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Effect of Abnormal Grain Growth and Heat Treatment on Electrical Properties of Semiconducting $BaTiO_3$ Ceramics

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ABSTRACT

Effect of abnormal grain growth and heat treatment time on the electrical properties of donor-doped semiconductive $BaTiO_3$ ceramics was examined. La-doped $BaTiO_3$ ceramics was sintered at 1340°C for different times from 10 to 600 min in order to change the volume fraction of the abnormal grains in samples. As a result, samples with different volume fraction of abnormal grain growth from 22 to 100% were prepared. The samples were annealed at 1200°C for various times. The resistivity of the samples at room and above Curie temperature was examined. The complex impedance measurement as functions of the volume fraction of abnormal grains and annealing time was conducted. Separation of complex impedance semicircle was observed in a sample in which abnormal and fine grains coexist. The results are discussed from a viewpoint of microstructure-property relationship.

Key words* : *Abnormal grain growth, Semiconducting, $BaTiO_3$, Heat treatment

1. Introduction

Barium titanate, a good ferroelectric material having a perovskite structure, is widely used as the electronic component material for multilayer capacitors, Positive Temperature Coefficient (PTC) resistors, grain boundary barrier layer capacitors, etc.[1-3] Since the electrical properties of $BaTiO_3$ vary widely with its microstructure, a number of investigations[4-8] have been conducted to understand its microstructural development during sintering and to control its final microstructure. When Abnormal Grain Growth (AGG) occurs,[9-11] a few large grains develop and grow fairly rapidly at the expense of the fine matrix grains, and the grain size distribution becomes bimodal.

The presence of liquid phase in the sintered ceramics, although recognized as being crucial, often has been overlooked. Its existence is particularly critical for the solid-state sintering of $BaTiO_3$ ceramics when several liquid eutectics are possible in the BaO-TiO_2 system,[12] and the well-known Al_2O_3-SiO_2-TiO_2 compositions.[13,14] AGG in the presence of a liquid is a phenomenon observed only when the grains are angular with flat interfaces. $BaTiO_3$[15,16] is one of the typical examples of angular grains which•exhibit AGG. If $BaTiO_3$ ceramics are sintered with a small excess of TiO_2, a liquid phase is formed above the eutectic temperature of 1332.[12] Consequently, densification is greatly enhanced and grain growth is accelerated, resulting in AGG and a bimodal grain size distribution. Then, whole fine matrix grains usually less than ~ 3 μm are replaced by coarse grains of ~ 100 μm within a few minutes. Once the fine matrix grains are completely replaced by coarse grains, further grain growth is retarded and a uniform grain size distribution is recovered.[17,18]

Although the abnormal grain growth is commonly occurred in $BaTiO_3$-based PTCR ceramics, a detail and precise understanding of electrical properties of donor-doped $BaTiO_3$ ceramics has not yet been conducted. Especially, it is known that the electrical properties of PTCR device are greatly affected by grain size and heat treatment condition. Therefore, the study of AGG in PTCR device is of great interest from academic point of view. In this study The effect of abnormal grain on the electrical properties of donor-doped $BaTiO_3$ ceramics was examined. Sintering temperature and sintering time were varied to obtain samples with different abnormal grain portions. Then the samples were annealed at 1200°C for different times. Resistivity and complex impedance measurements are analyzed with respect to the volume fraction of abnormal grains and heat treatment time.

2. Experimental

Samples with a formulation $Ba_{0.998}La_{0.002}TiO_3$ was prepared from the raw materials of $BaCO_3$(99.94%), TiO_2 (99.97%) and La_2O_3(99.999%). 0.002 mol% of excess TiO_2 was added to increase sinterability.[19,20] Raw materials were ball milled for 20 h in a polyethylene jar using Y-stabilized ZrO_2 balls and ethyl alcohol. After drying, the powder was calcined at 1150°C for 1 h. The calcined powder was ball-milled again for 20 h. The powder was mixed with 10wt% aqueous PVA solution and sieved to form granules. Green pellets with a diameter of 10 mm and a thickness of 3 mm were formed under the uniaxial pressure of 150 MPa. After binder burn out at 600°C for 5 h. the samples were sintered in air at 1340°C for different sintering times from 10 to 600 min. and then annealed at 1200°C for a period which was

