K and Ta, and the energy dispersive X-rays spectroscopy microanalysis clearly shows a K/Ta atomic ratio of ca. 1:1, indicating that crystal phase can be attributable to the perovskite $KTaO_3$. This is supported by the XRD pattern of the film.

By analyzing the XRD pattern of the film (Fig. 6), $KTaO_3$ aligned with a (100) out of plane orientation on the (100) oriented $SrTiO_3$ substrate. There is also evidence of a pyrochlore phase present in the film with (111) out of plane orientations, whereas pyrochlore phase is minor. It has also been reported that the X-rays peaks diffracted by the film

Fig. 2 SEM images of potassium tantalate powders hydrothermally synthesized at 400 °C after 2 h (**a**), 8 h (**b**), 24 h (**c**) and 48 h (**d**)



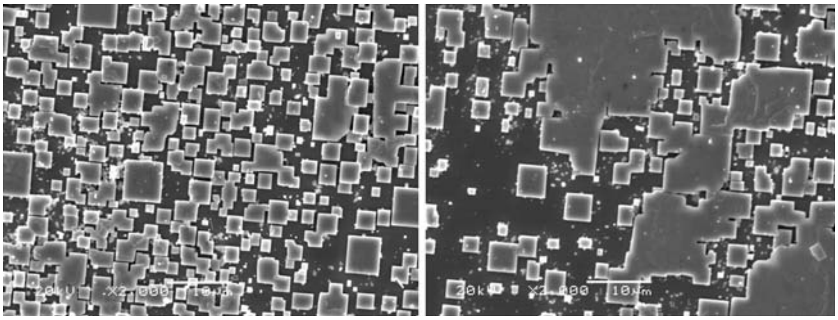


Fig. 4 SEM image of hydrothermally synthesized $KTaO_3$ crystals (sample no. 8 400 °C after 24 h) on the (100) $SrTiO_3$ substrate

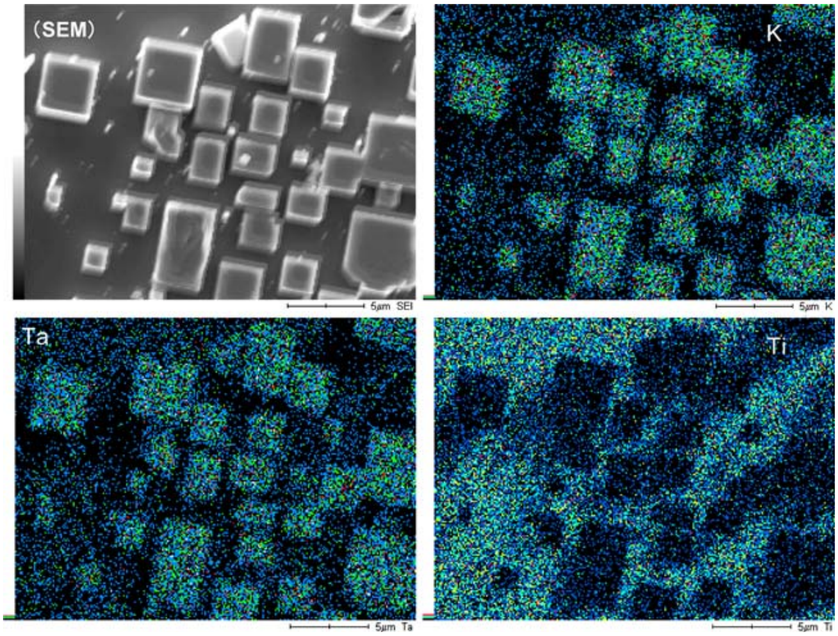


Fig. 5 SEM image and elemental (K, Ta, Ti) mappings of hydrothermally synthesized $KTaO_3$ crystals on the (100) $SrTiO_3$ substrate

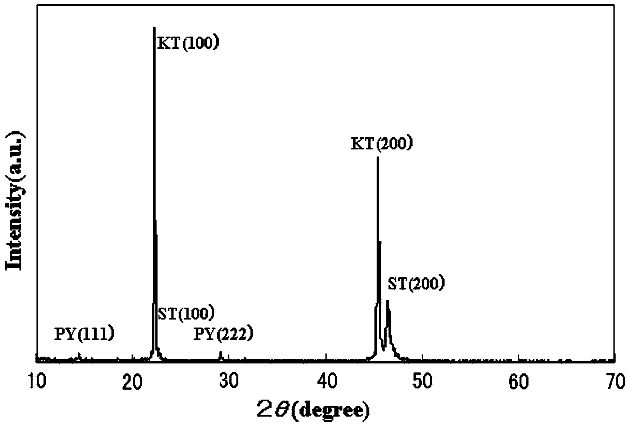


Fig. 6 XRD patterns of hydrothermally synthesized $KTaO_3$ film on the (100) $SrTiO_3$ substrate. PY: Pyrochlore, KT: Perovskite $KTaO_3$, ST: $SrTiO_3$

