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Preparation of barium titanate by homogeneous precipitation

SEUNGWON KIM
Department of Chemical Engineering, Yosu Fisheries University, Yosu 550-749, Korea
MOONHEE LEE, TAEYONG NOH, CHUL LEE
The Research Institute for Natural Sciences and Department of Chemistry, Hanyang University, Seoul 133-791, Korea

The barium titanyl oxalate, which was the precursor of barium titanate, was prepared by homogeneous precipitation using the diethyl oxalate as a precipitating agent. The oxalate dried at 80 °C was the crystalline phase, which was converted to amorphous-like phase after drying at 120 °C. The weight loss of oxalate was 47.3 wt%. The chemical formula of the oxalate could correspond to $BaTiO(C_2O_4)_2 \cdot 4H_2O$. The barium titanate obtained from the calcination of oxalate at 850 °C was a tetragonal phase with a particle size of 0.2 μm.

1. Introduction

Perovskite barium titanate ceramics are of interest owing to their ferroelectric and dielectric properties. These ceramics are widely used in the main constituents of passive electroceramic components such as multilayer capacitors and non-linear resistors [1, 2]. The most conventional technique for the preparation of barium titanate is a solid-state reaction between $BaCO_3$ and TiO_2 at a temperature of around 1350 °C [3]. In recent years, various preparation techniques have been tried to prepare the fine particle barium titanate. Clabaugh *et al.* [4] investigated the preparation of a high-purity barium titanate of nearly perfect stoichiometry by precipitating barium titanyl oxalate and subsequently converting this oxalate to barium titanate by a thermal decomposition. Since then, the wet preparation techniques for fine-particle barium titanate have been intensively studied [5–10].

In this study, we investigated whether barium titanyl oxalate, known as the precursor material of barium titanate, could be prepared by homogeneous precipitation using diethyl oxalate. The homogeneous precipitation has been applied to prepare zinc sulphide which is used as an attractive infrared window material [11, 12]. However, homogeneous precipitation has not yet been reported to have been used to prepare barium titanate. We report here the preparation of barium titanyl oxalate by homogeneous precipitation and the characterization of oxalate and barium titanate.

2. Experimental procedure

Aqueous solutions of barium chloride and titanium tetrachloride were chosen as the starting materials. Diethyl oxalate was employed as a precipitating reagent. The aqueous solution of titanium tetrachloride was prepared, following the process proposed by Kudaka *et al.* [13]. Distilled water was added slowly to the cool, stirred solution of titanium tetrachloride. The solution was clear and did not show any hydrolysis of titanium tetrachloride. It was found that titanium ions were easily hydrolysed and then formed titanyl hydroxide [14].

The prepared solutions of barium chloride and titanium tetrachloride were mixed in a mole ratio of Ba/Ti = 1.00. The diethyl oxalate was added to the mixed solution, keeping it constantly stirred. The quantity of diethyl oxalate was 30% in excess over the stoichiometric amount required for precipitation. The resulting solution was heated in a water bath to 65 °C. As the diethyl oxalate slowly decomposed, a white precipitated oxalate was formed. The decomposition of diethyl oxalate and precipitation of oxalate occurred by the following reactions

$$C_2H_5O_2CCO_2C_2H_5 + 2H_2O \rightarrow 2C_2H_5OH + C_2O_4^{2-} + 2H^+ \quad (1)$$

$$C_2O_4^{2-} + BaCl_2 + TiCl_4 \rightarrow \text{Ba–Ti–oxalate} \quad (2)$$

The precipitated oxalate was filtered and washed with pure ethanol several times, and then dried at temperatures of 80 and 120 °C. The dried oxalate was calcined to yield barium titanate at a temperature of 850 °C in air for 2 h.

The thermal decomposition of oxalate was analysed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC; Netzsch STA 409C). The oxalates dried at 80 and 120 °C were characterized by X-ray diffraction (XRD; Philips 1700) using nickel-filtered CuK_α radiation. The barium titanate obtained was also characterized by the X-ray diffraction and scanning electron microscopy (SEM; Jeol JAX-840).

Chemical analysis of the barium titanate was undertaken using the following process [7]. The barium

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titanate was dissolved in concentrated sulphuric acid by heating. After cooling, the dropwise titration of the distilled water brought about the precipitation of barium sulphate, which was used for the determination of the BaO content in barium titanate. The titanium ions, which were present in the filtrate, were analysed by ultraviolet spectrophotometry (HP 8452A) using hydrogen peroxide as a colouring agent and used for determining the TiO_2 content.

