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A new approach for the preparation of $SrTiO_3$ nanocubes

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Abstract

This paper describes the preparation of $SrTiO_3$ nanocubes with an average length of ~20 nm. $SrTiO_3$ nanoparticles were prepared using a solvothermal reaction at 240 °C for 18 h with $[(CH_3)_2CHO]_4Ti$ as a raw material and a little distilled water addition. X-ray diffraction measurements confirmed the presence of perovskite $SrTiO_3$ particles. The water served as an oxygen source for producing the perovskite structure. Furthermore, a new approach to nanocube formation using a mixture of raw materials as titanium sources was investigated. Dispersed $SrTiO_3$ nanocubes were successfully prepared using this approach and a solvothermal reaction performed at 260 °C for 18 h. $SrTiO_3$ was synthesized from a mixture that included $[(CH_3)_2CHO]_4Ti$ and TiO_2 as titanium sources. The $[(CH_3)_2CHO]_4Ti$ and TiO_2 contributed to rapid nucleation and crystal growth, respectively. Scanning electron microscopy observations revealed that the particles were nanocubes approximately 20 nm in size.

Keywords: $SrTiO_3$; Nanocube; Perovskite oxide; Solvothermal reaction

1. Introduction

Strontium titanate ($SrTiO_3$) is a perovskite oxide functional material that has been attracting attention as a dielectric for artificial superlattice films [1] and grain-boundary layer ceramic capacitors [2], and has demonstrated photocatalytic activity [3]. These functional ceramics require the synthesis of homogeneous nanoparticles, so wet chemical reactions are one reasonable approach. Various liquid phase reactions have been reported in the literature for the synthesis of $SrTiO_3$ nanoparticles. For example, Poth et al. [4] prepared $SrTiO_3$ crystallites up to sizes of 42 nm via combustion synthesis using aqueous solutions of metal nitrates, differing amounts of ethylene diamine tetraacetic acid (EDTA) as a reducing agent, and NH_4NO_3 as an oxidizing agent. In addition, Zhang et al. [5] controlled $SrTiO_3$ particle size by changing the crystallinity of a $TiO_2.nH_2O$ gel, and nanoparticles could be obtained under hydrothermal conditions. In the field of electric ceramics, studies attempting to control the size and shape of $SrTiO_3$ particles have been carried out in order to introduce new functionality. Calderone et al. [6] reported that the size and shape of $SrTiO_3$ particles synthesized by precipitation from an aqueous gel suspension prepared by hydrolyzing a $TiOCl_2$ solution with NaOH and adding $SrCl_2$ can be tailored in the range 80–1400 nm, and that cubic particles could also be produced by varying the temperature and the concentration. In addition, Rabuffetti et al. [7] obtained single-crystalline $SrTiO_3$ nanocubes with average edge lengths of 60 and 120 nm via sol-precipitation coupled with hydrothermal synthesis and a molten salt procedure, respectively. Mao et al. [8] prepared $SrTiO_3$ nanocubes with an edge length of 80 ± 10 nm by a novel, simple one-step solid-state chemical reaction in the presence of NaCl and a nonionic surfactant.

To synthesize homogeneous nanoparticles by a liquid-phase reaction, appropriate materials are necessary, such as a solvent reagent in the reaction media. Previous research involving a $SrTiO_3$ preparation using titanium alkoxide as a starting material has shown that nanoparticles can be formed by wet chemical methods [9–13]. For example, Kumar et al. [9] reported that the hydrolysis of titanium alkoxides under basic conditions was exploited to

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directly form homogeneous submicrometer powders of $SrTiO_3$ from a precursor solution. Furthermore, controlling the shape of the particles is very important in the creation of functional materials. In particular, nanocubes have attracted considerable attention due to their potential use in the creation of highly functional materials. However, it is well known that nanocube preparation, especially the preparation of perovskite oxides, is difficult [14,15]. In the present work, we investigated $SrTiO_3$ nanoparticles and nanocubes prepared by a solvothermal reaction. First, $SrTiO_3$ nanoparticles were prepared using titanium tetraisopropoxide ($[(CH_3)_2CHO]_4Ti$), a dissolved reagent in a reaction solution and strontium hydroxide ($Sr(OH)_2$). $[(CH_3)_2CHO]_4Ti$ and $Sr(OH)_2$ were used as starting materials because, once they were dissolved in ethanol and 2-methoxy ethanol as the reaction medium, $SrTiO_3$ nuclei were formed at an early stage at about 240 °C. However, insufficient oxygen in the autoclave for the formation of perovskite oxides was a problem because the sample preparation was carried out in a box filled with dry nitrogen gas before solvothermal treatment. To solve this problem, distilled water was added as an oxygen source to the reaction medium before the crystal was grown. Next, a new approach was investigated that used a mixture of raw materials, including both $[(CH_3)_2CHO]_4Ti$ and TiO_2, as titanium sources in order to prepare homogeneous $SrTiO_3$ nanocubes. The proposed technique allowed for efficient particle size and shape control, and produced dispersed $SrTiO_3$ nanocubes that are suitable for the creation of future electronic ceramics with new and enhanced properties.

