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JECS-10901; No. of Pages 6
ARTICLE IN PRESS
Journal of the European Ceramic Society xxx (2016) xxx–xxx
Contents lists available at www.sciencedirect.com
Journal of the European Ceramic Society
journal homepage: www.elsevier.com/locate/jeurceramsoc

Nanocrystalline semiconducting donor-doped $BaTiO_3$ ceramics for laminated PTC thermistor

Chao Gao [a,b], Qiuyun Fu [a,b,*], Dongxiang Zhou [a,b], Hao Zu [a,b], Tao Chen [a,b], Fei Xue [a,b], Yunxiang Hu [a,b], Zhiping Zheng [a,b], Wei Luo [a,b]

[a] School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan, 430074, China
[b] Engineering Research Center for Functional Ceramics, Ministry of Education, China

ARTICLE INFO

Article history:
Received 2 June 2016
Received in revised form 30 October 2016
Accepted 1 November 2016
Available online xxx

Keywords:
Nanocrystalline
Two-stage
Reduction-reoxidation
BaTiO3
PTC

ABSTRACT

This paper proposed a two-stage thermal processing method combined with the reduction-reoxidation procedure. Samples were firstly sintered in a reducing atmosphere by two stages and then reoxidized in air. Such two-stage thermal processing method was used to adjust density and grain size of ceramics separately. Finally, nanocrystalline semiconducting donor-doped $BaTiO_3$ ceramics were first successfully prepared. Samples with average grain size of 340 nm exhibited unexpectedly low room resistivity of 136 Ω cm and a significant PTCR effect, with a resistance jump of 4 orders of magnitude. In addition, depletion layer thickness of 40 nm and surface acceptor-state densities of 9.52×10^{13} cm^{-2} were also calculated. Such good properties had not been reported in former publications. It also means that smaller components based on semiconducting $BaTiO_3$ ceramics could be produced and more extensive application field could be proposed in the trend of miniaturization of electronic devices.

1. Introduction

Semiconducting ceramics exhibit distinct non-linear electrical properties, which results from different characteristics of grain boundaries and grains, and therefore have broad applications, such as thermistors [1,2], varistors [3,4], gas sensors [5,6] and grain-boundary barrier-layer capacitors [7] and so on. With the miniaturization of electrical components, laminated single-chip components have been gradually developed [8,9]. Thanks to its high melting point, low cost, excellent ohmic contact with semiconducting ceramics, the base mental, Nickel, was usually employed as inner electrodes for these laminated single-chip components [8,9]. Laminated semiconducting ceramic components with base metal inner electrodes should be sintered in a reducing or protective atmosphere to avoid oxidation of the base metal. However, semiconducting ceramics sintered in a reducing or protective atmosphere did not have non-linear electrical properties because the difference between grain boundaries and grain did not form. Thus a reoxidation process in air or oxygen is necessary to form potential barriers at grain boundaries to control their electrical properties. It is called the reduction-reoxidation method [7–11].

Grain size and density are the most concerned factors influencing properties of semiconducting ceramics prepared by the reduction-reoxidation method. Laminated miniaturized components prefer small grains but several electrical properties deteriorate with the decrease of grain size such as room resistivity of thermistors, breakthrough voltage of varistors and so on. In addition, the relative density should be in a certain range. It cannot be too low in order to obtain basic mechanical strength for applications. Meanwhile it cannot be too high in order to obtain good electrical properties through reoxidation. Generally, grain size and density of ceramics are correlated during the sintering. It is necessary to find out a way to control grain size and density separately.

Chen I-Wei [12] first used a two-stage sintering method to prepare dense nanocrystalline ceramics without final-stage grain growth. In the first-stage, samples were normally sintered for a short time. Then the sintering temperature was rapidly decreased and the samples were sintered at a relatively low temperature in the final-stage. The suppression of the final-stage grain growth was achieved by exploiting the difference in kinetics between grain-boundary diffusion and grain-boundary migration [12]. So far two-stage thermal processing method has been widely used to prepare all kinds of dense nanocrystalline ceramics, such as Y_2O_3, ZnO, $BaTiO_3$, Ni-Cu-Zn ferrite, BNT-BTO [12–15]. Therefore, such two-

* Corresponding author at: School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan, 430074, China.
E-mail address: fuqy@mail.hust.edu.cn (Q. Fu).

http://dx.doi.org/10.1016/j.jeurceramsoc.2016.11.001
0955-2219/

Please cite this article in press as: C. Gao, et al., Nanocrystalline semiconducting donor-doped $BaTiO_3$ ceramics for laminated PTC thermistor, *J Eur Ceram Soc* (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2016.11.001

