The effect of doping process on microstructure and dielectric properties of BaTiO$_3$-based X7R materials

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The effect of doping process on the dielectric properties, sintering behavior and microstructure were investigated on the BaTiO$_3$-Nb$_2$O$_5$-Co$_3$O$_4$ ternary system ceramic. Temperature stable dielectric ceramics were obtained by different doping processes if only appropriate Nb$^{5+}$ + Co$^{3+}$ amount and Nb$^{5+}$/Co$^{3+}$ ratio were adopted. The dielectric constant was enhanced to the largest extent by nanometer oxide doping and the temperature characteristic satisfied the X7R specification. Two kinds of grains were observed in all the samples: matrix grains (BaTiO$_3$) and the secondary phase grains (Ba$_6$Ti$_{17}$O$_{40}$) formed by the incorporation of Nb$^{5+}$ and Co$^{3+}$ into BaTiO$_3$ lattice and Ti$^{4+}$ segregation. The matrix grains were about 1 µm in diameter and showed little grain growth with increasing temperature in all the doped samples, whereas the sizes of the secondary phase grains were strongly dependent on the doping process. The secondary phase formed liquid phase during firing, but the liquid phase contributed little to the densification of ceramics.

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1. Introduction
Barium titanate (BT) is a well-known material for capacitors. Recently, BaTiO$_3$-based X7R dielectric materials have attracted much attention due to their high permittivity, stable temperature characteristic (TC) of the dielectric constant and non-polluting effect on the environment. Many kinds of additives, such as ZrO$_2$ [1], CdBi$_2$Nb$_2$O$_6$ [2], Nb$_2$O$_5$, Co$_3$O$_4$ [3–6], Sm$_2$O$_3$ [7], CeO$_2$ [8], have been used to make the dielectric temperature characteristic flat. Microstructure observed in these materials with flat TC can be characterized by small grains and chemical inhomogeneity that is called the “core-shell” microstructure with concentration gradients of additives in grain shell. Currently, BaTiO$_3$–Nb$_2$O$_5$–Co$_3$O$_4$ (BT–Nb–Co) ternary system materials are preferentially used for commercial X7R multilayer ceramic capacitor (MLCC) because the high permittivity and stable dielectric TC are easily obtained in this system. Many researchers have investigated the formation mechanism of the “core-shell” microstructure formed in the doped BaTiO$_3$ system [3–9]. Hennings and Rosenstein [2] brought forward a dissolution–precipitation mechanism to interpret the formation mechanism of the “core-shell” microstructure in bismuth-doped BT system. Also, Randal et al. [9] pointed out that the “core-shell” microstructure in BT-LiF ceramic was formed by dissolution–precipitation mechanism. However, Chazono and Kishi [4,5] reported that large amount of Nb$^{5+}$ + Co$^{3+}$ and large Nb$^{5+}$/Co$^{3+}$ ratio were favorable to yield flat TC in BT–Nb–Co system, and they further concluded that the refractory compound Ba(Co$_{1/3}$Nb$_{2/3}$)O$_3$ produced in the firing process was responsible for the formation of the “core-shell” microstructure.

In this study, we investigated the effect of doping process on the dielectric properties, sintering behavior and microstructure of BT–Nb–Co ternary system ceramics.

2. Experimental procedure
2.1. Preparation of samples
Barium titanate powder was synthesized by oxalate coprecipitation method and calcined at 1150°C for 2 h. The obtained powder had an average particle size of 0.5 µm in diameter and purity of 99.5%. In our work, we adopted three kinds of doping methods: submicrometer oxides doping, solution doping and nanometer oxides doping. Accordingly, the doped samples were abbreviated to Comp. A, Comp. B and Comp. C, respectively.

For Comp. A, reagent grade Nb$_2$O$_5$ and Co$_3$O$_4$ powders (SUDU Nano. Tech. Co., Chengdu, China), with particle sizes of ~ 0.3 µm and purity of 99.9%, were added to BaTiO$_3$.