2. Experimental procedure

$SrTiO_3$ was prepared by a solvothermal method. A mixture of ethanol (150 ml, Wako Pure Industries, Ltd., Japan) and 2-methoxy ethanol (100 ml, MERCK, Ltd.) was used as the solvent, while $[(CH_3)_2CHO]_4Ti$ (Kanto Chemical Co., Inc., Japan), TiO_2 (Ishihara Co., Ltd.), and $Sr(OH)_2$ (Ube Material Industries, Japan) were used as raw materials. In addition, water was used as an oxygen source. A mixed solution including the raw materials was transferred into a stainless-steel autoclave. This process was performed in a glove box filled with dry nitrogen gas because the alkoxide is extremely sensitive to CO_2 and moisture. The experiments were conducted in an autoclave with 500 ml volume (TPR-1 (SUS316, with a stirring system), Taiatsu Co., Ltd., Japan), and the filling factor was 50 vol%. Solvothermal synthesis was carried out in the range from 240 to 260 °C for 18 h, with a stirrer rotation speed of 300 rpm. After the autoclave cooled to room temperature, the powders were collected by a centrifugal separator using ethanol, which was also used for the rinse. Finally, the product was dried in a dryer at 50 °C overnight.

The crystallinity and phase purity of the prepared samples were analyzed by X-ray diffraction (XRD) using an UltimaIV (Rigaku Co.) diffractometer with CuKα radiation (wavelength 0.15406 nm) operating at 40 kV and 30 mA, at a scanning rate of $20^\circ\,\mathrm{min}^{-1}$ in the 2θ range of 20°–80° at room temperature. The morphology of the particles was examined by scanning electron microscopy (SEM; JSM-6500 F, JEOL, Ltd.) operating at 15 kV.

3. Results and discussion

The purpose of this work was to prepare $SrTiO_3$ nanocubes with an average length of ~20 nm. To do so, it was necessary to examine the potential for controlling the size and shape of the $SrTiO_3$ particles. First, control of the size of the $SrTiO_3$ was investigated. The addition of water during the preparation is very important. The starting materials and reaction medium lacked sufficient oxygen, which are necessary components of the perovskite structure. Furthermore, we consider that the crystal growth of $SrTiO_3$ is difficult with too little oxygen. Therefore, we added distilled water to the reaction medium as an oxygen source. The role of water is both to act as a source of oxygen during the formation of the perovskite structure and to promote crystal growth. The distilled water was added immediately before the solvothermal treatment.

An XRD pattern and an SEM micrograph of $SrTiO_3$ obtained using the solvothermal method with distilled water addition are shown in Fig. 1. The diffraction peaks can be assigned to the cubic lattice of $SrTiO_3$ with a perovskite structure (JCPDS No. 84-0444). Weak diffraction peaks of $SrCO_3$ were observed as a secondary phase. The diffraction peaks were narrower and sharper, and these peaks indicate the sizes of the particles in crystallinity. The average sizes of the particles were estimated from the (111) peaks using the Scherrer equation (Eq. (1))

$$D = (0.9\lambda)/(B\cos\theta) \tag{1}$$

where D is the crystal size in nanometers, λ is the wavelength of CuKα (wavelength 0.15406 nm), B is the full width at half maximum (FWHM) intensity in radians, and θ is the diffraction peak angle. The obtained B value of the diffraction line includes errors resulting from the experimental conditions, such as noise and the slit width of the X-ray diffractometer. The crystal size of the $SrTiO_3$ was 19 nm. The SEM observations indicated a particle size of ~20 nm, which is consistent with the XRD results. In addition, the particles were cube-shaped. Thus, the XRD and SEM results confirm

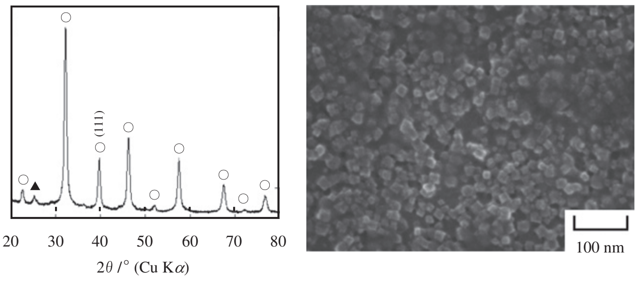

Fig. 1. XRD patterns and SEM micrographs of the products. Temperature, 240 °C; Time, 18 h; Starting material, $[(CH_3)_2CHO)]_4Ti$, 0.01 mol; $Sr(OH)_2$, 0.02 mol; water, 0.02 mol; ○, $SrTiO_3$; ▲, $SrCO_3$.

