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Hydrothermal synthesis of strontium titanate powders with nanometer size derived from different precursors

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Abstract

Nanocrystalline $SrTiO_3$ powders have been successfully synthesized under a moderate condition derived from different precursors by the hydrothermal method. Reaction conditions such as temperature, time and alkali concentration have been investigated and the product is characterized in detail by XRD, TEM and other techniques. Comparing with those from the conventional method, the hydrothermal $SrTiO_3$ powders with a simple mode of size distribution appear to have smaller particle size and a lower agglomeration, and can give the dense sintering bodies at lower temperature. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Strontium titanate, which has high capacity, high dispersion frequency constant, low dielectric loss and low temperature coefficient, is used to prepare the $SrTiO_3$ grain boundary layer capacitor ceramic ($SrTiO_3$-GBBLC).[1] Because of its higher conductivity than that of $BaTiO_3$–GBBLC as the semi-conductor, $SrTiO_3$–GBBLC is extensively applied to stabilize the electric voltage and current of the coupling circuit.

$SrTiO_3$ powder, derived from $SrCO_3$ and TiO_2, is traditionally prepared by the solid-state reaction at 900–1000°C.[2] K. Kudaka et al.[3] synthesized crystalline $SrTiO_3$ powders by the decomposition of oxalic co-precipitate in 1982 and this co-precipitation method was improved in the 1990s.[4–6] Compared to that by the solid-state reaction, the $SrTiO_3$ powder by the co-precipitation method has a more homogeneous chemical composition and a finer particle size. However, it is also difficult to prepare an electric device with excellent properties using these powders because high temperature treatment through the above processes readily leads to the agglomeration and inhomogeneity of the particles. With the improvement of the sol–gel chemistry, the decomposition method of metal alkoxide, first reported in 1970s,[7] is intensively studied at the end of 1980s.[8,9] The hydrothermal method is one of the most promising solution chemical methods and some ceramic powders [10–13] have been successfully prepared by this method. The particle size and morphology may be well-controlled.[14] Here, we report on the hydrothermal syntheses of $SrTiO_3$ powders by three routes at a low temperature.

2. Experimental

2.1. Preparation of the precursors

2.1.1. Precursor A

$Sr(OH)_2nH_2O$ ($n=4.6$) and acetylacetone (Hacac) are dissolved in 2-methoxyethanol (MOE) under N_2 atmosphere, in which the Sr concentration is 0.2 mol dm^{-3} and the molar ratio of Sr to Hacac is 1:1. The amount of $Ti(OC_4H_9)_4$ and Hacac is dropped into MOE and refluxed for 2 h, in which the Ti concentration is 0.2 mol dm^{-3} and the molar ratio of Ti to Hacac is 1:1. The above two solutions with equal volume are mixed together and refluxed for another half of an hour. Cooling to room temperature, the solution named precursor A is obtained.

2.1.2. Precursor B

Under stirring, the mixture of MOE and H_2O (volume ratio: MOE:H_2O is 4:1) is added into the precursor A in which the sum of Sr and Ti concentration is 0.1 mol dm^{-3} until the molar ratio of Ti:H_2O is up to

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1:6 at 60°C. After aging for a period, the solution gels. The gel is dried in vacuum at 45°C to transform to xerogel (precursor B).

2.1.3. Precursor C

Precursor A is added into a suitable alkali solution under N_2 atmosphere at room temperature and the suspension solution is obtained. The precipitate named as precursor C is obtained after filtration.

2.2. Synthesis of crystalline $SrTiO_3$

The precursor A is dropped slowly into an excessive KOH solution at a designed temperature under magnetic stirring and aged for several hours while the temperature is held constant. Cooling to room temperature, the product is obtained by filtration, washed with deionized water and dried under N_2 atmosphere.

The precursor B or C is added into the KOH solution to form a suspension solution, in which the sum of Sr and Ti concentrations is 0.1 mol dm^{-3}. 24.0 cm^3 of the suspension solution is poured into a 30 cm^3 stainless autoclave with a TEFLON liner and reacts at the designed temperature for several hours. After cooling to room temperature, the product is obtained by filtration, washed with hot deionized water and dried under N_2 atmosphere.

2.3. Characterization of the as-prepared powders

The XRD patterns of the product are recorded on a Rigaku D/MAX-III diffractometer. A JEM-100CXII transmission electron microscope is used to observe the particulate properties of the powder. A plasma spectrometer (ICP-1000) is applied to determine the Sr and Ti contents in the product.

