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Journal of the European Ceramic Society 24 (2004) 1227–1231
www.elsevier.com/locate/jeurceramsoc

Positive temperature coefficient of resistivity effect in niobium-doped barium titanate ceramics obtained at low sintering temperature

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Abstract

A positive temperature coefficient of resistivity (PTCR) effect was observed for low temperature sintered Nb-doped $BaTiO_3$ ceramics using YB_6 as a sintering aid. A semiconducting $BaTiO_3$ with good PTCR property was obtained at a low sintering temperature of 1150 °C because of the addition of YB_6. Addition of 0.2 mol% Nb_2O_5 and 1 mol% of YB_6 led to a low room-temperature resistivity and a resistivity jump of about 10^4. Room-temperature resistivity of the ceramics was controlled by the grain boundary resistivity which was related to the added amount of YB_6 and the sintering temperature. YB_6 only worked as a sintering aid to enhance the densification of semiconducting $BaTiO_3$ ceramics at low sintering temperature.

Keywords: $BaTiO_3$; Electrical properties; Grain boundary; Sintering; Thermistor

1. Introduction

It is well known that barium titanate ceramics ($BaTiO_3$) is a very important ferroelectric material. Besides its excellent dielectric properties, it can also be an n-type semiconductor exhibiting a strong positive temperature coefficient of resistivity (PTCR).[1,2] Until now, they have been widely used in electronic industries as temperature detectors, self-controlled heating devices, switch-on over-voltage current limiters and so on because of their excellent and useful PTCR effect. However, the electrical features of semiconducting $BaTiO_3$ ceramics depend crucially on the microstructure and characteristics of grain boundaries which was influenced by the composition and processing.[3]

Normally, semiconducting $BaTiO_3$ ceramics can be prepared by the mixed oxide solid-state reaction route. SiO_2 or an eutectic mixture of $Al_2O_3{\cdot}SiO_2{\cdot}TiO_2$ (AST) is commonly added as a sintering aid to form a liquid phase at a relatively lower temperature during sintering so as to control the microstructural development and to improve the PTCR effect.[4–6] Without them, donor-doped $BaTiO_3$ ceramics generally have high room-temperature resistance or even become insulators. But the sintering temperature of semiconducting $BaTiO_3$ ceramics with SiO_2 or AST is still higher than 1200 °C. However, it is possible to lower the liquid formation temperature even more by using some other sintering aids.[7,8] If semiconducting $BaTiO_3$ ceramics can be prepared at temperature lower than 1200 °C, the fabrication of cofired multilayer PTCR ceramics would be facilitated by using nickel ohmic paste as the electrode. However, since the electrical properties of semiconducting $BaTiO_3$ are sensitive to the composition of additives, most of these sintering aids affect the PTCR behavior, or may even turn the n-doped $BaTiO_3$ into an insulator. Only very few sintering aids are effective in the liquid-phase sintering of semiconducting $BaTiO_3$ ceramics.[9]

In our previous report,[10] it was found that the PTCR effect can be observed at a low sintering temperature of 1100 °C by adding an appropriate amount of YB_6 to Nb-doped $BaTiO_3$. In this study, we further investigated the positive temperature coefficient of resistivity effect in Nb-doped $BaTiO_3$ ceramics prepared at low sintering temperatures. The effects of varying the sintering temperature and YB_6 amount on the electrical properties and microstructure of 0.2 mol% Nb_2O_5-doped $BaTiO_3$ ceramics were also reported.

2. Experimental

Samples were prepared by a conventional solid-state reaction technique. $BaTiO_3$ (99% pure, Acros Organics,

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0955-2219/03/$ - see front matter
doi:10.1016/S0955-2219(03)00379-0

Lot. No. A014369001), Nb_2O_5 (99.9% pure, Acros Organics) and YB_6 (Aldrich Chem. Co.) were used as the starting materials. No additional SiO_2 or AST sintering aids were added. The amount of materials used was based on the following formula: $BaTiO_3 + xNb_2O_5 + yYB_6$ ($x = 0.1$–0.4 mol%, $y = 0.6$–1.2 mol%). The powders were mixed in a nylon pot with alcohol and ZrO_2 as the milling media. After milling, the slurry was dried and PVA was added as a binder. The powder was pressed into disks of 10 mm diameter and 3mm thick under a uniaxial pressure of 80 MPa. Then they were sintered at temperature ranging from 1100 to 1200 °C for 1 h in air. The cooling rate was 10 °C/min to 1000 °C and then 3 °C to 900 °C after which the samples were cooled naturally in the furnace.

