The Effect of Incorporating Method and Concentration of Niobium on the Properties of Barium Titanate Ceramics

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Abstract: Doping of barium titanate ceramics by aliovalent dopants leads to many changes in the material properties, such as the conductivity especially at high temperatures, the morphology, the dielectric behavior, etc. Since impurities and the lattice imperfections play a crucial role in these phenomena and peculiarities of other properties such as the PTCR effect, their investigation has attracted much attention. The mutual influence of impurities and lattice defects follows from the necessity of excess charge compensation. Barium titanate doped with donors is usually an n-type semiconductor, the conductivity of which, however, is considerably influenced by intrinsic defects. Therefore, not only the equilibrium behavior of these defects but also the defect formation and diffusion play an important role with respect to the semiconducting properties. It is known that the addition of a small amount of Nb has significant effects on the electrical properties of $BaTiO_3$. However, how Nb is distributed locally, and what structural variations it causes have not been studied in depth. With this in mind, the effect of dopants (Nb) ions on the microstructure and electrical properties of $BaTiO_3$ crystals was investigated. A series of doped barium titanate powders were prepared by two different methods and were examined by: XRD, HR-SEM, TEM, Particle size analysis techniques, Zeta potential measurements, Specific surface area, DSC measurements, Impedance Spectroscopy and, to investigate the dopant distribution, SIMS analysis and electron microscopy were performed. The influence of the preparation method on the properties of the powder is discussed.

Key words: defects, electrical properties, $BaTiO_3$, capacitor, sintering.

1. Introduction

Barium titanate (BT) is an important ceramic material in the electronics industry, and a typical perovskite. As an intrinsic ferroelectric material, it can be used in various applications, for example: as a dielectric material in multilayer capacitors, and in thermistors[1]. Addition of donor dopants such as Nb^{5+} at relatively low concentration results in room temperature semiconductivity with positive temperature coefficient of resistivity (PTCR), whereas higher donor contents leads to insulating materials with low concentration of oxygen vacancies and improved resistance to dielectric break down [2,3]. The transition from semiconductor behavior to insulator behavior beyond critical donor concentration is due to a shift from electron compensation to cation vacancy compensation. There are discrepancies in the reported properties of Nb doped BT in the literature, that result from complications in the preparation. The main complication consists in a slow rate of Nb incorporation into the BT lattice and a narrow temperature range at which the processing is effective[4]. Core shell structured BT is intentionally formed in X7R materials, which require a maximum deviation in the dielectric constant of ±15% from the 25ºC value over the temperature range of –55ºC to 125ºC. This can be achieved when the dopants are purposefully added to create a non-homogeneous crystal[5,6]. A concentration gradient paraelectric shell that contains most of the dopants surrounds a core of almost pure ferroelectric BT. Such a material is not in thermodynamic equilibrium and is obtained only under certain sintering conditions. Higher temperature or long sintering may promote a more homogenous distribution of dopants and cause a collapse of the core-shell structure[7]. In this work, we investigated the effect of the incorporating *method* on the properties of BT doped with various Nb concentrations.

2. Experimental procedure

BT powders were prepared by hydrothermal synthesis using a mixture of $BaCl_2 \cdot 2H_2O$ (99.6% purity) and $TiCl_4$ (99.9% purity) in deionized water. The solution resulted in a white colloidal sol after the addition of NaOH (2N). NaOH was added to produce a basic medium according to the stability conditions of BT in a solution (pH>12). Then the sol was transferred to a 300ml stainless-steel vessel. The sealed vessel was heated to 100°C for 5h. The resultant precipitate was cooled to room temperature, centrifuged, washed with water to remove excess Ba^{2+} and dried at 80°C for 12h in a vacuum oven. The Ba/Ti ratio of the as-prepared powder was 1:1. After this, the powder was pressed into pellets and sintered at 1300°C and 1350°C for 5h and 2h respectively with heating ratio of 3°C/min in air. The doped powders were prepared by two methods:

(1) Precipitation coating of niobium penta chloride ($NbCl_5$) onto the fine BT particles. BT particles are first dispersed in an aqueous solution. An additive solution is prepared from $NbCl_5$ and then slowly poured into the BT slurry. Precipitation coating is performed using pH adjustment.