formed on the $SrTiO_3$ (*hkl*) face are only $BaTiO_3$ perovskite peaks of the same *hkl* indices as those of the $SrTiO_3$ substrate. And heteroepitaxial growth of monolithic $BaTiO_3$ films were obtained as a highly smooth surface on $SrTiO_3$ (100) substrate, since a $BaTiO_3$ (100) face grows parallel to the surface of the substrate [25]. In the case of $KTaO_3$ film hydrothermally synthesized in 7 M KOH at 175 °C, it was reported that $KTaO_3$ film had an epitaxial, cube-on-cube relationship with the $SrTiO_3$ substrate, (100)[001]$KTaO_3$//(100)[001]$SrTiO_3$ [13]. The thickness of the $KTaO_3$ was estimated from the ratio of the film to substrate XRD intensities for the (200) peaks. The film had a lattice parameter of 3.987 Å and a full-width at half maximum (FWHM) of 0.20°, compared to 0.04° for the $SrTiO_3$ substrate. Since a lattice parameter of $SrTiO_3$ is 3.905 Å (JCPDS 35-734) and oxygen-oxygen distances in $SrTiO_3$ and the perovskite $KTaO_3$ are 3.905 Å$\sqrt{2}$ and 3.987 Å$\sqrt{2}$, respectively, a lattice mismatch can be estimated to be 2.1% at ambient temperature. The average crystal size (D) of the film and powder was calculated according to the Scherrer equation: $D_{calcd} = K\ \lambda/\beta \cos\theta$, in which β is the FWHM and θ is the diffraction angle. The peak at 22.3° was used for the calculation of the crystallite size. The average crystal size of $KTaO_3$ film and powder were calculated to be 53.9 and 66.9 nm, respectively, indicating that there is not much different between the crystallite size in the solution and that on the substrate. Crystallite sizes are much smaller than the grain sizes as shown in the scanning electron micrographs. $KTaO_3$ particles and films might be composed of small crystals by self-assembling and align in the (100) directions.

Electron backscatter patterns for the $KTaO_3$ crystals are identical with that for the $SrTiO_3$ substrate, indicating that $KTaO_3$ crystals growth in the (001)[100] orientation which is the same as $SrTiO_3$ substrate. Accordingly, epitaxial crystal growth of $KTaO_3$ can be achieved on the (100) $SrTiO_3$ substrate under supercritical water conditions.

As mentioned above, the reaction between the Ta_2O_5 precursor powder and KOH solution first produces an intermediate defect pyroclore phase. The pyrochlore phase then dissolves and reacts with KOH to synthesize the more stable perovskite phase. It is found that the reaction temperature, time and KOH concentration strongly effect on the formation of the potassium tantalate films. Only defect pyrochlore potassium tantalate film was formed on tantalum substrate under galvanostatic conditions in KOH solutions (0.5–5.0 M) at temperatures from 50 to 150 °C [10–12]. In the case of $KTaO_3$ film hydrothermally synthesized in 7 M KOH at 175 °C, a pyrochlore-free $KTaO_3$ film could be grown by delaying the introduction of $SrTiO_3$ substrate into the synthesis solution after substantial amounts of Ta_2O_5 had reacted to form the pyrochlore powder, reducing the tendency for further nucleation of the pyrochlore phase on the substrate [13]. However, solvating power of the media also affects the formation of perovskite phase. Solvothermal preparation of $KTaO_3$ particles was achieved using 1.0 M KOH in water–ethanol mixed solvents [14]. In the hydrothermal process, the hydroxyl ion activity was critical effect promoting the formation of the perovskite phase [1]. Since water is the solvent which has strong salvation by forming hydrogen bonds with ions, the hydroxyl ion in the KOH solution can be shielded by the H_2O molecules and make hydroxyl ion activity decrease. Compared with water, ethanol has weaker salvating power. Thus, hydroxyl ion activity in ethanol solution is much greater than in water solution with the same KOH concentration in each. Since hydrogen bonds are weaken under supercritical water conditions, the reactivity of the KOH solution in the supercritical water is enhanced as well as the solvothermal reactions. Thus, the $KTaO_3$ formation on the $SrTiO_3$ substrate is more pronounced in 0.5 M KOH solution under supercritical water conditions, since crystal growth prepared using long reaction time are preferable than those adopting relatively short reaction time using highly concentrated KOH.

Conclusion

In summary, perovskite $KTaO_3$ crystals have been successfully prepared by hydrothermal reaction in 0.34–1.0 M KOH solution under supercritical water conditions. Besides, $KTaO_3$ films were achieved on the (100) $SrTiO_3$ substrate in 0.5 M KOH aqueous solution using supercritical water. The $KTaO_3$ film grew epitaxially on a (100) oriented single-crystal $SrTiO_3$ substrate with the orientation relation of (100)[001]$KTaO_3$//(100)[001]$SrTiO_3$. Using supercritical water conditions, the KOH concentration required to form the perovskite phase is far lower (<0.5 M) than that previously reported for conventional hydrothermal conditions (>7.0 M). This supercritical water processing provides an environmentally benign route to directly synthesize well-crystallized perovskite potassium tantalate films without highly alkaline aqueous KOH solutions or organic solvents.

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