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Study of Nb–Zn co-doped Ba(Ti,Zr)O_3 ceramics

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The surface coating processing technique was used to modify hydrothermally synthesized-Ba(Ti,Zr)O_3 (BTZ) with an Nb-organic compound and Zn-organic compound in an organometallic precursor (Nb-EDTA and Zn-EDTA), which were coated on the powders uniformly. The sintering temperature was decreased and dense ceramics were obtained with well-developed grain growth at 1300 °C. Both increasing the amount of Nb–Zn and decreasing the Nb/Zn ratio greatly promoted grain growth. On increasing the Nb/Zn ratio, the Curie point temperature was markedly lowered, accompanied by a large decrease in the corresponding dielectric maximum and a simultaneous enhancement of the ferroelectric relaxor characteristic. At Nb/Zn = 2, the Curie temperature was monotonously lowered with increasing Nb–Zn content. The shift rate of the phase transition point of Nb–Zn co-doped BTZ was 6.5 °C/mol %. The corresponding dielectric maximum was enhanced rapidly from 9020 for a 0.35 mol % Nb–Zn doped sample to more than 12000 for a 0.90 mol % Nb–Zn doped sample.

Key words: *barium titanate zirconium; Nb–Zn co-doped; microstructure; dielectric property*

1. Introduction

Barium titanate zirconium Ba($Ti_{1-x}Zr_x$)O_3 (BTZ) ceramics, based on a solid solution of $BaZrO_3$ and $BaTiO_3$, have been widely studied and adapted to meet the Y5V and Z5U specifications of multilayer ceramic capacitors, owing to their very high and broad relative permittivity maximum at the ferroelectric Curie point [1, 2]. Owing to the solid-state reaction during sintering, the sintering temperature of BTZ ceramics is always above 1350 °C [3]. Therefore, it is of great importance to select a proper technique and additives in order to acquire high-performance ceramics based on BTZ.

Aliovalent cations incorporated in the perovskite lattice serve as donors or acceptors, capable of greatly affecting electrical characteristics even though their solubilities remain on a trace level [4–7]. The distribution of these additives in the starting

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powder is usually realized by milling but achieving a uniform distribution of the additives by this method is difficult, particularly if the main component is a submicrometer powder. It has been anticipated that this problem can be solved by coating the surface of the powder with appropriate additives using a chemical method [8]. In general, chemically prepared powders have high purity submicrometer particle sizes, and much better compositional uniformity than those made with the traditional method of mixing solid constituents followed by calcination [9].

In this paper, a surface coating processing technique was used to modify hydrotherrmally synthesized $Ba(Ti,Zr)O_3$ with an Nb-organic compound and Zn-organic compound in an organometallic precursor (Nb-EDTA and Zn-EDTA), used as the donor and acceptor dopants, respectively. Nb^{5+}-donors were compensated by Zn^{2+} -acceptors on Ti sites and the complex $[Nb_{2/3}Zn_{1/3}]^{4+}$ was substituted for Ti^{4+}. The effect of co-doped Nb–Zn on the microstructure and dielectric properties of BTZ ceramic was then investigated and the possible mechanism discussed.

2. Experimental

The main starting material was commercial $Ba(Ti_{0.90}Zr_{0.10})O_3$ (GuoTeng Co., Ltd.), synthesized by the hydrothermal method. All reagents used were of reagent grade and used directly without any further purification. Homogeneous and stable Nb–Zn metal -organic compounds were prepared in aqueous solutions by a complex route, with their soluble inorganic compounds as metal ionic sources and EDTA as the complex chelate agent.

The typical experimental procedure can be described as follows. According to the required concentrations of Nb–Zn, precisely measured amounts of the metal-organic compounds were added and adjusted so that the concentration of BTZ in solution was 10 wt. % and the amount of Nb–Zn was 0–0.90 mol %. pH of the solution was then adjusted to about 10 using 1 mol/dm^3 NH_4OH. The BTZ powders were added into the aqueous solutions of the metal-organic compounds, and ultrasonically dispersed for 15–20 minutes. The gelation time was longer than 2 h. During the sol-gel process, electromagnetic stirring was used. The sol temperature was kept at 80 °C. After coating, the slurry was dried in a vacuum oven at 50 °C for 24 h. The modified powders were cold-pressed uniaxially into disks 10 mm in diameter and 1 mm thick under 3 MPa and sintered at 1260–1300 °C for 1 h in air and cooled in the furnace. Then, disk samples were electroded by applying silver paste on opposing surfaces and fired at 750 °C.

