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Defects and microstructure of a hydrothermally derived $(Bi_{1/2}K_{1/2})TiO_3$ powder

Manabu Hagiwara*, Makoto Ito, Shinobu Fujihara

Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

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ABSTRACT

Fine powders of bismuth potassium titanate $(Bi_{1/2}K_{1/2})TiO_3$ (BKT) synthesized by hydrothermal reactions have been reported to have good sinterability and high chemical stability against long-time sintering. In this study, detailed chemical and structural characterizations were performed on a hydrothermal BKT powder sample to identify the origin of such properties. The results of X-ray diffraction, infrared transmittance, and diffuse reflectance measurements revealed that the hydrothermal BKT particle contained high concentrations of lattice hydroxyl group and Bi vacancy, whereas the observation by transmission electron microscope showed that its surface was covered with numerous Bi_2O_3 nanoparticles to achieve the overall stoichiometric cation ratio of BKT. We found that the unique composite nanostructure of the hydrothermal BKT powder led to a large suppression of Bi evaporation during high-temperature sintering, thereby contributing to its superior chemical stability.

1. Introduction

Bismuth-based lead-free perovskite ferroelectrics have been extensively studied as alternatives to lead-based piezoelectric materials represented by $Pb(Zr, Ti)O_3$ because of the similar electronic configurations of Bi^{3+} and Pb^{2+} ions [1]. Among them, bismuth potassium titanate $(Bi_{1/2}K_{1/2})TiO_3$ (BKT) is of particular importance because, as in the case of $PbTiO_3$, it has a tetragonal crystal symmetry at room temperature [2]. However, the synthesis and sintering of phase-pure BKT is known to be difficult owing to its low melting point and the high volatility of Bi and K [3,4], resulting in a poor understanding of its basic properties.

It has been reported that the ferroelectric and piezoelectric properties of BKT are decreased in fine-grained ceramics with grain sizes lower than 1 μm [5,6]. Thus, preparing ceramic samples with large grain sizes over 1 μm is necessary for studying the intrinsic properties of BKT. To obtain such coarse-grained ceramics, a prolonged sintering is required because the melting point of BKT limits the sintering temperature below 1070 °C, at which the grain growth rate is very slow. However, BKT powders synthesized by conventional solid-state reactions have been reported to decompose into K-rich and Bi-rich secondary phases upon prolonged sintering longer than 20 h, resulting in the degradation of the electric insulation property of these sintered ceramics [3,7]. On the other hand, we have reported that BKT powders derived by hydrothermal methods show good sinterability owing to their fine particle size (~150 nm) and high chemical stability against prolonged sintering [6,8,9]. Sintering this hydrothermal powder for long periods (up to 100 h) can yield dense BKT ceramics with controlled grain sizes up to 1 μm without noticeable formation of secondary phases [6,9]. Some other reports have also suggested that hydrothermally derived BKT powders are suitable for preparing phase-pure and dense ceramics [10,11]. Although it can be assumed that the chemical composition, defects, or microstructures of hydrothermal BKT powders are responsible for their suitability for providing high-quality ceramic samples, the detailed reasons behind this behavior remains unknown so far. With the aim to gain insights into this question, we performed, herein, detailed chemical and structural characterizations of hydrothermally-derived BKT powders annealed at varying temperatures.

2. Experimental procedure

A BKT powder was synthesized following the hydrothermal process reported elsewhere [8]. 1.198 g of anatase TiO_2 (99.9%, Toho Titanium) and 1.950 g of $Bi(OH)_3$ (99.9%, Kojundo Chemical Laboratory) were ultrasonically dispersed in 10 mL of deionized water.

* Corresponding author.
E-mail address: hagiwara@applc.keio.ac.jp (M. Hagiwara).
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Then, 50 mL of a 14.4 mol/L KOH solution was rapidly dropped into the mixture under magnetic stirring in an ultrasonic bath. The resulting suspension was heated to 160 °C in a Teflon-lined autoclave and immediately cooled down and kept at 110 °C for 6 h while stirring at 400 rpm. After the hydrothermal reaction, the products were filtered, washed twice with 100 mL of ethanol, and finally dried at 60 °C for 12 h. The resulting powder was subsequently heat-treated at varying temperatures (200–1000 °C) for 30 min in air. For comparison, another BKT powder was also synthesized by a conventional solid-state method following the procedure reported by König et al. [3].

The following characterizations were performed on the sample powders. The microstructure of the samples was observed by field-emission transmission electron microscopy (FE-TEM; TECNAI F20, Philips) equipped with an energy dispersive X-ray (EDX) spectrometer and by field-emission scanning electron microscopy (FE-SEM; JSM-7600F, JEOL). The composition of the hydrothermal powder was measured with an X-ray fluorescence (XRF) spectrometer (XGT-2700, Horiba) using the solid-state powder as a reference. The crystal structures of the powders were examined by X-ray diffraction (XRD). XRD patterns were recorded in a diffractometer (AXS D8-02, Bruker) with Cu Kα radiation from 20° to 80° and analyzed by a Rietveld refinement program RIETAN-FP [12] to determine the lattice parameters. The diffuse reflectance spectra were measured with a spectrophotometer (FLH-740, JASCO). The Fourier transform infrared (FT-IR) spectra were measured in a range of 400–4000 cm^{-1} using an infrared spectrometer (ALPHA, Bruker) by the KBr pellet method. Thermogravimetric (TG) analysis was carried out using a Shimadzu DTG-60 instrument at temperatures ranging from room temperature to 1000 °C (heating rate: 5 °C/min) in air. Prior to the IR and TG measurements, the sample powders were vacuum-dried at 100 °C overnight to minimize the influence of the surface-adsorbed water.