3. Results and discussion

The X-ray diffraction patterns of the oxalates dried at temperatures of 80 and 120 °C are shown in Fig. 1. The oxalate dried at 80 °C was crystalline phase (Fig. 1a), which was consistent with that of barium titanyl oxalate reported by Kudaka *et al.* [13]. However, this crystalline oxalate became an amorphous-like phase (Fig. 1b) after drying at 120 °C. The result agrees with the report of Fang and Lin [15], in which the irregular diffraction patterns dominated in most directions with the increased drying temperature.

Fig. 2 shows the results of TGA–DSC measurements for the oxalate. The analysis was performed up to a temperature of 1000 °C with a heating rate of 4 °C min^{-1}. The weight loss of oxalate was 47.3 wt %. This weight loss is closer to the values reported by Gallagher and Schrey [16] and Yamamura *et al.* [7]. Therefore, the chemical formula of the oxalate could correspond to $BaTiO(C_2O_4)_2 \cdot 4H_2O$, the weight loss of which was calculated to be 48.1 wt %. The DSC curve shows the endothermic loss of water in the temperature region 100–250 °C and the exothermic reaction at a temperature of 350 °C, which are closer to the results of Gallagher and Schrey [16] and Tunkasiri and Rujijanagul [17], who observed a phase change at approximately 700 °C. In this work, however, an endothermic reaction of the phase change corresponding to the formation of $BaTiO_3$ was observed at a temperature of 660 °C. No exothermic reaction associated with a cubic–tetragonal phase transition [18] was detected at temperatures between 900 and 1000 °C.

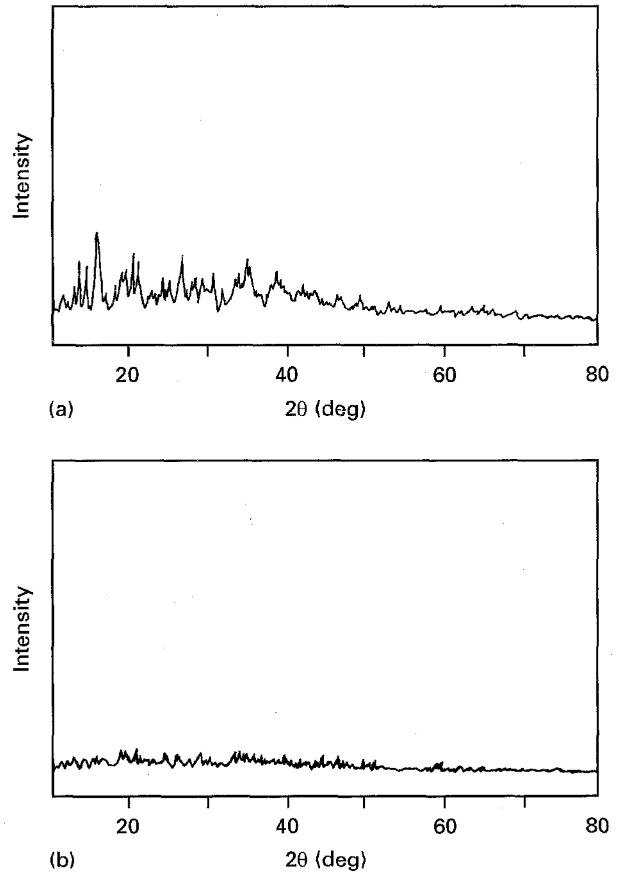

Figure 1 X-ray diffraction patterns of oxalates dried at temperatures of (a) 80 °C and (b) 120 °C.

The results of chemical analysis for barium titanate are given in Table I. It can be seen that barium titanate is almost stoichiometric, but slightly barium deficient. It may be speculated that this barium deficiency originates from the incomplete precipitation of barium at a relatively low pH of 1.5 [19].

Fig. 3 shows the scanning electron microscopic observations of the oxalate and barium titanate obtained by the calcination of the oxalate at 850 °C. The particle sizes of oxalate and barium titanate were around 0.4 and 0.2 μm, respectively. The oxalate was constituted of aggregates of particles, which disappeared at the low calcining temperature of 850 °C.

The X-ray diffraction pattern of the barium titanate is shown in Fig. 4. The lattice constants and c/a ratio were calculated using Cohen's method [20]. The lattice constants were found to be $a = 0.4003$ nm and $c = 0.4020$ nm. The c/a ratio of 1.004 was a slightly lower tetragonality than that reported previously [7, 8]. The low c/a ratio might originate from the barium deficiency.