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varied from 0 to 900 min. Then the samples were furnace cooled. The abnormal grain portion was obtained by Point Counting method,[21] and the volume of pores are excluded. The resistance of each sample was measured by two prove dc measurement technique. Good ohmic contacts were obtained by using an In/Ga alloy in the ratio of about 2/1. Complex impedance measurement,[22] which allows separation of the contributions of the grains and grain boundaries to the total impedance, was conducted at room temperature using an Impedance Gain Phase Analyzer (model, HP4194A).

3. Results and Discussion

Fig. 1 shows the microstructures of samples sintered at different temperatures in the range of 1320 – 1500°C for 1 h. When the sample was sintered at 1320°C for 1 h (Fig. 1(a)), abnormally grown grains with the size around 60-100 μm are observed. When the sintering temperature increased to 1330°C (Fig. 1(b)), more abnormal grains are developed. However, in the case when the samples are sintered at 1370 and 1500°C, normal grain growth proceeded and homogeneous grain size distribution achieved with the mean grain size of 13 and 23 μm, respectively. Larger grain size in the sample sintered at 1500°C than that sintered at 1370°C is believed due to promoted diffusion of materials at elevated temperature. The evolution of the microstructure as a function of sintering temperature can be explained by the nucleation rate, which is a function of temperature. Because nucleation rate increases greatly as the temperature increased, large number of nucleation might be formed at the same time when the samples are sintered above 1370°C. Then, further grain growth is retarded that results in a normal grain growth with a uniform grain size distribution.[17,18] From this experiment, the optimum sintering temperature to control the volume fraction of abnormal grain growth is determined as 1340°C.

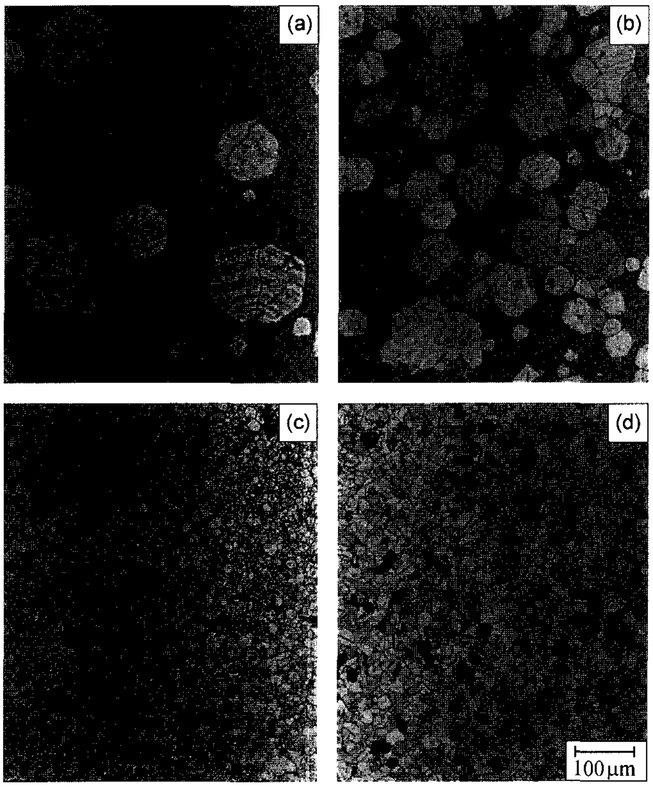

Fig. 1. Microstructure of samples sintered at (a) 1320°C, (b) 1330°C, (c) 1370°C and (d) 1500°C for 1 h.

