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Sintering process of barium titanate prepared by homogeneous precipitation method

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균일침전법에 의해 제조한 티탄산 바륨의 소결 과정

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Perovskite barium titanate ceramics are of interest in electronic devices because of their dielectric and ferroelectric properties. These electronic devices using barium titanate are widely applied in the positive temperature coefficient (PTC) thermistor, multilayer capacitor (MLC) and grain-bouary barrier layer (GBBL) capacitor [1, 2]. The barium titanate was prepare by the conventional mixed metal oxide synthesis using barium carbonate and titanium dioxide [3]. But, metal oxide synthesis usually lead to the defects such as low purity, ununiform particle size and easy mixing of impurities. Recently, there have been many investigations in an attempt to prepare a fine particle and stoichiometric barium titanate using chemical wet techniques such as hydrothermal [4], spray-drying [5], oxalate coprecipitation [6-8], homogeneous precipitation [9] and sol-gel [10,11].

In this study, the sintering process of barium titanate prepared by homogeneous precipitation method was investigated by measurements of density (sintered, apparent and bulk) and apparent porosity.

The homogeneous precipitation method of barium titanate was described in previous paper [9]. In brief, the solutions of barium chloride, titanium tetrachloride and diethyl oxalate were used as starting materials. Diethyl oxalate as precipitating reagent was added to a mixed solution of

barium chloride and titanium tetrachloride, keeping it constantly stirred. The mole ratio of Ba/Ti was controlled as unity. And, the mixed reactant solution was heated in a water bath to 65℃. As the diethyl oxalate was slowly decomposed, white precipitates were formed. The white precipitates were barium titanyl oxalate, $BaTiO(C_2O_4)_2 \cdot 4H_2O$, known as the precursor material of barium titanate [9]. The precipitates were filtered and washed with pure ethanol, and then dried at 80℃ for 12 h. The dried precipitates were calcined to obtain barium titanate at a temperature of 850℃ in air for 2 h. The barium titanate obtained by homogeneous precipitation method had a tetragonal phase with c/a of 1.004 and Ba/Ti ratio of 0.98-0.99. This slight barium deficiency might originate from the incomplete precipitation of barium at a relatively low pH of 1.5 [9, 12].

The calcined powders were ball-milled with zirconia balls and distilled water in a polyethylene vessel for 6 h and then dried. The dried powders were pressed into pellets of 20 mm diameter and 2.0 mm thickness under a pressure of 1500 kg/cm^2. The pressed pellets were sintered in the temperature range of 1200 to 1350 ℃ for 2 h. The heating and cooling rate were 5℃/min and 4℃/min, respectively.

Sintered density was measured from the weight and volume of the sintered pellets. Apparent density, bulk density and apparent porosity of the sintered pellets were measured by the following method defined in American Society for Testing and Materials Specipication (ASTM), C373 [13]. A dried weight (W_d) was measured in the pellets sintered in the various temperatures. The sintered pellets were boiled in water for 5 h and weighed in water (W_w) at 25℃. Excess water on the surface of the pellets was wiped off with wet gauze and the pellets were weighed (W_s). Apparent density, bulk density and apparent porosity were calculated as [13,14],

$$\text{Apparent density} = W_d/(W_d-W_w) \quad (1)$$

$$\text{Bulk density} = W_d/(W_s-W_w) \quad (2)$$

$$\text{Apparent porosity (\%)} = 100\times(W_s-W_d)/(W_s-W_w) \quad (3)$$

Figure 1 shows the variation of the sintered density, apparent density and bulk

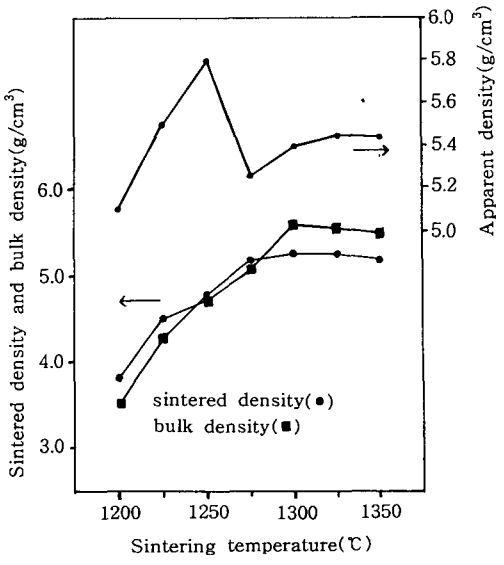

Fig. 1. Variation of the sintered density, apparent density and bulk density against the sintering temperature.

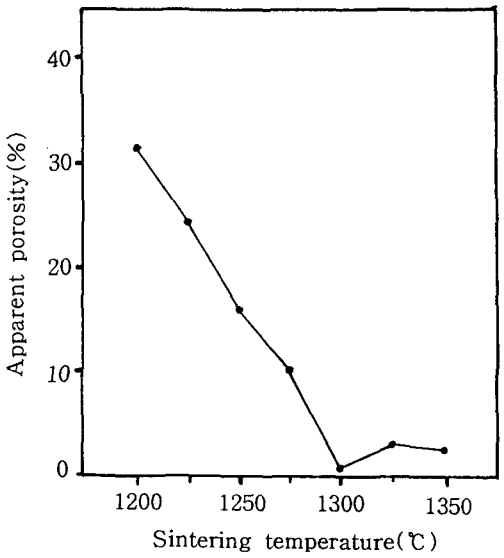

Fig. 2. Variation of the apparent porosity against the sintering temperature.

density against the sintering temperatures. The sintered density increased with sintering temperature up to 1300℃. The barium titanate sintered at 1300℃ had a sintered density of 5.6 g/cm^3, which was 92 % of the theoretical density (6.08 g/cm^3). The bulk density also increased with the sintering temperatures as the sintered density. The behavior of the bulk density is similar to the result in the sintering process of the semiconductive $Ba_{0.776}Sr_{0.22}Y_{0.004}TiO_3$ reported by Yoneda et al [14].

The variation of the apparent porosity against the sintering temperatures is shown in Fig. 2. The apparent porosity decreased with the increasing of the sintering temperature, which of 1300℃ showed the minimum apparent porosity. It means that a compact sintering of barium titanate prepared by homogeneous precipitation method was obtained at the sintering temperature of 1300℃.

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