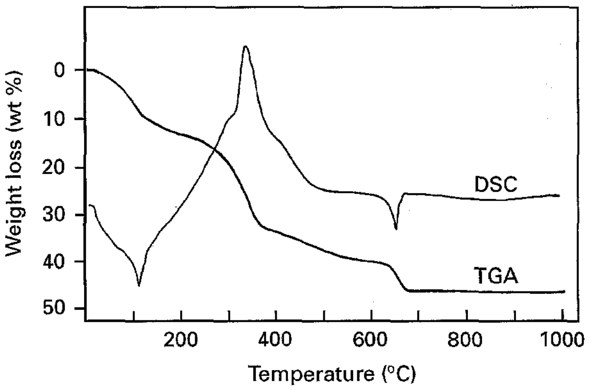

Figure 2 TGA–DSC measurements for the oxalate.

TABLE I Results of chemical analysis of $BaTiO_3$ powders

Sample	BaO (wt %)	TiO_2 (wt %)	Mole ratio of Ba/Ti
1	65.4	34.2	0.996
2	65.3	34.1	0.998
3	65.2	34.4	0.987

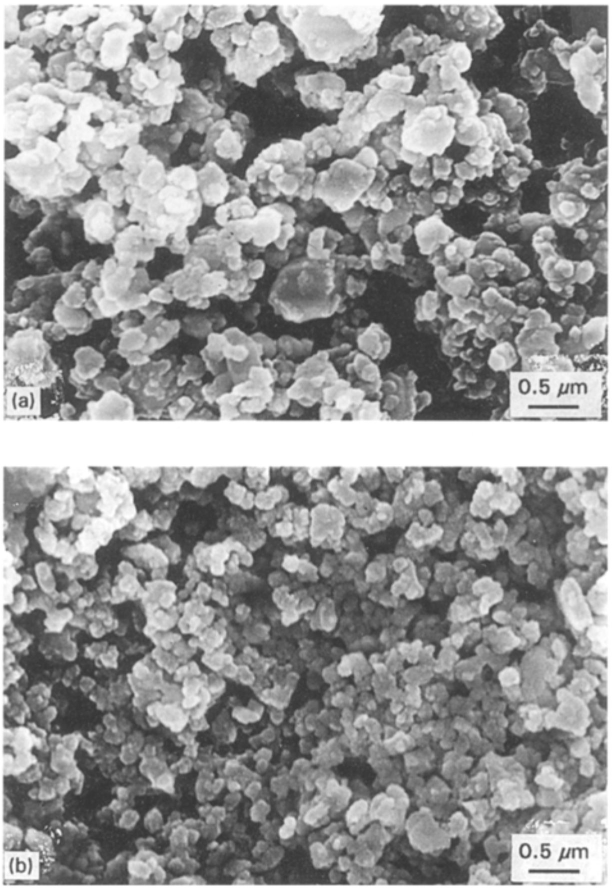

Figure 3 Scanning electron micrographs of (a) the oxalate and (b) the barium titanate calcined at 850 °C.

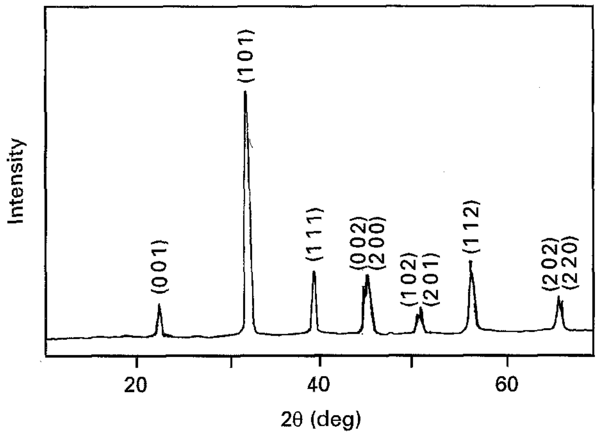

Figure 4 X-ray diffraction pattern of the barium titanate.

4. Conclusion

Homogeneous precipitation was applied to prepare the barium titanyl oxalate which is the precursor of perovskite barium titanate. Barium chloride and titanium tetrachloride were used as starting materials for the barium and titanium components. Diethyl oxalate was used as a precipitating agent. The oxalate dried at 80 °C was found to be $BaTiO(C_2O_4)_2 \cdot 4H_2O$ with a crystalline phase, which was converted to an amorphous-like phase after drying at 120 °C. The oxalate converted to the stoichiometric barium titanate with a tetragonal phase. The barium titanate obtained had a very fine particle of size around 0.2 μm.

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