(2) Preparing the doped powders under hydrothermal conditions while adding the dopant atoms (Nb^{5+}) from the beginning of the reaction. A series of doped powders with Nb concentrations between 0.1-3mol% were examined.

3. Results and discussion

The manufactured BT powder has a cubic crystalline structure before sintering; mono dispersed and uniformly distributed particles with an average particle size of 20 nm. Specific surface area of the pure powder was 62 m^2/g. Figure 1 shows a HR-SEM photograph of spherical and homogenous distribution of the as-prepared powder. From ζ-potential measurements of the powders in different pH values, the isoelectric point (i.e.p.) is found at $pH \approx 11 \pm 0.5$ for all the as-prepared samples. After calcination, there is a significant shift towards lower pH values of the i.e.p., probably due to less barium carbonate on the surface.

Nitrogen adsorption isotherms measured at 77K for samples doped with 1mol% Nb by the two methods were determined and are presented in Figure 2. The B.E.T. isotherms indicate that the adsorbent has relatively large pores. The adsorption curves have the same general shape except that adsorbed volume rises more rapidly in the intermediate zone in samples doped by chloride mixing (denoted as HS) and shows a wide hysteresis loop instead of nearly retracing the adsorption curve. This behavior is typical of mesoporous and macroporous materials. The presence of niobium on the surface of samples doped by coating (denoted as PC) causes a decrease in the adsorption capability. This suggests that niobium fills the pores and hence decreases the adsorption volume.

Figure 3 shows DSC curves, which describe the phase transition peak at the Curie point for samples doped with 0.3mol% Nb by the two methods. For HS samples, only one peak was detected at 116ºC as anticipated. However, two peaks were detected for PC samples, a broad one at 112°C and another one at 121°C. This could be explained by the core-shell structure that is formed only in the PC samples. The Nb concentration at the shell is higher than the nominal concentration, while at the core it is lower than the nominal concentration. The Curie point is known to be a very sensitive probe for various changes in the bulk material; hence, the two different noticeable peaks suggest noticeable core-shell structure.

In order to investigate the sintering process, isothermal shrinkage measurements were performed using dilatometer. Figure 4 shows the shrinkage–temperature diagram of doped BT specimens prepared by the two different methods. For samples doped by chloride mixing, appreciable shrinkage begins at 850ºC. For samples doped by coating, the thermal shrinkage begins much later, at 1100ºC due to the presence of niobium atoms on the surface of the BT grains that hinder the sintering process. The maximum temperature of 1100°C was chosen to prevent lamination of the samples to alumina parts of the dilatometer.

Figure 5 shows SEM micrographs of samples doped with 0.1mol% Nb, prepared by the two methods and sintered at 1300ºC for 5h in air. The differences in the grain growths between these samples are caused because of the different distributions of dopant atoms and of internal defects due to self-compensation, in the grains[8,9]. This is in accord with our observation that oxygen vacancies are crucial in the early stage of the sintering of nano-BT[10].

Figure 6 shows the depth profile concentrations measured by SIMS, of Nb, Ba and residual carbon in BT samples doped with 1mol% Nb and sintered at 1300°C. The concentration of Nb atoms is constant for HS samples. In the case of PC samples, the concentration at the surface is higher, and decreases until a constant value is obtained in a depth of approximately 50nm.

Capacitance as a function of temperature at two different frequencies: 1kHZ and 1MHZ, for samples doped with 3mol% Nb by coating and by chloride mixing and sintered at 1300ºC for 5h were done. The addition of niobium by coating resulted at a flatter C(T) curve. The capacitance temperature dependence of the PC sample with 3mol% Nb meets the X7R specifications. For HS samples, larger temperature dependences were detected.