To examine the evaporation of Bi and K during sintering, the hydrothermal and solid-state powders were pressed into pellets (11 mm in diameter and 1 mm in thickness) using 2 wt% of poly(vinyl butyral) as an organic binder. After the binder was burnout at 800 °C for 1 h, the pellets were sintered at 1050 °C for 5 h, and the weight of the pellets was subsequently measured after cooling. This procedure of sintering together with the subsequent weight measurement was repeated until the total sintering time reached 30 h. The composition of the pellet samples after the sintering for 30 h was also examined by using the XRF analysis.

3. Results and discussion

The EDX characterization data confirmed that the as-prepared hydrothermal BKT powder had an overall stoichiometric composition. The XRD profiles for the as-prepared and heat-treated hydrothermal BKT powders are shown in Fig. 1(a) and (b). All diffraction peaks of the as-prepared powder can be indexed to a single phase with tetragonal perovskite structure, although its tetragonality (c/a, 1.058) is much larger than the reference data (c/a = 1.024, ICDD PDF #00-036-0152 [13]). Such a large tetragonal distortion can be also seen in most of the previously reported XRD patterns of hydrothermal BKT [8,10,11,14,15]. The (00l) peaks of the as-prepared powder were significantly broader as compared to the (h00) peaks, implying the existence of a large strain in the crystal lattice along the c axis. The powders heated at different temperatures maintain the single-phase perovskite structure in all cases, although the lattice parameters drastically vary with the heat treatment temperature (Fig. 1(c)). The lattice parameter c drastically decreases and approaches to the lattice parameter a with the heat treatment temperature, resulting in a monotonical decrease in c/a down to 1.007 at a heat treatment temperature

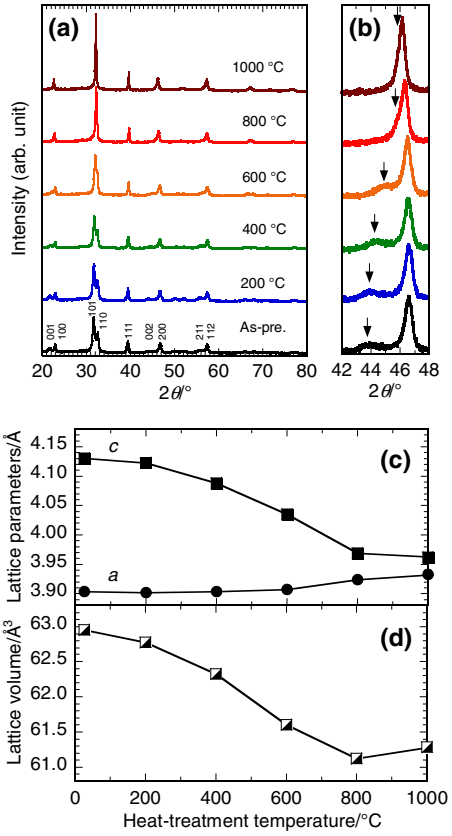

Fig. 1. (a) XRD patterns of the as-prepared and heat-treated hydrothermal BKT powders, (b) magnified profiles of the (002) and (200) peaks, and heat treatment temperature dependences of (c) the lattice parameters and (d) the lattice volume. The arrows in (b) indicate the position of the (002) peaks.

of 1000 °C. Similar variations of the lattice parameters have been reported by Krad et al. [11] The lattice volume also decreases with the heat treatment temperature up to 800 °C, then slightly increases from 800 to 1000 °C (Fig. 1(d)). Fig. 2 shows the FE-SEM images of these as-prepared and heat-treated hydrothermal BKT powders. The as-prepared sample is composed of fine particles with a size of 150–200 nm formed by the attachment of smaller cubic particles. No obvious change in the morphology of the particles is found in the samples heat-treated at 200–1000 °C. This indicates that the observed variation in the lattice parameter by the heat treatments is not originated from the morphological change.

Fig. 3 shows the FT-IR spectra of the as-prepared and heat-treated hydrothermal BKT powders. The as-prepared powder exhibits a sharp absorption band at 2930 cm^{-1}, which may be attributed to the stretching of C–H bond of the ethanol used as the washing media, and a strong absorption band around 3300 cm^{-1} ascribed to the stretching of O–H bond. The intensity of this O–H band gradually weakens with the heat treatment temperature up to 1000 °C, whereas the C–H band disappears after the heat treatment at 200 °C. The diffuse reflectance spectra of the same samples are presented in Fig. 4. All samples show sharp onset of interband absorption around 340 nm, indicating nearly constant band gap energy around 3.7 eV for these samples, which is the normal value for Ti^{4+}-oxide compounds. No obvious visible-light absorption is observed in the as-prepared powder, whereas the powders heat-treated at 400–800 °C show a broad absorption shoulder around 400 nm. Correspondingly, we observed that the color of the samples turned from white to faint yellow. Such a light absorption around 400 nm has been previously reported for TiO_2 (anatase) annealed in N_2 atmosphere and attributed to the existence of

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