

Dielectric properties of barium titanate ceramics doped by B₂O₃ vapor

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(Received 20 July 2004; accepted 17 September 2004)

The effects of B₂O₃ vapor doping on the dielectric properties of barium titanate ceramics were studied. After the doping, the Curie point of BaTiO₃ ceramics was increased from 128 °C to 130 °C and the maximum dielectric constant was considerably increased. X-ray diffraction showed that both the grain lattice parameters and the tetragonality were increased by the boron oxide vapor doping. It was proposed that boron interstitial was introduced into the grain lattice of barium titanate ceramics by B₂O₃ vapor doping and the dielectric properties were thus obviously changed. © 2004 American Institute of Physics. [DOI: 10.1063/1.1814167]

Barium titanate is one of the most important and widely used ferroelectrics, and extensive researches have been conducted on it ever since it was discovered in 1943. Barium titanate-based ceramics usually are sintered at temperatures above 1300 °C and many of the researches have been devoted to lowering the sintering temperatures of barium titanate based ceramics.^{1–3} B₂O₃-based flux additions, as a liquid phase provider at high temperatures, have received much attention to decrease the sintering temperature of BaTiO₃ based ceramics.^{4–10} Rhim *et al.* found that the dielectric and ferroelectric properties of Ba_{0.7}Sr_{0.3}TiO₃ samples with 0.5 wt % of B₂O₃ sintered at <1150 °C were as good as those of undoped Ba_{0.7}Sr_{0.3}TiO₃ sintered at 1350 °C.⁷ Prakash *et al.* found an addition of the ZnO-B₂O₃ flux to BaTiO₃ lowered the sintering temperature and improved its dielectric properties.⁸ Lee *et al.* reported that various boron source compounds, such as BaB₂O₄, greatly lowered the starting temperature of densification by formation of liquid phases around 900 °C, lowered room temperature resistivity ρ_r , and improved positive temperature coefficient resistivity (PTCR) effect of Y-doped BaTiO₃ ceramics.⁹ However, B₂O₃ has rarely caused attention as a dopant rather than flux addition. Because B₂O₃ vaporizes easily at high temperatures, it can be adopted as a vapor dopant. In donor doped BaTiO₃ ceramics, the B₂O₃ vapor dopant can improve the PTCR effect distinctly^{11,12} and decrease the sintering temperature.¹³ These effects were benefited from the introduction of boron interstitial in the perovskite lattice. In this paper, we focus our attention on the dielectric properties of barium titanate ceramics doped by B₂O₃ vapor.

High purity commercial BaTiO₃ (99.99%, Advanced Nano Products Co., Ltd., Chungcheongbuk-do, Korea), and B₂O₃ (99.99%, Beijing Chemical Plant, Beijing, China) were adopted as starting materials. The barium titanate powders were pressed into small disks 1 mm thick and 10 mm in diameter with hydrostatic pressure of 98 MPa. The disks were placed in two bottom-up alumina crucibles marked as

A, B, respectively. B₂O₃ powders of 0.25 mol % (nominally) were placed beside the samples in crucible B. The samples were sintered at 1250 °C for 2 h in air, then furnace cooled to room temperature. The samples in crucibles A and B were sintered in different runs to avoid cross contamination. The microstructure of the samples was studied by scanning electron microscopy (Leica Stereoscan 440). The lattice parameters were measured by an x-ray diffractometer (Philips PW 3719) with Cu K α radiation. The ceramic samples were polished and silver paste electrodes were fired on both surfaces. The dielectric constant and the dielectric loss of the samples were measured through an impedance analyzer (Model HP 4192A LF, Hewlett-Packard Co., U.S.A.) from room temperature to 200 °C.

As temperature decreases, barium titanate undergoes three successive phase transitions: From paraelectric cubic phase to ferroelectric tetragonal phase and then to ferroelectric orthorhombic phase and finally to low-temperature rhombohedral phase.¹⁴ The transition from cubic phase to tetragonal at 127 °C is important because it is a transition from paraelectrics to ferroelectrics, and the transition temperature is called Curie point. The Curie point can be shifted by the doping of Pb ion to replace Ba to high temperature and by the doping of Sr to low temperature. It is found that the tetragonality, or c/a , of BaTiO₃ based materials at room temperature is related to their Curie point. A larger c/a corresponds to a higher Curie point. Figure 1 shows the temperature dependence of dielectric constant and dielectric loss (1 kHz) of two samples from crucible A (sample A) and crucible B (sample B), respectively. It can be seen that through the doping of B₂O₃ vapor, the maximum dielectric constant k_m was considerably increased, and the Curie point was increased slightly from 128 °C in sample A to 130 °C in sample B.