Figure 7 shows TEM micrographs for samples sintered at 1300ºC for 5h (a) HS and (b) PC. The difference in the microstructures for samples with the same dopant concentration prepared by the two different methods is observed; in (b) the core shell structure can be seen.

Electrical measurements were obtained by impedance analyzer and lockin-amplifier at different frequencies and temperatures[11]. The analysis of these impedance spectroscopy measurements is done by a novel technique that retrieves the time constant distribution function, developed in our lab[12,13]. Figure 8 shows the distributions of the time constant for (a) HS and (b) PC samples at two different temperatures, 300ºC and 350ºC, where the wider the peak the less homogenous the structure. For samples doped by chloride mixing the peaks are narrower and their position is more sensitive to temperature changes; on the other hand, the distributions of the time constants for samples doped by coating are wider and less sensitive to temperature, hence better for MLCC application.

4. Summary and Conclusions

In this work, the microstructural development and electrical properties of Nb-doped BT ceramics was analyzed, focusing on the effects of the doping method on the properties. Beyond a critical concentration, niobium inhibits the grain growth of BT. Different microstructures were observed in samples that have the same nominal dopant concentration but are prepared by different methods, and for those doped by coating, a core shell structure was obtained. DSC detected two T_C peaks for samples doped by coating when the Curie point at lower temperature referred to the shell and the other peak referred to the core. Electrical measurements show more distributed time constant and less sensitivity for temperature changes in samples doped by coating which have the core shell structure. Samples doped by chloride mixing have a narrower time constant distribution and more temperature dependence. It is shown that the incorporation method greatly influences the properties of the sintered samples, suggesting strong kinetic effects.

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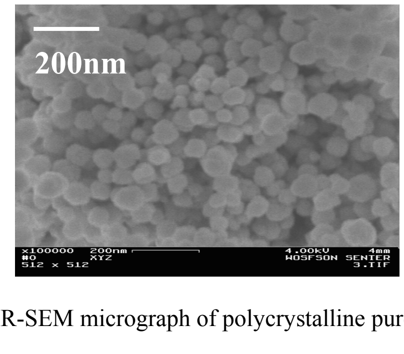

Figure 1. HR-SEM micrograph of polycrystalline pure $BaTiO_3$ powder.

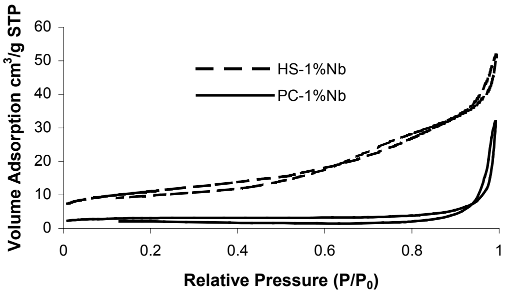

Figure 2. Nitrogen Adsorption isotherms of barium titanate doped with 1%Nb.

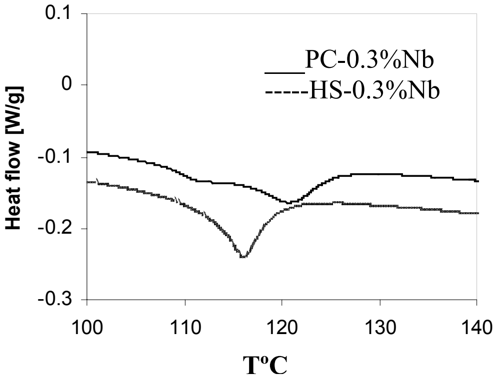

Figure 3. DSC curves for samples doped with 0.3% Nb sintered at 1300ºC.

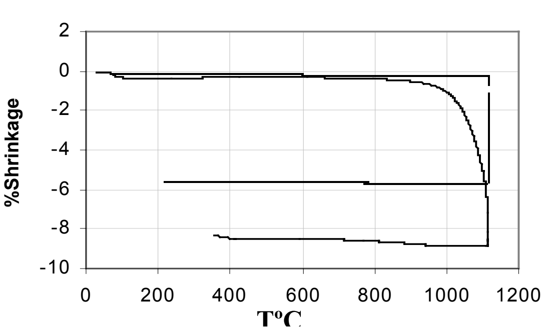

Figure 4. Shrinkage behavior of samples doped with 0.1%Nb heated to 1100ºC.