The densities of the sintered disks were measured using the Archimedes method. The microstructure was observed using a scanning electron microscope (SEM-Leica Stereoscan 440).

The sintered samples were electroded by rubbing In–Ga alloy on the surfaces. The electrical resistivity was measured as a function of temperature using a digital multi-meter in a temperature-programmable muffle oven at a heating rate of 2 °C/min. Complex impedance analysis was conducted in the frequency range of 5 Hz–13 MHz to obtain the resistivity of grains and grain boundaries using an HP-4194A impedance analyzer.

3. Results and discussion

It was found that the room-temperature resistivity ρ_v of low temperature sintered Nb-doped $BaTiO_3$ ceramics with 1.0 mol% YB_6 as sintering aid depends strongly on the amount of Nb_2O_5 donor. At about 0.2 mol% Nb_2O_5-doped amount, ρ_v has a minimum value of 193Ω·cm. The possible reasons for that resistivity increase with the amount of donor include vacancies of barium[11] or titanium,[12] and segregation of the donor[13] near the grain boundary. Y^{3+} can be a donor element if it enters the Ba site in the $BaTiO_3$ lattice. However, in this study, Y in YB_6 was found to exist in amorphous intergranuar phase between some grain boundaries and no diffusion of Y into $BaTiO_3$ grain was detected.[10] Furthermore, the lattice parameter ratio c/a is almost the same for the samples with different amounts of YB_6 added from X-ray measurement. Therefore, YB_6 functions in lowering the sintering temperature rather than acting as a donor in the test. Only Nb_2O_5 works as a donor dopant in the composition. Nb^{5+} ion substitutes for Ti^{4+} ion in the $BaTiO_3$ lattice: $[Nb^{5+}] = [V_{Ti}'''''] + e$, where $[Nb^{5+}]$ and $[V_{Ti}''''']$ are the concentration of Nb ion and Ti ion vacancy.

Fig. 1 shows the density as a function of the sintering temperature for 0.2 mol% Nb_2O_5-doped $BaTiO_3$ with 0.8, 1.0 and 1.2 mol% of YB_6. The densification rate at low firing temperature depends on the amount of YB_6 added. Addition of more YB_6 leads to a faster increase in density. However all the samples have the close density when the sintering temperature reaches around 1080 °C. YB_6 promotes the densification process probably by reacting with $BaTiO_3$ to create a liquid phase at relatively low temperature during sintering.[10]

The influence of the amount of YB_6 and sintering temperature on the room-temperature resistivity ρ_v of 0.2 mol% Nb_2O_5-doped $BaTiO_3$ ceramicsis illustrated in Fig. 2. It can be seen that ρ_v decreases with increasing sintering temperature before reaching saturation. At higher sintering temperature, less amount of YB_6 is required to gain low room-temperature resistivity. In contrast, at lower sintering temperature, increase in the amount of YB_6 is necessary to obtain similar ρ_v. The microstructures of the samples with 1 mol% YB_6 sintered at different temperatures are shown in Fig. 3.

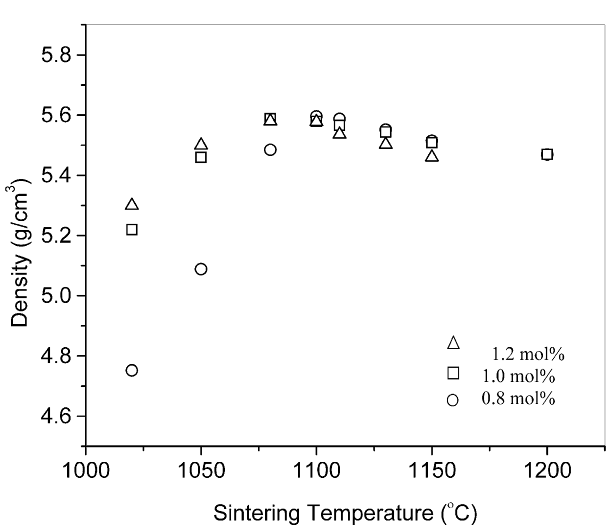

Fig. 1. Density as a function of sintering temperature for 0.2 mol% Nb-doped $BaTiO_3$ ceramics with different amounts of YB_6.