The density of the sintered compacts was measured by the Archimedes method with water as the liquid medium. Electric permittivity as a function of the temperature of the sintered disks was measured using an automatic measurement system with an LCR (HP4291A) at 1 kHz. The phase compositions were characterized by powder X-ray diffraction (XRD), using a Rigaku X-ray diffractometer equipped with CuK_α radiation (λ = 1.5418 Å). Microstructures of fracture surfaces were observed by a scanning electron microscope (SEM), JSM-6301F.

3. Results and discussion

Sintering behaviour. The densities of BTZ ceramic samples doped with various amounts of Nb–Zn are shown in Fig. 1. As observed, the densities of sintered samples became high at temperatures above 1260 °C. This indicates that the additives decrease the sintering temperature of the studied powder. Maximum density was achieved at 1300 °C, and at sintering temperatures above 1320 °C the densities of all samples decreased. This decrease has been attributed to the increased intragranular porosity resulting from discontinuous grain growth [10]. It is obvious that the densification of BTZ ceramics is improved by increasing the amount of Nb–Zn and by decreasing the Nb/Zn ratio. Therefore, it can be concluded that the densification of BTZ ceramics is greatly affected by Nb–Zn co-doping.

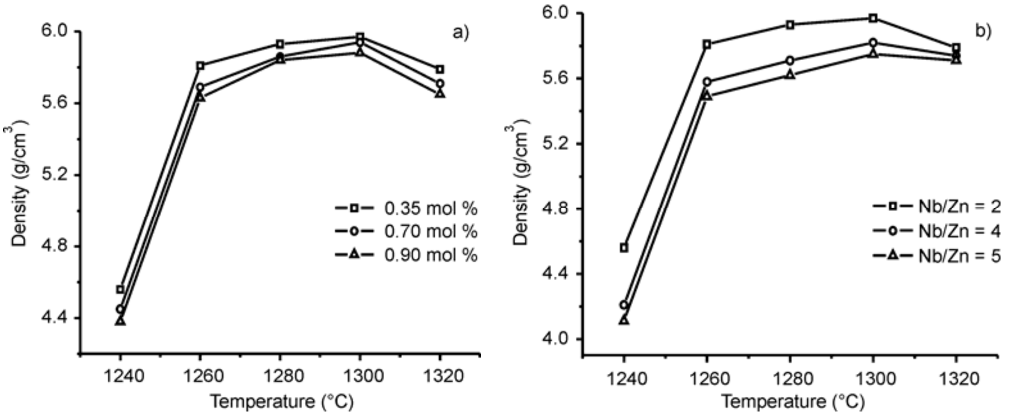

Fig. 1. The influence of sintering temperatures on the densities of BTZ ceramic samples doped with various: a) Nb–Zn amounts, b) Nb/Zn ratios

Phase identification. Figure 2 shows X-ray diffraction patterns of the disk surface fired at 1300 °C for 1 h. BTZ solid solutions were formed after sintering and there existed no secondary phase in the XRD of the solution. This indicates that Nb and Zn ions were dissolved in BTZ. The crystal structure of BTZ solid solutions was pseudocubic for all samples. Lower-angle (200) and (002) diffraction lines separated each other on the tetragonal system merged in this system (see the insert of Fig. 2a). We interpreted these results as the substitution reactions of $[Nb_{2/3}Zn_{1/3}]^{4+}$ for Ti-site cations, leading to the distortion of the perovskite lattice. The interstices between oxygen octahedra diminished with increasing barium vacancies, and the *c*/*a* ratio was lowered as well [5].