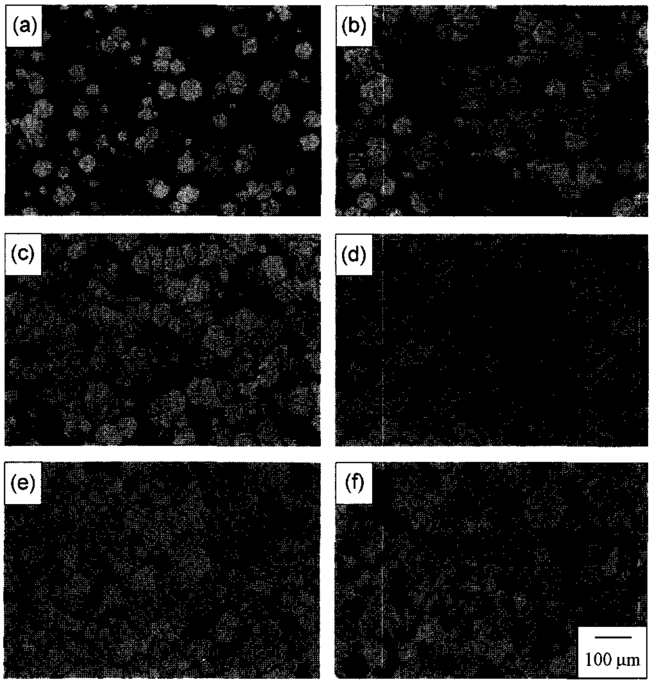

Fig. 2. Microstructure of samples sintered at 1340°C for (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min, (e) 60 min and (f) 600 min.

The microstructures of samples sintered at 1340°C for various times from 10 to 600 min are shown in Fig. 2. When the sample was sintered for 10 min, few abnormal grains were appeared as shown in Fig. 2(a). The evaluated volume fraction of the abnormal grains increased gradually as the sintering time increased. In the case of (e), which was sintered for 60 min, the entire sample is composed of abnormal grains and pores. When the fine matrix grains are completely replaced by abnormal grains, further grain growth is retarded and a uniform grain size distribution is recovered. In this case, we will designate it 100% of abnormal grain growth even though the sample contains pores. Based on the assumption, the volume fractions of abnormal grains in the samples are 22, 44, 67, 83, 100 and 100% for the corresponding sintering time of 10, 20, 30, 40, 60 and 600 min, respectively. No great change in microstructure between (e) and (f) was observed due to the retarded grain growth as expected.

Fig. 3 shows the ρ_{min} and ρ_{max} of the samples evaluated from temperature-resistivity curves of PTCR effect. Therefore, ρ_{min} is the resistivity at room temperature and ρ_{max} is the resistivity above Curie temperature, which is directly related to the PTCR jump. Because the conductivity of large

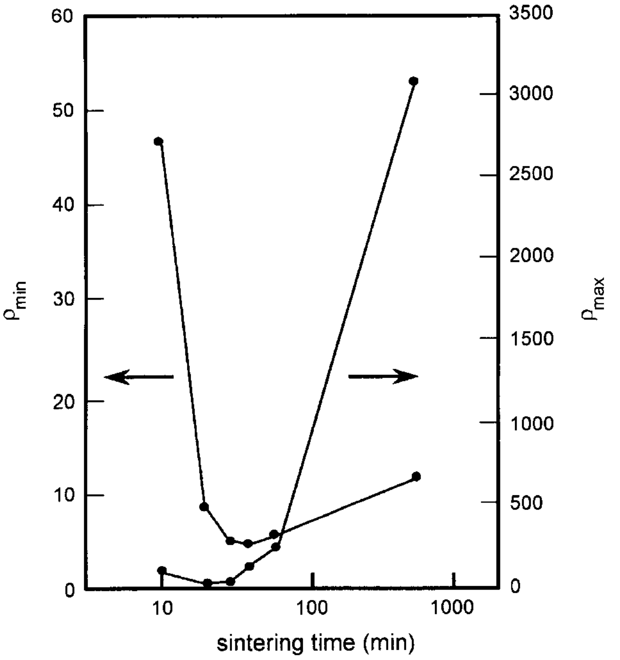

Fig. 3. ρ_{max} and ρ_{min} as a function of sintering time at 1340°C.