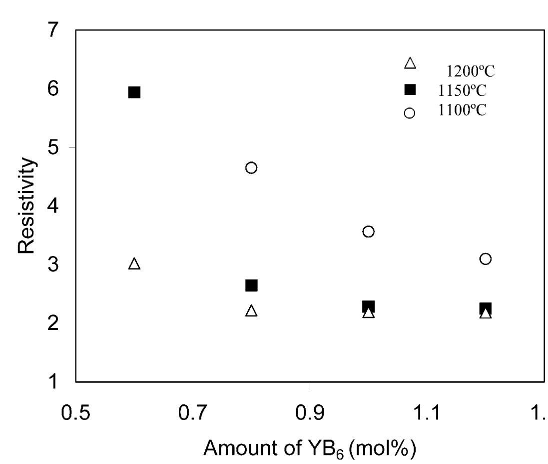

Fig. 2. Room-temperature resistivity as a function of amount of YB_6 for 0.2 mol% Nb-doped $BaTiO_3$ ceramics sintered at different temperature.

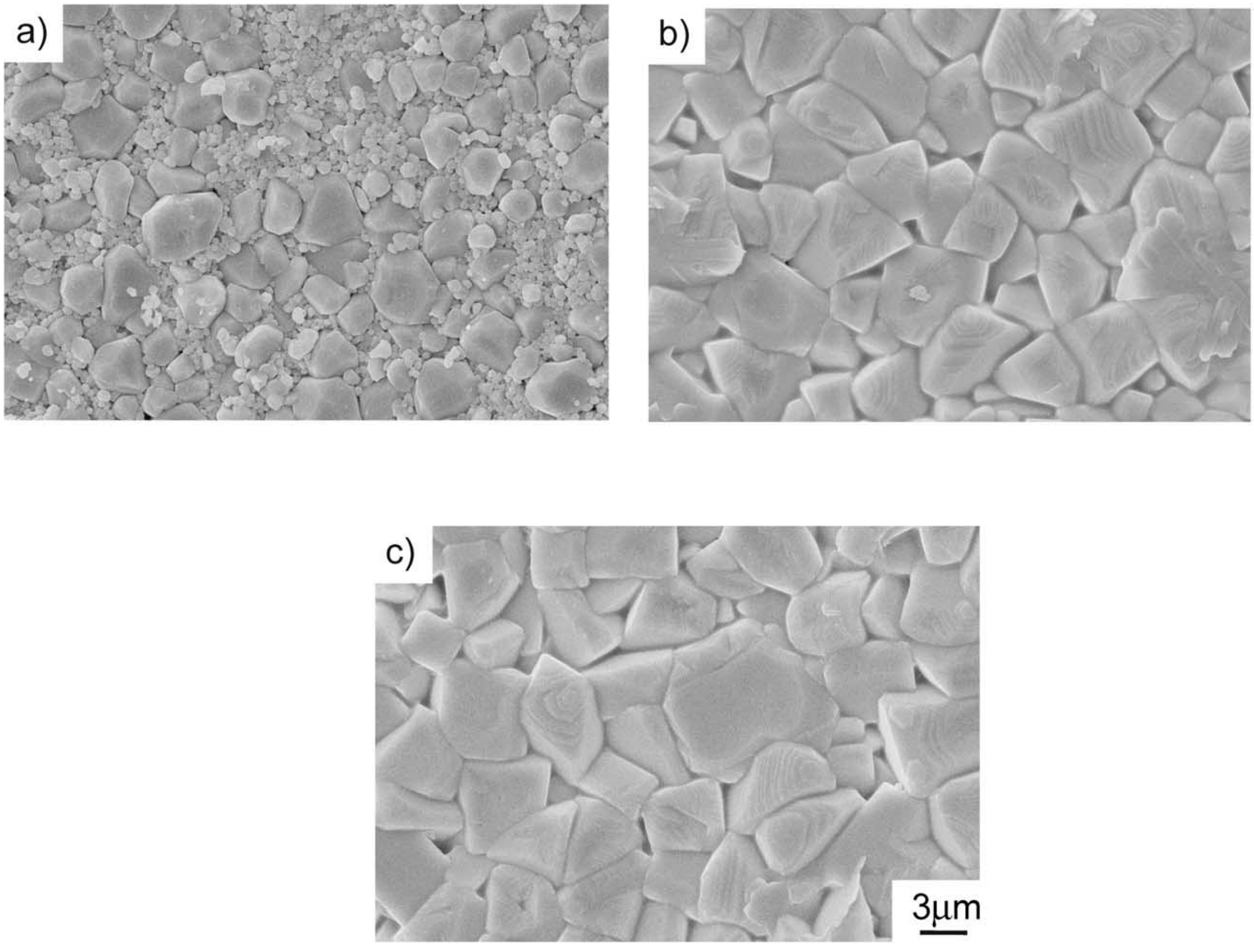

Fig. 3. SEM micrographs of 0.2 mol% Nb-doped $BaTiO_3$ ceramics with 1 mol% YB_6 sintered at (a) 1100 °C, (b) 1150 °C and (c) 1200 °C for 1 h.

When the sintering temperature is 1100 °C, there are many fine grains in the samples (Fig. 3a) although the sample is well densified (Fig. 1) and hence suppression of anomalous grain growth and a large number of grain boundaries. This may be the cause of the high room-temperature resistivity. When the sintering temperature is augmented to 1150 °C, the uniform grain growth is enhanced so that a significant reduction in room-temperature reisistivty