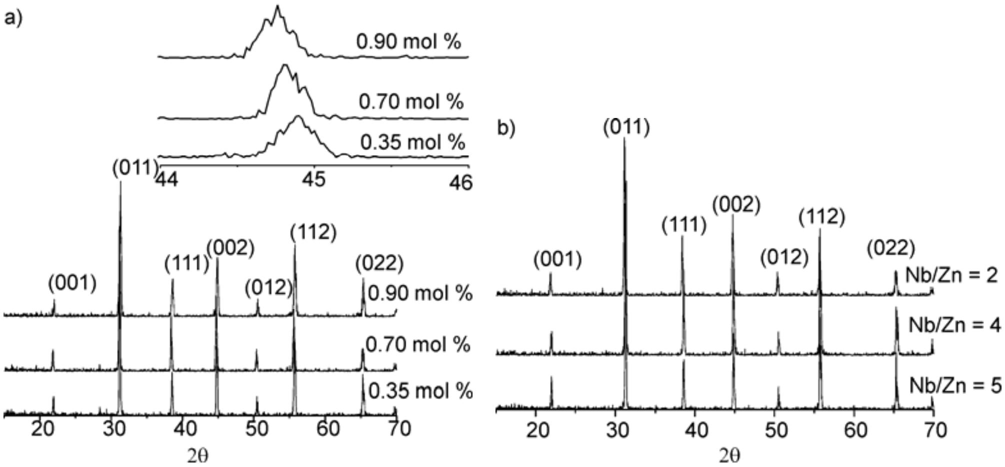

Fig. 2. XRD patterns of BTZ ceramics doped with various:
a)Nb–Zn amounts, b) Nb/Zn ratios, sintered at 1300 °C for 1 h

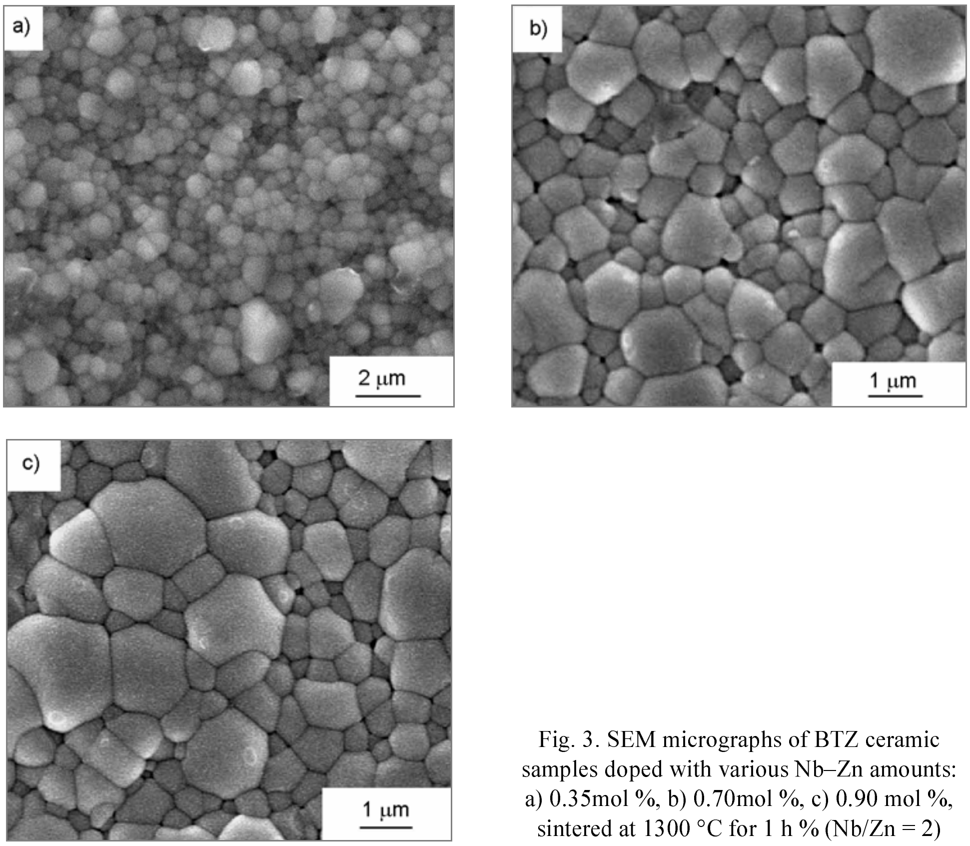

Fig. 3. SEM micrographs of BTZ ceramic samples doped with various Nb–Zn amounts: a) 0.35mol %, b) 0.70mol %, c) 0.90 mol %, sintered at 1300 °C for 1 h % (Nb/Zn = 2)