For Comp. B, niobium oxide hydrogen peroxide and cobalt nitrate solutions were prepared and added to BaTiO$_3$ that was premilled for 6 h. The slurries were stirred uniform and dried as quickly as possible in order to decrease solution delaminating. Then the mixtures
were calcined at 500°C to decompose niobium oxalate and cobalt nitrate to corresponding oxides.

For Comp. C, niobium ethoxide ethyl glycol solution needed to be prepared first. Then homogeneous sol could be obtained by adding cobalt nitrate solution to niobium ethoxide and then changed to gel when heated at 60°C. Nb2O5-Co3O4 composite oxide was synthesized by calcining the dry gel at 500°C for 1 h. The average particle size of Nb2O5-Co3O4 composite oxide was about 70 nm in diameter observed by transmission electron microscopy (TEM). Then the Nb2O5-Co3O4 composite oxide was added to BaTiO3.

In Comp. A–C, the same Nb5+/Co3+ amount of 2.8 at % and Nb5+/Co3+ ratio of 3 were adopted. Both Comp. A and C was ball milled in deionized water for 6 h, and then dried and screened. Finally, all mixed powders were pressed into discs of 10 mm diameter and 1 mm thickness, then disks were sintered at 1280–1340°C for 2 h at a heating rate of 200°C/h.

2.2. Measurement
X-ray diffraction (XRD) analyses were carried out for phase identification using a Rigaku diffractometer over the 20 range of 20–70°. Microstructures of the sintered samples were investigated using a Hitachi S-530 scanning electron microscope (SEM). After samples were fired at 700°C with silver paste on both sides, the dielectric properties were measured at 1 kHz with an LCR meter (HP 4192A) at temperatures ranging from –25 to 130°C.

3. Results and discussion
3.1. Dielectric properties
Fig. 1(a) compares the temperature dependence of dielectric constant of Comp. A–C sintered at 1280°C with 2 h soak. It was obvious that the overall dielectric constant of Comp. B and C could be enhanced greatly. The room temperature dielectric constant increased more than 500 by nanometer oxides doping than by submicrometer oxides doping. However, as shown in Fig. 1(b), Comp. B and C exhibited a little larger variation rate of capacitance than Comp. A, which could be calculated by the formula of (C – C25°C)/C25°C over the measuring temperature.

3.2. Sintering behavior
Fig. 2(a)–(c) show the influence of firing temperature on the TC of Comp. A–C. The firing temperature had different effects on the shape of TC curves for all the samples. Variation rate of capacitance of Comp. A did not exceed X7R specification even Comp. A was sintered at 1340°C. However, over high firing temperature resulted in large variation rate of capacitance for Comp. B and C. The dielectric constant peak located at about 40°C in all the cases. As shown in Fig. 2(a) and (c), when firing temperature increased, the dielectric constant of Comp. A and C first increased and then declined when firing temperature was as high as 1340 or 1320°C. However, as shown in Fig. 2(b), the dielectric constant peak of Comp. B was continuously heightened when firing temperature increased. The experiment proved that different doping processes could produce temperature stable dielectric ceramics, if only appropriate Nb5+/Co3+ amounts, Nb5+/Co3+ ratio and firing temperature were adopted. Moreover, it was favorable by nanometer oxides doping to make the system hold high dielectric constant and still satisfy the requirement of EIA X7R specification. It has been noticed that the formation of microstructure depended on the doping process, as well as Nb5+/Co3+ ratio [4]. Thus, it was necessary to investigate the differences of microstructure among the samples.

3.3. Microstructure
Fig. 3 shows the sketch map of microstructures of Comp. A and C. It was reasonable to suggest that the dopants with submicrometer size could not homodisperse in BaTiO3 powder with comparative particle size so that the quantity of grains that composed of grain core and grain shell was limited. On the contrary, large quantities of grains formed chemically inhomogeneous ‘core-shell’ microstructure resulted from the uniform distribution of nanometer dopants in BaTiO3 grain boundaries. Therefore, it could be inferred that the average thickness of grain-shell in Comp. C was smaller than that in