2.4. Sintering of the as-prepared powders

The typical $SrTiO_3$ powders were mixed with 0.5% poly(vinylalcohol), pelletted and sintered at 1200° C by stepwise heating in a programmed furnace. The samples were soaked for 2 h at the final sintering temperature of 1200°C. The densities were determined by the Archimede's techniques. The bulk densities of the sintered pellets were measured according to the literature.[15]

3. Results and discussion

3.1. Synthesis

To study the crystallization processes of the precursors A, B and C, the effects of the KOH concentration, reaction temperature and time are investigated.

Fig. 1 shows the crystallization of the precursor A at different temperatures while the KOH concentration is held at 0.8 mol dm^{-3} for 10 h. The crystallization takes place at 70°C and the fully-crystallized product is obtained at 85°C. Further experiments indicate that the $SrTiO_3$ phase can form at 85°C when the aging time is as long as 4 h. Prolonging the reaction time to 8 h, a well-crystallized product precipitates. The crystallinity of the product greatly depends on the KOH concentration. Full-crystallized $SrTiO_3$ precipitates when the KOH concentration ranges from 0.6–4.0 mol dm^{-3}, lower or higher concentration always results in the decrease of the crystallinity of the products. Thus, the optimal condition for the crystallization of precursor A is that the reaction carried out at 85°C for 8 h with the KOH concentration of 0.6–4.0 mol dm^{-3}.

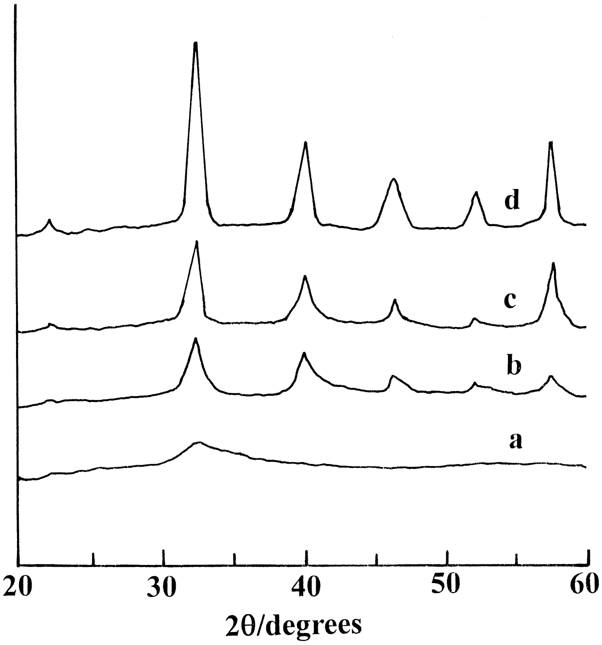

Fig.1. XRD patterns of the product derived from precursor A at different temperatures; a: 60°C; b: 70°C; c: 80°C; d: 85°C.

The XRD patterns of the hydrothermal product, derived from precursor B corresponding to different KOH concentrations while the reaction temperature is held at 140°C for 2 h are shown in Fig. 2. It reveals that the $SrTiO_3$ phase forms when the KOH concentration is as high as 0.8 mol dm^{-3} and the $SrTiO_3$ powder fully crystallizes until the KOH concentration up to 1.2 mol dm^{-3}. However, the crystallinity of the product decreases when the concentration is higher than 6.0 mol dm^{-3}. Thus, the KOH concentration at the range of 1.2–6.0 mol dm^{-3} is necessary to prepare $SrTiO_3$ from precursor B. Similar to precursor B, the full-crystallized $SrTiO_3$ can be synthesized at the KOH concentration range of 1.2–7.0 mol dm^{-3} for precursor C.

Fig. 3 gives the crystallinity of the precursors B and C at different temperatures while other reaction conditions are held constant. It shows that the crystalline $SrTiO_3$ precipitates when the temperature is higher than 130°C