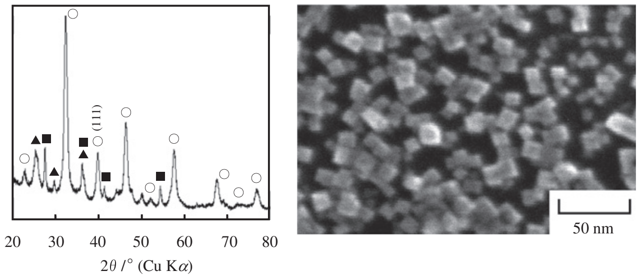

Fig. 2. XRD patterns and SEM micrographs of the products. Temperature, 260 °C; Time, 18 h; Starting material, $[(CH_3)_2CHO)]_4Ti$, 0.005 mol; TiO_2, 0.005 mol; $Sr(OH)_2$, 0.02 mol; ○, $SrTiO_3$; ■, TiO_2; ▲, $SrCO_3$.

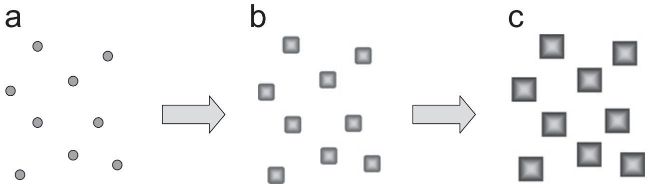

Fig. 3. Formation of homogeneous $SrTiO_3$ nanocubes from a mixture of raw materials, including both $[(CH_3)_2CHO]_4Ti$ and TiO_2 as titanium sources.

that water participates in the formation of the perovskite structure and promotes crystal growth of $SrTiO_3$.

Next, the shape of the $SrTiO_3$ nanoparticles was examined. Previous reports showed that $SrTiO_3$ nanocubes were formed using a solvothermal reaction with a mixed solution of ethanol and 2-methoxy ethanol as a reaction medium [16]. However, it is necessary to have particles of a more homogeneous shape and size, so we prepared homogeneous nanocubes from a mixture of raw materials that included $[(CH_3)_2CHO]_4Ti$ and TiO_2 as titanium sources. We expected that $[(CH_3)_2CHO]_4Ti$ and TiO_2 would contribute to rapid nucleus formation and crystal growth, respectively. Because TiO_2 can serve as an oxygen source, we did not add distilled water to the solution. The XRD pattern and SEM micrograph of the $SrTiO_3$ obtained using the above solvothermal method and mixture of raw materials are shown in Fig. 2. The obtained powder was a mixture of $SrTiO_3$, $SrCO_3$, and TiO_2. The diffraction peaks of the resulting $SrTiO_3$ could be assigned to the cubic phase, as shown in Fig. 1. In addition, TiO_2 remained even though $SrTiO_3$ was formed. Regarding the shape of the particles, nanocubes with sharp corners were formed from a mixture of raw materials that included $[(CH_3)_2CHO]_4Ti$ and TiO_2 as titanium sources. The crystal size of the $SrTiO_3$ was 13 nm, as estimated from the (111) peaks using the Scherrer equation. It was found that the addition of TiO_2 as a raw material is an important factor in the preparation of nanocubes with sharp corners.

Finally, we will discuss the formation mechanism of the nanocubes (Fig. 3). Before heat treatment, $[(CH_3)_2CHO]_4Ti$ was completely dissolved in the reaction medium. When the temperature reached approximately 260 °C, nuclei were rapidly formed (Fig. 3(a)). The homogenous nucleus formation is noteworthy because the homogeneous nuclei resulted in homogenous $SrTiO_3$ nanocubes. On the other hand, the TiO_2 was not dissolved in the reaction medium before heat treatment. When the solution was heated, the TiO_2 slowly dissolved in the reaction medium. This dissolved TiO_2 contributed to the crystal growth of $SrTiO_3$ nanocubes (Fig. 3(b) and (c)). Furthermore, the oxygen contained in the TiO_2 was used to form the perovskite structure.

4. Conclusions

$SrTiO_3$ nanoparticles were prepared using a solvothermal reaction at 240 °C for 18 h with $[(CH_3)_2CHO]_4Ti$ as a raw material. XRD measurements confirmed the presence of perovskite $SrTiO_3$ particles. Added water served as an oxygen source for the formation of the perovskite structure. Furthermore, a new approach based on a mixture of raw materials as titanium sources was investigated. $SrTiO_3$ nanocubes were successfully prepared using this approach and a solvothermal reaction at 260 °C for 18 h. Dispersed $SrTiO_3$ was synthesized from a mixture of raw materials, including $[(CH_3)_2CHO]_4Ti$ and TiO_2 as titanium sources. The $[(CH_3)_2CHO]_4Ti$ and TiO_2 contributed to rapid nucleus formation and crystal growth, respectively. SEM observations revealed that the resulting particles were nanocubes approximately 20 nm in size. The proposed technique allowed for efficient particle size and shape control in the present study, and prepared $SrTiO_3$ nanocubes that may enable the creation of new functional ceramic materials with enhanced properties.

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