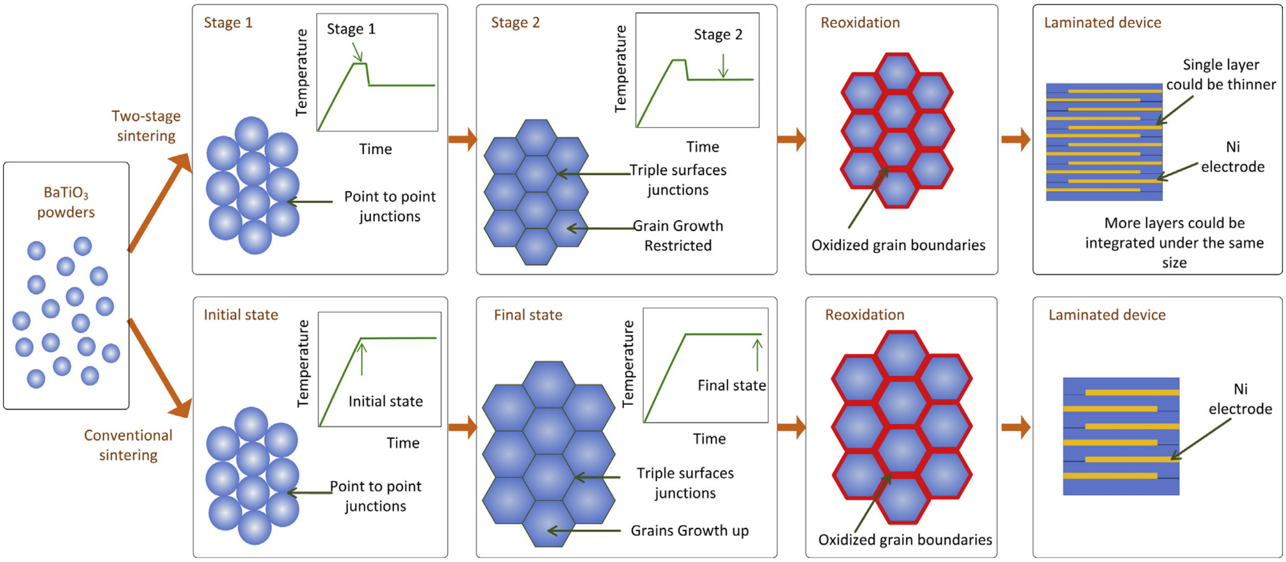

Fig. 1. Comparison of the two-stage sintering and conventional sintering based on the reduction-reoxidation method.

stage thermal processing method could be suitable for controlling grain size and density separately.

Based on the above method, this paper proposed a two-stage thermal processing method combined with the reduction-reoxidation procedure to prepare nanocrystalline semiconducting donor-doped $BaTiO_3$ ceramics for laminated PTC thermistor. Samples were firstly sintered by two stages in a reducing atmosphere to prevent the oxidation of Ni inner electrodes and then reoxidized in air to adjust their electrical properties. Such two-stage thermal processing method can be used to adjust density and grain size of ceramics separately. It can also be applied to preparing other nanocrystalline semiconducting ceramics and integrated passive components.

2. Experimental procedure

In our previous work, BN and Mn were successfully added as sintering aids and acceptors respectively [16]. Therefore, they were used again in this experiment.

Sample preparation: firstly, hydrothermal $BaTiO_3$ (particle size of 100 nm), La_2O_3, $Mn(NO_3)_2$ and BN (analytical reagent) were weighed according to the mol ratio of 1:0.002:0.0005:0.02. They were mixed by ball milling for 6 h in deionized water with zirconia balls, then dried and sieved to obtain the initial powder.Secondly, the initial powder was mixed with a dispersant, a solvent (including anhydrous ethanol and toluene) and a defoamer by ball milling for 8 h in a nylon pot and then a binder was added to it. The mol ratio of initial powder, dispersant, anhydrous ethanol, toluene and defoamer is 1:0.005:0.005:0.32:0.2:0.2. The slurry was acquired after ball milling for another 12 h and then cast into green sheets with thickness of 50 μm per layer by the doctor-blade method. These green sheets were baked at 80 °C for 2 min and stacked 20 layers to obtain 1 mm thick tape. Then the tape was stacked under an isostatic pressure of 30 MPa at 50 °C. Then, the samples were cut into standard size of 1206 (1.2 inch × 0.6 inch). Thirdly, the samples were heated at 280 °C in air for 72 h to remove the binder with heating and cooling rates of 10 °C/h, respectively. Then a two-stage thermal processing method combined with the reduction-reoxidation method was used. The green ceramics were sintered at a relatively high temperature for only 10 min, and then quickly cooled down to a lower temperature and held for a much longer soaking time.Finally, the reduced ceramics were reoxidized in air at 800 °C for 2 h with heating and cooling rates of 5 °C/min, respectively.

The measurements and calculations of physical and electrical characteristics: Density of samples was measured by the Archimedes method. Different samples were quenched to room temperature after different holding time for density measurements. The microstructure of the ceramics was observed using a scanning electron microscope (FEI Nova 630 SEM; FEI, Hillsboro, OR). Cross sections of the different samples were polished and quenched in air to observe the internal structure of the ceramics. Due to the particularity of the two-stage process, the quenching temperature should be carefully selected. For samples sintered at 990 °C in the first stage and held at 940 °C in the second stage, the suitable quenching temperature should be around 970 °C. When the quenching temperature was above 980 °C, re-crystallization occurred. In contrast, when the quenching temperature was below 950 °C, grain boundaries would be difficult to be distinguished. The In-Ga alloy (60: 40) electrodes were pasted on the surfaces of the ceramics for electrical measurements. The resistance was measured by a digital multimeter and the temperature dependence of resistance was measured in a temperature-programmable furnace (ZWX-B, Huazhong University of Science and Technology, China) at a heating rate of 2 °C/min. Complex impedance spectroscopy over the range 20 Hz–30 MHz was carried out using an impedance analyzer (6530B, Wayne Kerr, UK) at 25 °C. The potential barrier height, acceptor-state density, and thickness of the depletion layer was calculated and discussed based on the above tests. Numerical uncertainties (standard deviation) were also added in the corresponding figures.

3. Results and discussions

The two-stage thermal processing method proposed here combined with the reduction-reoxidation procedure was compared with the conventional sintering procedure as shown in Fig. 1. The sintering processes (including both Stage 1 and Stage 2) were performed in nitrogen to obtain ceramics with certain grain size and density, and then samples were reoxidized in air to control electrical properties.

In conventional sintering procedures, samples were heated at a predetermined rate, and then held at a fixed temperature until the expected densification level was acquired. The two-stage ther-