grains per unit volume is higher than that of small grains in semiconductive $BaTiO_3$ ceramics, it is necessary to employ mixing rules[23,24] when the large and small grains are mixed. Percolation limit is a point where dispersed particles link up to form a 3-dimensional network.[23] Therefore, when the abnormal grains are dispersed and isolated by the small grained matrix in the microstructure, the connectivity of the abnormal grains changes from 0-3 to 3-3 at the percolation limit. In a mixture of conductor and insulator, percolation limit could be a minimum volume percent of conductor that can make a conduction path through the matrix. It is reported that the percolation limit in diphasic mixture is approximately 40%.[25] Concerning the ρ_{min}, when the sample was sintered for 10 min, the microstructure has 0-3 connectivity[26] because the volume fraction of small and large grains is 78 : 22. In this case, ρ_{min} revealed high value. When the volume fraction of small and large grains is 54 : 44 by sintering for 20 min, it forms a 3-3 conduction connectivity, which greatly drop the ρ_{min}. Further sintering up to 600 min slowly increased the ρ_{min} in room temperature and drastic increase in ρ_{max} above Curie temperature. This phenomena can be explained by the Daniels' model that suggested donor compensation by cation vacancies introduced during sintering and/or cooling.[27,28]

All samples with different volume fraction of abnormal grains were annealed at 1200°C for various times from 0 to 900 min. The annealing process did not change the microstructures of the samples. The complex impedance patterns of a sample composed of 100% of abnormal grains sintered at 1340°C for 60 min is given in Fig. 4(a). Regardless of the annealing time only one impedance semicircle was observed, which signifies that two resistance components exist in the

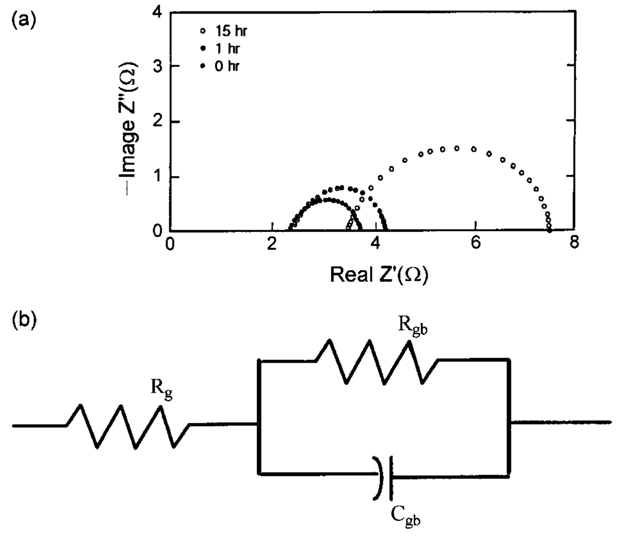

Fig. 4. (a) Complex impedance spectra of samples sintered at 1340°C for 60 min with a various annealing time at 1200°C and (b) its equivalent circuit.

sample; i.e., the resistance originated from grain and grain boundary. When the annealing time is increased from 0 to 1 h, the semicircle extended to the right signifying the grain boundary resistance increased. When the annealing time increased to 15 h, the size of semicircle increased and shifted to the right. In Fig. 4(b), an equivalent circuit is suggested corresponding to the sample. R_{gb} and C_{gb} are the resistance and capacitance of grain boundaries and R_g is the conductive grain resistance.

In the case when the sample is sintered at 1340°C for 20 min, in which abnormal grains and fine grains are coexist, complex impedance patterns as a function of annealing time at 1200°C is shown in Fig. 5(a). As the annealing time increased, the semicircle began to separate into two, and the grain boundary

