Charge compensation mechanism in yttria-doped barium titanate

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Abstract

A commercial TiO2-excess BaTiO3 powder doped with Y2O3 has been pressureless-sintered using conventional tube furnace and CO2-laser, and the room-temperature electrical conductivity determined. Grain-growth inhibition is found to occur at ~0.40 mol% Y2O3 where the refined microstructure of an average grain size of ~1 μm is obtained from sintering at 1215 °C. The principal charge compensation mechanism in Y2O3-doped BaTiO3 depending upon temperature can be divided into three characteristic regimes. The mechanism is predominantly of the cation vacancy compensation at temperatures <1210 °C, a mixed mode at 1210–1500 °C, and the electron compensation when sintering temperature exceeds 1500 °C. Sintering using the CO2-laser has enabled the retention of the high temperature defect equilibrium which renders the room-temperature conductivity of ~10^-2 (Ω mm)^-1 to the ceramics. The sintering of Y2O3-doped BaTiO3 ceramics is improved since densification is enhanced by faster barium diffusion via the extrinsic cation vacancy and coarsening suppressed by high Y2O3-content due to reduced grain-boundary mobility by second-phase (Y2Ti2O7) pinning.

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1. Introduction

A cation vacancy mechanism for principal charge compensation is usually taken to argue for enhanced densification in donor-doped BaTiO3 ceramics observed experimentally in the solid-state sintering [1,2]. Effective grain-growth inhibition for donor-doping occurs between ~0.20 and 0.40 mol% such as La2O3 [1,2], and Sb2O3 [3]. The lower donor concentration has been conveniently termed the grain-growth inhibition threshold (GGIT) [4]. The sintering of BaTiO3 ceramics is enhanced and the microstructure refined simultaneously to an average grain size (Gav) of ~1–3 μm with dopant content exceeds GGIT. However, eutectic liquids [5,6] forming at temperatures below 1350 °C [1,2] have interfered with the interpretation of the sintering kinetic data [6], arguing for densification enhancement in the solid state. Furthermore, the ceramics with donor–dopants in this range had low electrical conductivities, often became insulators [1].

The coincidence of the room-temperature conductivity maximum and the onset of grain-growth inhibition suggested [1] a correlation between the vacancy compensation and grain-growth control. It was postulated [7] that the barium vacancy (V_Ba) [6] formed upon cooling in an oxidising atmosphere is the most important intrinsic defect. The principal charge compensation defect being V_Ba was implied and later considered [8] to be kinetically more mobile, although others [9] have indicated that the formation of the titanium vacancy was favourable thermodynamically. In fact, an enrichment of Ti relative to Ba was found [10] on the surface of slowly cooled Nb-doped BaTiO3 ceramics, indicating excessive barium vacancies on the surface. It was suggested [7] that the principal charge compensation mechanism depends upon the temperature and the oxygen partial pressure, pO2, in the sintering atmosphere. The overall charge neutrality in the ceramics is maintained by a mixture of cation vacancy and electron, i.e. mixed mode, regardless of the donor oxide and its concentration [1,2,7].

More specifically, the principal charge compensation mechanism of three distinctive schemes, depending on the sintering temperature (T) for donor-doped BaTiO3 sintered...
and cooled to room temperature in air was proposed before [3,7]. It is summarised below,

| (I)  | \( T < 1220 \, ^\circC \) | \( N_D \approx 2[V_{Ba}^n] \) | Vacancy compensation |
| (II) | \( 1220 \, ^\circC < T < 1500 \, ^\circC \) | \( N_D = 2[V_{Ba}^n] + n \) | Mixed mode |
| (III) | \( T > 1500 \, ^\circC \) | \( N_D \approx n \) | Electron compensation |

where \( N_D \) is the concentration of donor cation and \( n \) is the concentration of electron.

Yet, donor-doped BaTiO3 sintered at 1220–1500 °C in air has produced semiconductors as well as insulators [1,2,7]. Thus, a kinetically controlled mechanism of equilibrium restoration has been proposed to account for the limited electrical conductivity of donor-doped BaTiO3 at room temperature [3,7]. The ability to restore equilibrium upon cooling is determined kinetically by the diffusion of barium vacancy inwards to the grain interior from surface. Defect distribution depending on the cooling rate is inhomogeneous across the grains and each grain would have contained a rim of barium vacancy with frozen-in defects in the grain interior. However, the proposed temperature-dependent charge compensation regimes have not been verified experimentally.