can be seen. But the further increase in the sintering temperature only leads to a slight change in microstructure and the room-temperature resistivity becomes steady. Therefore, the influence of YB_6 addition on room-temperature resistivity is related to its effects on the microstructure. In the presence of YB_6, the sintering process can be a liquid-phase sintering in terms of dissolution and precipitation of materials. The formation of microstructure depends strongly on the amount of liquid phase. Increase in YB_6 amount and sintering temperature is favorable for generation of more liquid phase facilitating uniform microstructural

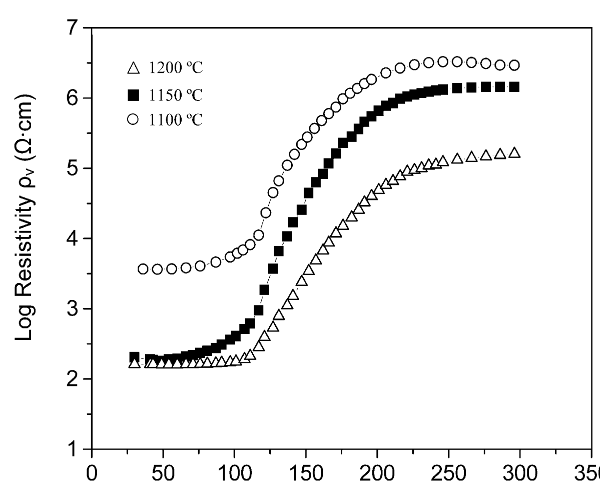

Fig. 4. Temperature dependence of resistivity of 0.2 mol% Nb-doped $BaTiO_3$ ceramics containing 1 mol%YB_6 sintered at different temperature.