Figure 2 shows the x-ray diffraction (XRD) profile of two samples from crucibles A and B, respectively. Both samples were found to exhibit a tetragonal phase at room temperature. XRD patterns of (111), (002), and (200) planes of the samples shown in Fig. 2 demonstrate peak shifts due

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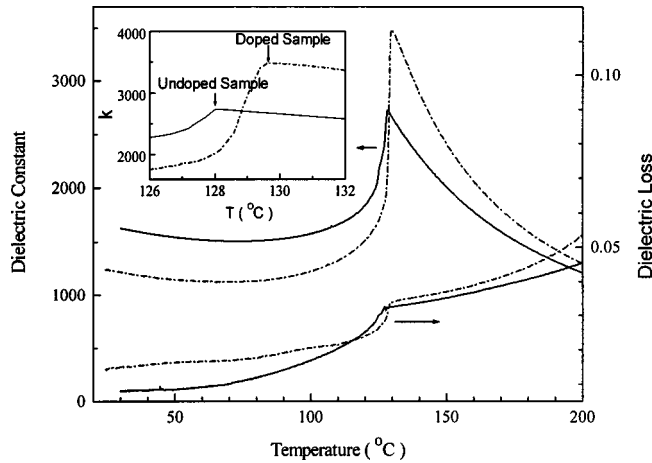


FIG. 1. Temperature dependence of dielectric constant and dielectric loss (1 kHz) of two samples from crucible A (sample A, solid line) and crucible B (sample B, dot dash line), respectively.

to the vapor doping, indicating a lattice expansion in the ceramics due to the vapor doping. The lattice cell parameters and the c/a ratio can be calculated from the XRD data according to the Bragg equation:

$$\lambda = 2d \sin 2\theta, \quad (1)$$

where d is distance of diffraction plane, λ the wavelength of x ray ($\lambda = 1.5418 \text{ \AA}$ for Cu K_{α}), and θ the diffraction angle. The results of BaTiO_3 ceramics with and without B_2O_3 vapor doping are listed in Table I. Both a and c were obviously increased after the doping of B_2O_3 vapor.

According to previous papers, the maximum dielectric constant of BaTiO_3 based ceramics was depressed after the addition of B_2O_3 or its inclusion as flux through conventional doping process, while the lattice parameters or the Curie point was not influenced. In this study, the doping of B_2O_3 vapor obviously showed quite different effects. In conventional doping, B_2O_3 forms liquid phase in the early sintering stage, reacts with BaTiO_3 and forms secondary phases at the grain boundary. While in vapor doping, B_2O_3 is placed separate from BaTiO_3 so its vapor is present not only in the early sintering stage but also during and after the maximum temperature stage, accompanying the formation of grain boundary. We believe that B_2O_3 vapor promotes the sintering

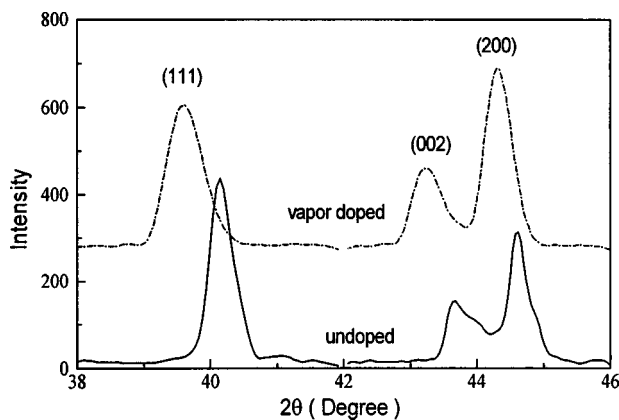
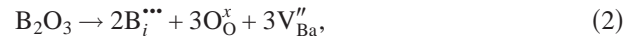


FIG. 2. XRD profile of two samples from crucibles A and B, respectively.

TABLE I. Lattice cell parameters of BaTiO_3 ceramics with and without B_2O_3 vapor doping.