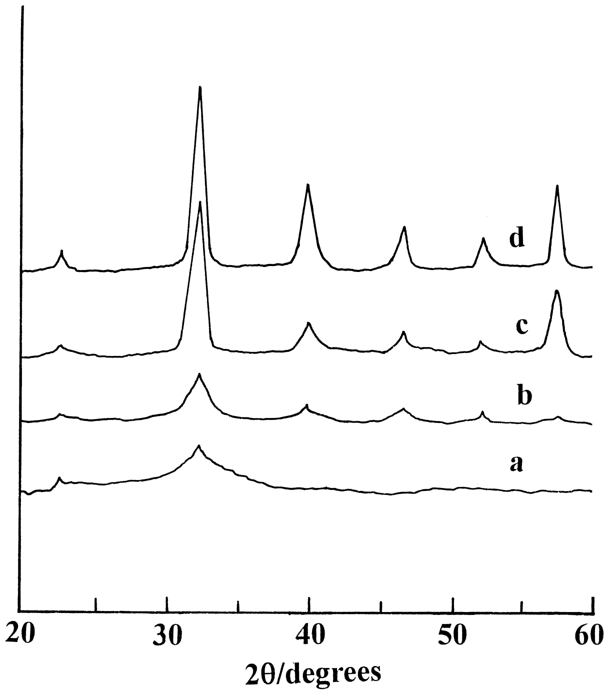

Fig. 2. XRD patterns of the product derived from precursor B corresponding to different KOH concentrations. (a) 0.6 mol dm^{-3}; (b) 0.8 mol dm^{-3}; (c) 1.2 mol dm^{-3}; (d) 1.6 mol dm^{-3}.

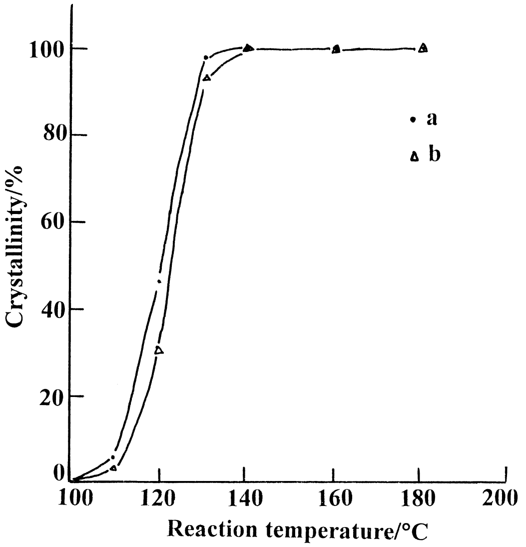

Fig. 3. Crystallinity of the products derived from precursor B and C at different temperatures. (a) Precursor B; (b) Precursor C.

for precursor B. As a comparison, a reaction temperature higher than 140°C is necessary for preparing $SrTiO_3$ crystallite using precursor C under the same KOH concentration and reaction time. Further experiments (Fig. 4) show that the $SrTiO_3$ phase forms after reacting for 8 h for precursor B, while 12 h is necessary for precursor C. The results reveal a higher reaction activity of precursor B than that of precursor C.

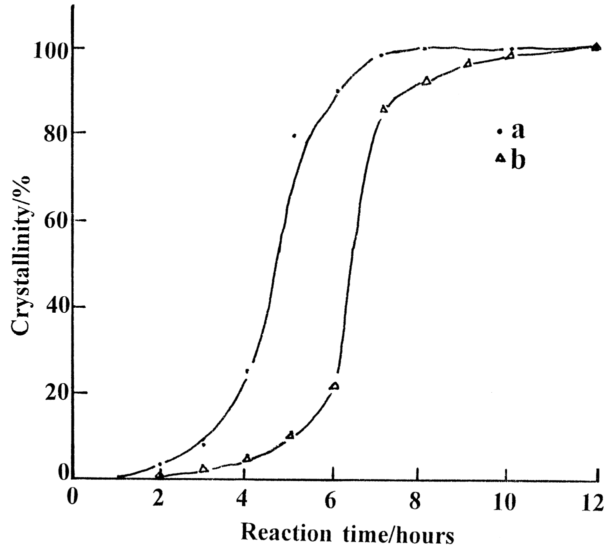

Fig. 4. Crystallization curves of as-prepared products derived from precursor B and C. (a) Precursor B; (b) Precursor C.

The suitable reaction conditions for preparing $SrTiO_3$ derived from precursors A, B and C are listed in Table 1. It is obvious that the reactive activity is precursor $A > B > C$. For example, $SrTiO_3$ may be synthesized at a lower temperature from precursor A and the crystallinity of the product from precursor B is higher than that from precursor C under the same reaction conditions. The Sr and Ti atoms in precursor A and B have the homogeneity at the molecule level, and the Ti atoms may have a similar complex environment to those in $SrTiO_3$ structure, which leads a small energy barrier and a short diffusion distance of Sr^{2+} to form $SrTiO_3$ nuclei. Precursor C is a hydrate metal oxide co-precipitate, the part dissolution of Sr makes a long diffusion distance, and the hydrate TiO_2nH_2O has a lower reaction activity than its gel. [16] Furthermore, the system has a low dielectric constant for the existence of organic materials, which also influences the diffusion of Sr^{2+}. Thus, a lower reaction activity of precursor C than precursor A and B is observed in the hydrothermal processes. In the hydrothermal process, the hydrolysis of the precursor is the first stage, and results in complex hydrous metal oxides. The conversion of complex hydrous metal oxides to the $SrTiO_3$ phase might take place through intermediates such as amorphous $SrTiO_3$ solid solution, which depends on the hydrolysis temperature. The activities of the intermediates at different temperatures are disparity and result in the difference in the activities of the precursor A and B. In addition, the conversion dynamics might be one of the factors.

