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Influence of donor Nd and sintering conditions on dielectric property of $BaTiO_3$-based ceramics

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ABSTRACT

A series of $Ba_{0.8}Sr_{0.2}Zr_{0.1}Ti_{0.9}{\cdot}xNd_2O_3$ solid solutions with average size of 50nm were synthesized by microwave method. XRD demonstrated that the compounds were mutually miscible in the solid solution. The dielectric constant in different sintering temperature was discussed. The result showed that the sample reached a high dielectric constant (about 140000) when the doping content of Nd_2O_3 was 0.2%and the sintering temperature was 1240^0C. The effect of sintering to microstructure was studied by means of SEM, and the mechanism was also discussed.

KEYWORDS

Nano-$BaTiO_3$;
Preparation;
Dielectric property;
Sintering.

INTRODUCTION

The outstanding dielectric, ferroelectric and piezoelectric properties of $BaTiO_3$ make it the desirable primary materials for a variety of applications including multiplayer capacitors, thermistors and electro optic devices[1]. But $BaTiO_3$ has the highest dielectric constant (~10^4) at the Curie temperature (120^0C), while at room temperature the dielectric constant decreases to 2000~3000, and the dielectric loss is very high, which greatly limits its applications. It is supposed theoretically the Curie point of $BaTiO_3$ may be lowered and broadened when the active ions Ti^{4+} are partially replaced by the inactive Sn^{4+} or Zr^{4+}[2]. But traditional solid-state adulterating is not only uneven, but also easily introduce some impurities into the product. So it can't meet the need of the modern electronic industries. In order

EXPERIMENTAL

Material and apparatus

$TiCl_4$, $Sr(OH)_2{\cdot}8H_2O$, $Ba(OH)_2{\cdot}8H_2O$, $ZrOCl_2{\cdot}8H_2O$ and $NdCl_5$ are analytical reagents. All experiments were carried out in the double-distilled water.

Y-2000 X-ray Diffractometer (Dandong), JEM-100SX Transmission Electrical Microscope (Japan), KYKY-2800B Scanning Electron Microscope (USA), 769YP-24Z Table Oil Press (Tianjin), Automatic LCR Meter and Reactor (Britain), SRJX-4-13 Automatic Controlling Temperature Stove (Tianjin), Whirlpool (USA) etc.

Synthesis of $Ba_{0.8}Sr_{0.2}Zr_{0.1}Ti_{0.9}O_3{\cdot}xNd_2O_3$ solid solutions

By the method in refs.[3,4], a stoichiometrical amount of $ZrOCl_2{\cdot}8H_2O$ and $NdCl_5$ were dissolved in 100 ml water, a suitable amount of $TiCl_4$ solution was slowly added into the above solution. The PH value of the solution was adjusted to 7 by using $NH_3 \cdot H_2O$, Then reacted with the alkaline solution of $Sr(OH)_2$ and Ba $(OH)_2$ quantitatively in the whirlpool for 25 minutes. The solid solution powder of $Ba_{0.8}Sr_{0.2}Zr_{0.1}Ti_{0.9}O_3 \cdot xNd_2O_3$ (the values of x are 0.00075, 0.001, 0.0015, 0.002, 0.0025, 0.003 respectively) was obtained after filtering, washing and drying for 24h at100^0C.

Preparation of ceramics

The sample was mixed with suitable amount of adhesive (8% PVA aqueous solution) and ground evenly. The resulting powder was pressed into a disc at a pressure of 6~8Mpa. The disc was heating at 800^0C to remove the binder, then sintered at 1180^0C~1270^0C. Its electric capacity value (C) and dielectric loss (tanδ) were measured by the Automatic LCR Meter at room temperature(1KHz). Then the dielectric constants were calculated.

RESULTS AND DISCUSSION

XRD analysis

As shown in figure 1, the doped $BaTiO_3$ solid solution powder had the same XRD pattern as pure $BaTi0_3$ phase and both of them belonged to the cubic system. The peaks shifted a little owing to the mixing effect of the doping additives.

TEM analysis

TEM showed that the solid solution particles were substantially spherical with the average size of 50nm in diameter.

The relationship between component and dielectric property

The dependences of dielectric constant(ε) and composition of $Ba_{0.8}Sr_{0.2}Zr_{0.1}Ti_{0.9}O_3 \cdot xNd_2O_3$ solid solution are shown in figures 3. It can be seen from these figures that after the adulterated Nd evenly enters into the matrix lattice, which results in much higher dielectric constant at room temperature.

This was because Zr^{4+} was different with Ti^{4+}. Zr^{4+} did not change its chemical valence while Ti^{4+} was changeful at high temperature. In the powder of $Ba_{0.8}Sr_{0.2}Zr_{0.1}Ti_{0.9}O_3$, the electric bond of Ti-O was broken due to the Zr-doped, so it was hard to form

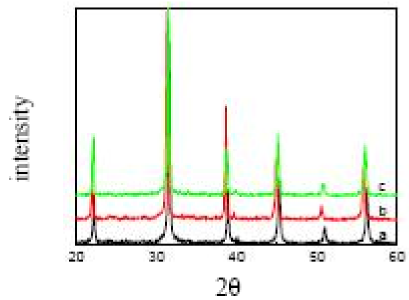


Figure 1: XRD pattern of the sample (a) $BaTiO_3$; (b) $Ba_{0.8}Sr_{0.2}Zr_{0.1}Ti_{0.9}O_3$; (c) $Ba_{0.8}Sr_{0.2}Zr_{0.1}Ti_{0.9}O_3 \cdot xNd_2O_3$