In a preliminary study of the \( \text{Y}_2\text{O}_3 \)-doped BaTiO3 compositions sintered at 1350 °C, a large discrepancy of the electrical conductivity by ~10^5 was found in the ceramics of similarly refined microstructure with an average grain size \( G_{av} \approx 15–18 \, \mu \text{m} \). It demonstrates that laser sintering has produced BaTiO3 ceramics with significantly higher electrical conductivity at room temperature. The fast cooling rate from sintering temperatures afforded by CO2-laser appears to be a determining factor. The implication is that the room-temperature conductivity is determined by a kinetic process [3,7] occurred upon cooling from sintering temperatures. We, therefore, studied the room-temperature electrical conductivity of BaTiO3 ceramics doped with \( \text{Y}_2\text{O}_3 \) adopting pressureless-sintering technique of two vastly different cooling rates. The conductivity data reported here confirm the existence of the three-charge compensation regimes proposed by Wernicke [3] and Daniels [7].

2. Experimental procedure

A commercial TiO2-excess 0.997 nonstoichiometric BaTiO3 powder (Ticon^\text{®} HPB) supplied by Ferro (Penn Yan, NY, USA) was used in this study. Reagent grade \( \text{Y(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} \) (Merck, Darmstadt, Germany) was mixed with 1 wt% polyvinyl butyral (PVB) binder in absolute alcohol before milling in a polypropylene (PP) jar with nylon-coated steel balls for 2 h. The mixed slurry was oven-dried, de-agglomerated using an agate mortar and pestle, then passed through a ~74 µm mesh. An appropriate amount of powder was die-pressed to discs of 5 mm in diameter in a WC-inserted steel die by applying uniaxial pressure of 100 MPa. Samples were then sintered in a conventional tube furnace by the heating rate of 5 °C min\(^{-1}\) or using a CO2-laser (PRC, FH-3000, Landing, NJ, USA). The experimental detail of adopting CO2-laser for sintering was reported before [11].

Sintered density was determined by applying the Archimedes technique when distilled water was used as the immersion medium. Sintering kinetic curves are established by plotting the final sintered density against sintering time. The room-temperature electrical conductivity was determined using a two-point probe on polished sample surface coated with In–Ga electrodes using an electrometer (model 617, Keithley, Cleveland, OH, USA).

Sintered samples were mechanically ground and polished with SiC grits successively before diamond lapping to 1 µm surface roughness for microstructure observation. Grain boundaries were delineated with thermal etching at 1200 °C, or chemical etching using 1% HF solution where appropriate. Average grain size was determined on SEM micrographs, taken from JEM6400 (JEOL, Tokyo, Japan), adopting the linear intercept technique [12]. Thin foils for TEM were prepared by the standard procedures of slicing, ultrasonic drilling, polishing followed by dimple grinding and Ar^+-beam thinning to electron transparency. Observations were performed in a JEOL AEM3010 operating at 300 kV.

3. Results

3.1. Sintering behaviour and microstructures

Fig. 1 shows the sintering curves of \( \text{Y}_2\text{O}_3 \)-doped BaTiO3 by furnace-sintering at 1215 °C for up to 150 h. Sintering of the ceramics has been improved and higher final density (described in relative density, \( \rho_{rel} \)) obtained by donor-doping. An increase of \( \Delta \rho_{rel} \approx 16% \) was obtained by adding 0.80 mol% \( \text{Y}_2\text{O}_3 \). However, it also appears that the sintered density was improved only insignificantly with \( \text{Y}_2\text{O}_3 \)-doping.
between 0.15 and 0.50 mol%. The sudden increase of final sintered density from the undoped to 0.15 mol% doped samples, and again from the 0.50 to 0.80 mol% doped samples can easily be discerned (Fig. 1). The increasing trend differs characteristically from that reported [11] for the La$_2$O$_3$-doped samples where the sintered density increased progressively with the dopant concentration.

Pressureless-sintering of doped samples containing Y$_2$O$_3 < 0.30$ mol% at low temperatures (1215 °C for 100 h) in a conventional furnace produced a bimodal

![Image of microstructures](image_url)

Fig. 2. Microstructures of Y$_2$O$_3$-doped BaTiO$_3$: (a) 0.30 mol%, (b) 0.40 mol%, (c) 0.80 mol% pressureless-sintered at 1215 °C for 100 h, (d) 0.80 mol% laser-sintered at 1450 °C for 60 s, (e) 1.0 mol% Y$_2$O$_3$ pressureless-sintered at 1300 °C for 15 h, and (f) 0.15 mol% Y$_2$O$_3$ laser-sintered at 1450 °C for 60 s (SEM-SEI).
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