3.2. Characterization

Within analysis error, the ICP-1000 results are in agreement with the formula $SrTiO_3$ and there are no metal impurities found in the products.

The particle sizes of the typical samples prepared at different conditions are shown in Tables 2–4, respectively. The results indicate that the nanocrystallites have a narrow grain size distribution. The particle size gradually enlarges with the prolonging of reaction time due to the dissolution of smaller grains and the growth of larger ones. Higher KOH concentration favors the grain growth for precursor B and C. The powder from precursor C is larger than that from precursor A and B under the same reaction conditions. The result indicates that the nucleation rate of precursor A or B is faster than that of precursor C through the hydrothermal processes. Raising the reaction temperature leads to the enlargement of the crystallites for precursor A, while there is no obvious changes for precursor B and C. Thus, higher temperature greatly accelerates the grain growth of crystalline $SrTiO_3$ in the hydrolysis and crystallization process of precursor A. Above results may be explained as follows: the hydrothermal reaction includes nucleation and grain growth of the product, which compete through the hydrothermal processes. The two processes depend on the reaction conditions. The grain growth might be faster than the nucleation process at higher temperature and higher KOH concentration is favorable to grain growth.

Table 1
Reaction conditions for synthesis of $SrTiO_3$ powder

Precusor	Temperature (°C)	Reaction time (h)	KOH concentration (mol dm^{-3})
A	$\geqslant 85$	$\geqslant 10$	0.6–4.0
B	$\geqslant 130$	$\geqslant 8$	1.2–6.0
C	$\geqslant 140$	$\geqslant 12$	1.2–7.0

Table 2
particle size of the product derived from precursor A

No.	Temperature (°C)	Aging time (h)	Particle size (nm)
1	85	10	30 ± 5
2	85	16	50 ± 10
3	85	20	60 ± 10
4	100	10	50 ± 5
5	100	16	70 ± 10
6	100	20	100 ± 20

Table 3
Particle size of the product derived from precursor B

No.	Temperature (°C)	Time (h)	KOH concentration (mol dm^{-3})	Particle size (nm)
7	140	12	1.2	30 ± 5
8	140	24	1.2	50 ± 10
9	160	12	1.2	30 ± 5
10	160	24	2.0	80 ± 10
11	160	24	2.8	100 ± 20

Table 4
Particle size of the product derived from precursor C

No.	Temperature (°C)	Time (h)	KOH concentration (mol dm^{-3})	Particle size (nm)
12	140	10	1.6	80 ± 10
13	140	18	1.6	100 ± 20
14	160	10	1.6	80 ± 10
15	160	18	2.4	140 ± 30
16	160	18	3.2	180 ± 30

Table 5
Bulk and apparent densities of the sintered bodies[a]

Sample	Density (g/cm^3)	
	Bulk	Apparent
A	5.04	5.09
B	5.02	5.06
C	4.98	5.06

[a] The samples A, B and C are prepared from the hrdrothermal powders Nos. 3, 9 and 15 respectively.

3.3. Sintering

The bulk and apparent densities of the typical as-prepared $SrTiO_3$ powders are given in Table 5. The results show that the nearly theoretical densities were achieved with the hydrothermal powders. The sintering temperature was lower than that of the $SrTiO_3$ powder by the conventional method.[17] The hydrothermal particles with a small particle size and a simple mode of size distribution appeared to lead to good densification of sintered bodies. Earlier studies[18] on the sintering properties of the hydrothermal powders supported the above results, although the $SrTiO_3$ particles used here were much smaller than the $BaTiO_3$ particles. The fine sintering property might attribute to the lower agglomeration and uniform size of the hydrothermal particles.

4. Conclusions

The main conclusions of the present paper are as follows.

1. Nanocrystalline $SrTiO_3$ powder is synthesized by the hydrothermal method under moderate conditions from different precursors. The crystallization of the product greatly depends on the reaction temperature, time and alkali concentration.
2. Compared to other methods, the as-prepared product has the superior particulate properties such as a small particle size and a simple mode of size distribution. The reaction time and the KOH concentration affect the particle size.

3. The hydrothermal powders have a fine sintering property and can be calcined at 1200°C to give the dense sintered bodies.

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