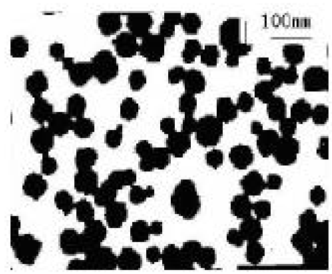


Figure 2 : TEM photograph of $Ba_{0.8}Sr_{0.2}Zr_{0.1}Ti_{0.9}O_3 \cdot 0.002Nd_2O_3$

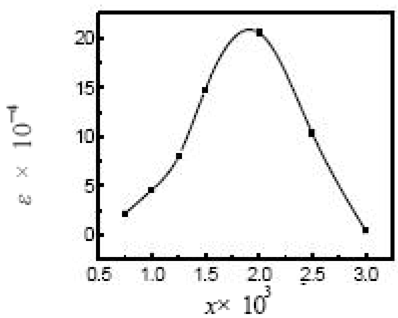


Figure 3 : Relationship betweenεand x of $Ba_{0.8}Sr_{0.2}Zr_{0.1}Ti_{0.9}O_3 \cdot xNd_2O_3$

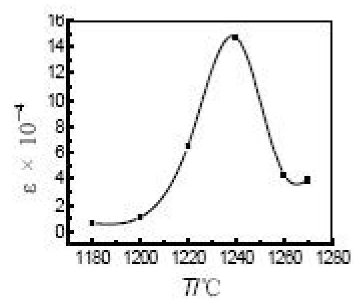
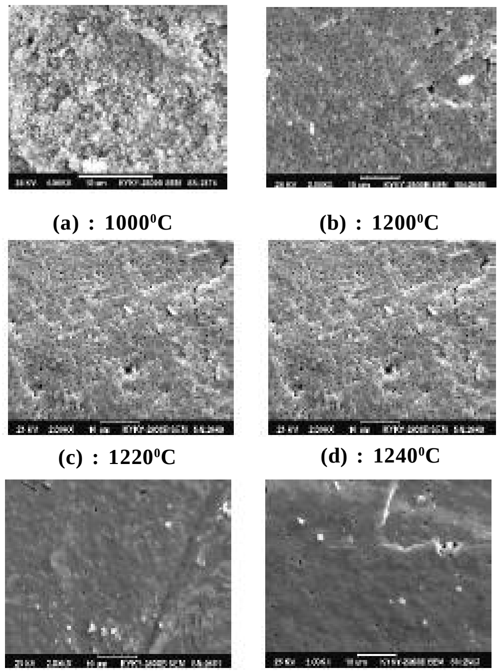


Figure 4 : Relationship betweenεand sintering temperature of $Ba_{0.8}Sr_{0.2}Zr_{0.1}Ti_{0.9}O_3 \cdot 0.002Nd_2O_3$



(a) : 1000^0C (b) : 1200^0C
(c) : 1220^0C (d) : 1240^0C
(e) : 1260^0C (f) : 1280^0C

Figure 5 : SEM photograph of the ceramics at different sintering temperature

conductance because the doped ion could only move among several atoms. Influenced by the spontaneous polarization, the localized atoms were far away from the balance position and polarized, the mixing effect made the ferroelectric composition increase, and improved the dielectric constant. Another reason was that Nd had a different chemical valence, a significant change could occur with little doping. When the adulterant of Nd_2O_3 was little, the concentration of the localized electrons increased with adulterant increasing, so did the dielectric constant. Vacancy compensation and lattice distortion would occur with adulterant increase, which led to the decrease of dielectric constant.

Effect of sintering temperature

A dense and fine grain microstructure was formed during the sintering process. Different sintering methods influenced the performance of the ceramic.

Sintering temperature was a very important and rigid factor in the process of sintering ceramics. The material performance would degrade if the sintering temperature was higher or lower than the optimum. Figure 4 showed the temperature dependence of dielectric constant of the sample.

It could be seen that the dielectric constant increased with temperature increasing, and reached the maximum (140000) at 1240^0C, whereas decreased as the temperature increased higher.

SEM micrographs of the ceramic at different sintering temperature were shown in Figure5. From the photos we could see that the particles and the pores changed a lot during the sintering process. There were always a great deal of pores in the ceramic disc, the contact among particles would augment gradually due to the surface tension from point to interface and form crystal boundary finally (Figure 5(a,b)). The liquid phase appeared with temperature increasing, whose surface tension gave pressure to the particle on the contact point. The distortion of the crystal lattice near the contact point led to the increase of solubility (Figure 5(c,d)). The secondary crystallization occurred with the excessive sintering, the crystal grew rapidly and some pores in the inner could not eject , which made the decrease of the dielectric constant (Figure 5 e,f).

CONCLUSIONS

1. A series of nano-$Ba_{0.8}Sr_{0.2}Zr_{0.1}Ti_{0.9}\cdot xNd_2O_3$ solid solutions were synthesized by microwave method. By controlling the reaction conditions, dispersed and uniform nanopowders were obtained with average size 50nm.The reaction time reduced to only 25 min.
2. After adulteration of appropriate amount of Sr^{2+},Zr^{4+} and Nd^{3+} in $BaTiO_3$ by chemical method, the adulterated ions entered into matrix lattice evenly. The dielectric constant of the material improved significantly, reaching to about 140000. This material could be used in miniaturized multilayer ceramic capacitor.
3. Sintering temperature had a great effect on the properties of the ceramic. It was found that the material could achieve a dense microstructure and a high dielectric constant at 1240^0C.

ACKNOWLEGMENTS

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thesized by normal pressure liquid-phase method, the dielectric constant can reach to about 15000[3]. To meet the request of miniaturization in microelectronic devices, a series of ceramic nanopowders with high dielectric constant were synthesized doped with Nd by microwave method.

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