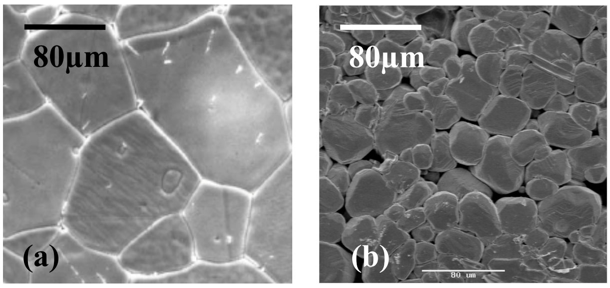

Figure 5. SEM micrographs of samples doped with 0.1%Nb after sintering at 1300ºC for 5h in air (a) prepared by chloride mixing (b) prepared by coating.

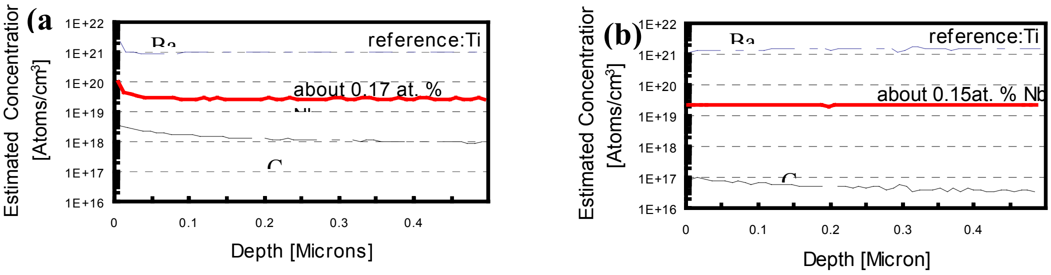

Figure 6. SIMS curves the estimated concentration of Nb as a function of the depth in (a) samples doped by coating (b) samples doped by chloride mixing.

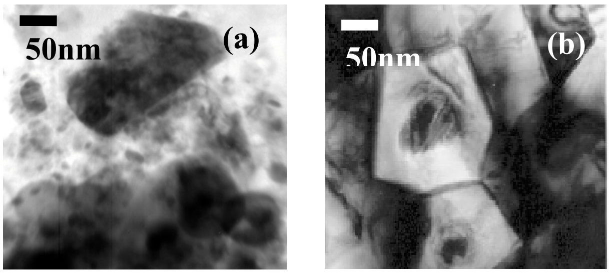

Figure 7. TEM images for samples doped with 0.3%Nb by two methods sintered at 1300ºC for 5h in air (a) chloride mixing (b) coating.

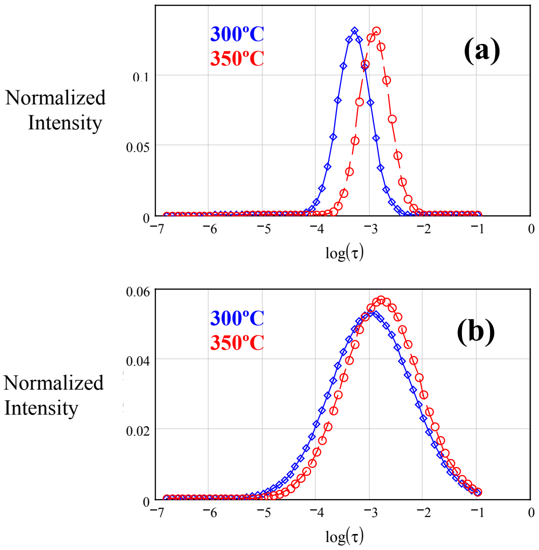

Figure 8. Distribution of time constants for samples doped with 0.3mol% Nb (a) chloride mixing (b) coating, in two different temperatures.

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