Microstructure. Figure 3 shows the microstructure of samples with various compositions sintered at the same conditions (1300 °C/h). It can be seen that the grain size was decisively affected by the dopant content. Both an increasing amount of Nb–Zn and decreasing Nb/Zn ratio greatly promoted grain growth. The grain size changed from 0.7 μm for the sample with Nb/Zn = 2 to about 0.5 μm for the sample with Nb/Zn = 5. When Nb/Zn is equal to 2, the grain size changed from 0.4 μm for the 0.35 mol % Nb–Zn doped sample to about 1.2 μm for the 0.90 mol % Nb–Zn-doped sample. These alterations demonstrate that appropriate amount of Nb–Zn additive and Nb–Zn ratio can improve the microstructure of BTZ ceramics.

The substitution of $[Nb_{2/3}Zn_{1/3}]^{4+}$ complexes for Ti sites in the perovskite lattice seems to account for the influence of the stoichiometry (Nb/Zn ratio). When Nb/Zn is above 2, the positively charged donor centre can be compensated by the cation vacancies of Ba ions [11]. At this point, mass transport was reduced and grain growth was also greatly restrained. In addition, excess Nb ions possibly segregate on the grain boundary and restrained grain growth. When Nb/Zn is equal to 2, however, both Nb^{5+} and Zn^{2+} not only serve as modifying aids, but also as sintering aids that contribute to mass transport and grain growth.

Dielectric properties. The temperature dependence of the relative electric permittivity for Nb–Zn co-doped BTZ ceramics sintered at 1300 °C/h is illustrated in Fig. 4. It is clear that both the Nb/Zn ratio and amount of Nb–Zn have a large influence on dielectric properties. With increasing Nb/Zn ratio, the Curie point temperature is lowered from 68 °C for the sample with Nb/Zn, from 2 °C to 42 °C for the sample with Nb/Zn = 5, accompanied by a large decrease in the corresponding dielectric maximum and an enhancement of the ferroelectric relaxor characteristic. At Nb/Zn = 2, the obvious phase transition point shifts towards lower temperatures with increasing Nb–Zn amount.

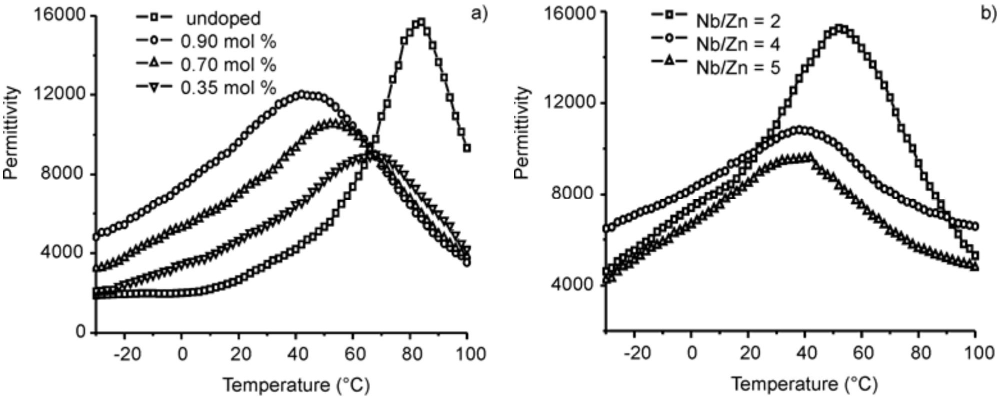

Fig. 4. Temperature dependence of electric permittivity for BTZ ceramic samples doped with various: a) Nb–Zn amounts, b) Nb/Zn ratios, sintered at 1300 °C for 1 h

It can be seen that increasing the amount of Nb–Zn from 0 to 0.9 mol % lowers the Curie temperature monotonously from 85 °C to 42 °C. The shift rate of the phase transition point of Nb–Zn co-doped BTZ was –46.5 °C/mol % (Fig. 5). The corresponding dielectric maximum, however, was enhanced rapidly from 9020 for the 0.35 mol % Nb–Zn doped sample to more than 12 000 for the 0.90 mol % Nb–Zn doped sample.