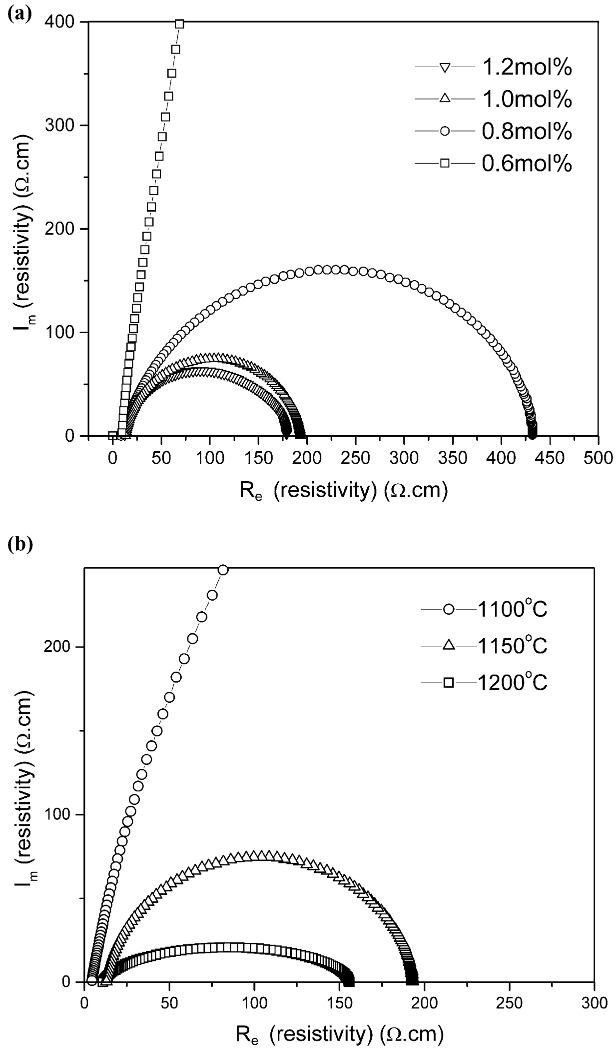

Fig. 5. Impedance analysis at room temperature of 0.2 mol% Nb-doped $BaTiO_3$ ceramics (a) with different amount of YB_6 sintered at 1150 °C for 1 h and (b) containing 1 mol% YB_6 sintered at different temperature for 1 h.

development, which results in a low room-temperature resistivity.

Fig. 4 shows the temperature dependence of the resistivity ρ_v of 0.2 mol% Nb_2O_5-doped $BaTiO_3$ ceramics with 1 mol% YB_6 prepared at different sintering temperature for 1h. The samples obtained showed a blue color and were semiconducting, but the magnitude of the resistivity ρ_v jump changed with the sintering temperature. The highest jump about 10^4 in the ρ_v was observed in the samples sintered at 1150 °C. In addition, the change in sintering temperature nearly does not shift the temperature at which dramatic increase in ρ_v begins. However, the temperature of ρ_v maximum (T_m) for the samples sintered at different temperature is different. For the sample sintered at 1200 °C, T_m is higher than the other two samples.

Fig. 5 shows that the imaginary part of the resistivity vs the real part of the resistivity of the samples. In general, the resistance in donor-doped $BaTiO_3$ semiconducting ceramics is governed by the grain and grain boundary resistance which can be obtained from the intercept on the real axis in the resistivity spectra.[14,15] From Fig. 5a, with an increase in the amount of YB_6 added, the grain resistivity remains small, while the grain boundary resistivity decreases greatly. Fig. 5b also shows the dependence of the grain boundary resistivity on the sintering temperature. The sample sintered at 1100 °C shows the high grain boundary resistivity. When the sintering temperature increases, the obvious decrease in grain boundary resistivity is observed. As mentioned above, one can conclude that the decrease in the room-temperature resistivity with increasing amount of YB_6 and sintering temperature can be ascribed to a reduction in the grain boundary resistivity. The effect of YB_6 amountand sintering temperature on the room-temperature resistivity mainly concerns with their effect on the microstructure of the samples as well as the characteristics of the grain boundaries.

4. Conclusion

Semiconducting $BaTiO_3$ ceramics have been prepared at sintering temperature below 1200 °C in air. Addition of YB_6 led to a significant decrease in the sintering temperature. The amount of YB_6, Nb_2O_5 content and the sintering temperature affect the room-temperature resistivity, resistivity jump and microstructure of the samples. 0.2 mol% Nb_2O_5-doped $BaTiO_3$ ceramics containing 1 mol% YB_6 sintered at 1150 °C exhibits good PTCR properties. The dramatic increase in room-temperature resistivity of the samples obtained at different sintering temperature starts at the same temperature. Increasing YB_6 amount and sintering temperature almost don't change the grain resistivity, but reduces the grain boundary resistivity significantly. YB_6 works well as a sintering aid for Nb-doped $BaTiO_3$ ceramics, but it does not diffuse into the grains during sintering.

Acknowledgements

This work was supported by the postdoctoral Fellow Scheme and the Centre for Smart Materials of the Hong Kong Polytechnic University.

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