Sample	$a(\text{\AA})$	$c(\text{\AA})$	$a^2c(\text{\AA})^3$	c/a
BT	4.0002	4.0426	64.689	1.011
B-BT	4.0137	4.0598	65.402	1.012

in two ways: One is that some active liquids are formed near grain boundaries by the condensation of B_2O_3 vapor. Grains in fresh surfaces of B_2O_3 vapor doped BaTiO_3 had been observed to exhibit protuberant edges near the grain boundaries,¹¹ which was not observed in samples from crucible A. The other is that some defects and distortions of lattice are formed in vapor doped samples so the activation energy of bulk diffusion is decreased. In vapor doping, B_2O_3 can vaporize as a single molecule and be doped into the perovskite lattice. A particular impurity in perovskite lattice of formula ABO_3 may act as an acceptor, a donor, or an uncharged impurity, depending on the site it occupies. Because B^{3+} (0.2 \AA) is too small to occupy the cation ($\text{Ba}^{2+} 1.35 \text{ \AA}$, $\text{Ti}^{4+} 0.68 \text{ \AA}$) sites of BaTiO_3 , B_2O_3 usually acts as a glass-forming agent in BaTiO_3 ceramics. If B^{3+} ions are incorporated in the lattice of BaTiO_3 , they should form boron interstitials due to their very small ion size. The defect chemistry equation, in Kroger-Vink notation, is written as



where $\text{B}_i^{\bullet\bullet\bullet}$ stands for an interstitial boron with three positive charges, O_O^x for an oxygen ion on an oxygen site, and $\text{V}_{\text{Ba}}^{\prime\prime}$ for a barium vacancy with two negative charges. The observed lattice expansion can be explained by the formation of interstitial boron ions.

Hydrogen ion is one of the most common interstitials in perovskite lattice and it has been studied by many researchers. Kapphan *et al.*¹⁵ and Aggarwal *et al.*¹⁶ proposed two preferable positions for interstitial hydrogen ion: One is the

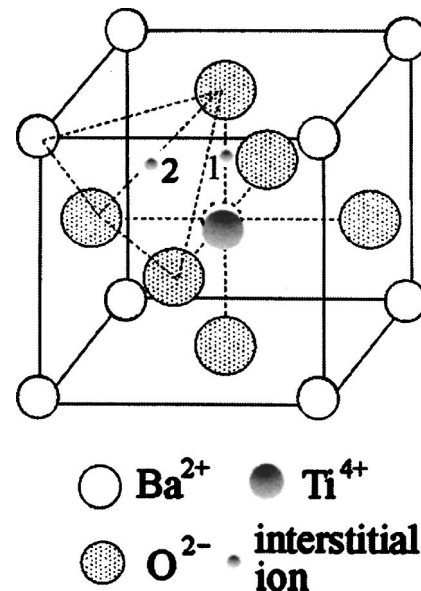


FIG. 3. BaTiO_3 crystal structure showing possible locations of boron interstitial.

center of the tetrahedral sites and the other is the site between an apical oxygen ion and Ti as shown in Fig. 3. Here, the dash circle represents the center of oxygen octahedral, and Ti ion is displaced from the center which gives rise to the spontaneous polarization. Because the boron ion is also very small (with a radius of 0.23 Å), we believe that it occupies a similar position in perovskite as hydrogen ion does. The boron ion carries as high as 3 positive charges and the dielectric constant was not observed to be depressed after the boron interstitial introduction in our experiments, so it should occupy the tetrahedral site “2” rather than the site “1” between the apical oxygen ions and Ti. Because there is attraction between boron ion and oxygen ion, boron ion will move away from the barium ion and approaches the three oxygen ions in the tetrahedron and repulses the titanium ion in the center of oxygen octahedron, hence the tetragonality of the lattice cell, c/a ratio, increases when the boron interstitial is introduced in the lattice. It is well known that in the system of SrTiO₃-BaTiO₃ or BaTiO₃-PbTiO₃, the Curie point increases with increasing tetragonality. This rule is also valid for B₂O₃ vapor doped BaTiO₃. The tetragonality of the vapor doped sample is greater than that of undoped sample at room temperature so the Curie point is shifted to 130 °C after the doping of B₂O₃ vapor.

In summary, B₂O₃ showed quite different effects on BaTiO₃ ceramics when it was added as a vapor dopant rather than a flux: The Curie point was increased from 128 °C to 130 °C and the maximum dielectric constant was considerably increased. The grain cell expanded and the tetragonality, or the c/a ratio, increased. In vapor doping, the presence of

a relatively high pressure of B₂O₃ vapor through the sintering process led to the formation of interstitial boron ions in perovskite lattice and promoted sintering.

ACKNOWLEDGMENTS

This work was supported by the Postdoctoral Research Fellowship Scheme and the Centre for Smart Materials of The Hong Kong Polytechnic University.

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