The sintering temperature had little effect on the Curie temperature for certain amounts of Nb–Zn doped BTZ ceramics, while it can influence the dielectric constant maximum to a considerable extent. It appeared that the samples sintered at 1300 °C had the highest dielectric constant and the ones sintered at 1260 °C had the lowest dielectric constant in the mass. The dielectric losses of all samples were less than 1.0 %, and resistivities were about $10^{11}\Omega\cdot$cm.

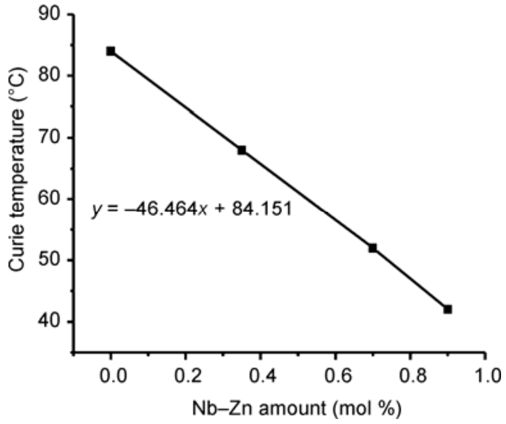

Fig. 5. The Nb–Zn amount dependence of the Curie temperature for BTZ ceramics

The influence of the Nb–Zn co-doping on the dielectric properties of BTZ ceramics was first attributed to the promotion effect of the dopants on the sintering of the ceramics. When doped with a proper Nb–Zn content, fully densified ceramics can be obtained with well-developed grain growth, which was helpful for the improvement of the dielectric properties of BTZ ceramics. Secondly, the substitution reactions of $[Nb_{2/3}Zn_{1/3}]^{4+}$ for Ti-site cations lead to the distortion of the perovskite lattice. The interstices between oxygen octahedra diminished with increasing barium vacancies, and the *c*/*a* ratio decreased as well. Therefore, the spontaneous polarization was depressed due to the restraint of B-site cations, and as a result the Curie point of the BTZ ceramics descends steeply. On the other hand, the distortion of the perovskite lattice can strengthen the structure fluctuations in the materials, which may account for the diffusion phase transition characteristics of doped BTZ ceramics.

4. Conclusions

The sintering behaviour, microstructure, and dielectric characteristics of Nb–Zn co-doped barium zirconium titanate ceramics were investigated. Sintering temperature was decreased by this technique and dense ceramics were obtained with well-developed grain growth at 1300 °C. Ba(Ti,Zr)O_3 solid solutions were formed after sintering, and no secondary phase was found in the XRD of the solution. Both increasing of the amount of Nb–Zn and decreasing the Nb/Zn ratio seriously promoted grain growth. The influence of dopants on the sintering characteristics of BTZ ceramics was attributed to the substitution tendency of $[Nb_{2/3}Zn_{1/3}]^{4+}$ for Ti-site cations in the perovskite lattices. With increasing Nb/Zn ratio, the Curie temperature decreased significantly, accompanied by a large decrease in the corresponding dielectric maximum and an enhancement of the ferroelectric relaxor characteristic. At Nb/Zn = 2, the Curie temperature monotonously decreased with increasing Nb–Zn content. The shift rate of the phase transition point of Nb–Zn co-doped BTZ was 6.5 °C/mol %. The corresponding dielectric maximum was enhanced rapidly from 9020 for the 0.35 mol % Nb–Zn doped sample to more than 12 000 for the 0.90 mol % Nb–Zn doped sample.

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