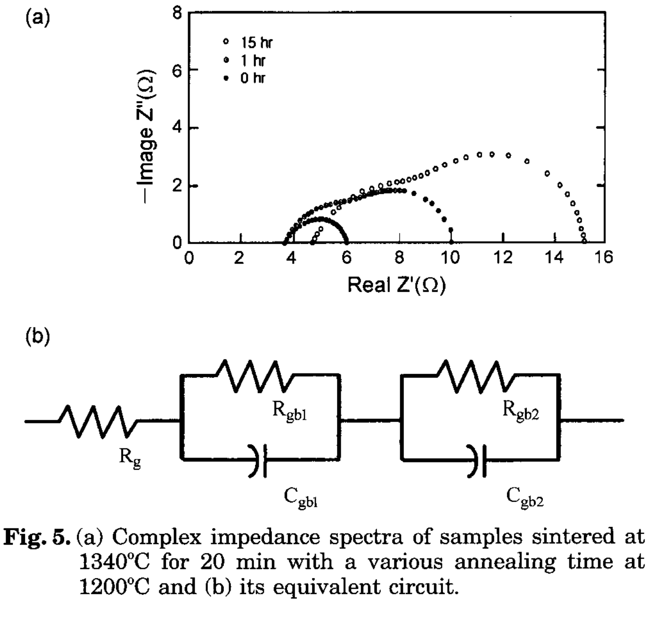

Fig. 5. (a) Complex impedance spectra of samples sintered at 1340°C for 20 min with a various annealing time at 1200°C and (b) its equivalent circuit.

resistance increased greatly up to 15 Ω comparing with the Fig. 4(a). The separation of the semicircle implies that another resistance and capacitance components are show up, and its corresponding equivalent circuit is suggested in Fig. 5(b).

The PTCR(Positive Temperature Coefficient of Resistance) effect in donor-doped $BaTiO_3$ ceramics has been understood to be characterized by its grain boundary properties since Haywang[29,30] proposed the grain boundary-layer model. It is proposed that the acceptor acting cation vacancies appear along the grain boundaries during cooling process, and it can electrically compensates the donors around the grain boundaries and then, potential barriers form on the grain boundaries.[27,28] The cation vacancy diffusion from grain boundary into grain make the insulating layer near the grain boundary because cation vacancy compensates the extra donor charge. They also found that the concentration of cation vacancies depends on the oxygen partial pressure during sintering, sintering temperature and cooling rate. Annealing at 1200°C introduces cation vacancies at grain boundaries and prolonged annealing encourage generation of the cation vacancies as well as inward diffusion of the vacancies into the grains. Based on this viewpoint, therefore, the increased grain and grain boundary resistance by annealing time is understood.

On the other hand, the separation of impedance semicircle observed in Fig. 5(a) can be explained by its duplex microstructure shown in Fig. 6. Fig. 6 shows the SEM photograph of a sample sintered at 1340°C for 20 min. In the microstructure, small grains of 1~2 μm exist in between two abnormal grains. Daniels *et al.* suggested that total vacancy compensation takes places at about 1220°C. Thus, an inward diffusion of a depletion layer, richer in Ba vacancies than in donor, towards the center of the grain would be expected to take place during the annealing process below 1220°C. If the cation vacancies are V_{Ba}'', the diffusion coefficient of V_{Ba}'' obtained by Daniels *et al.*[28] predicts that the diffusion depth of V_{Ba}'' is about 3 mm for 1 h annealing and 12 μm for 15 h annealing at 1200°C.

Fig. 7 shows the schematic diagram of microstructure for an explanation of cation vacancy diffusion by heat treatment.

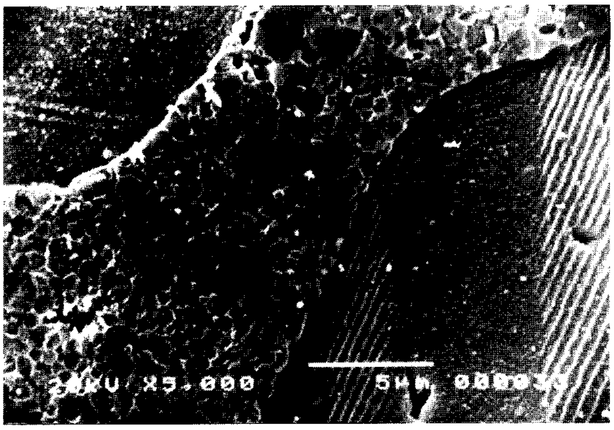

Fig. 6. SEM photograph of a sample sintered at 1340°C for 20 min.

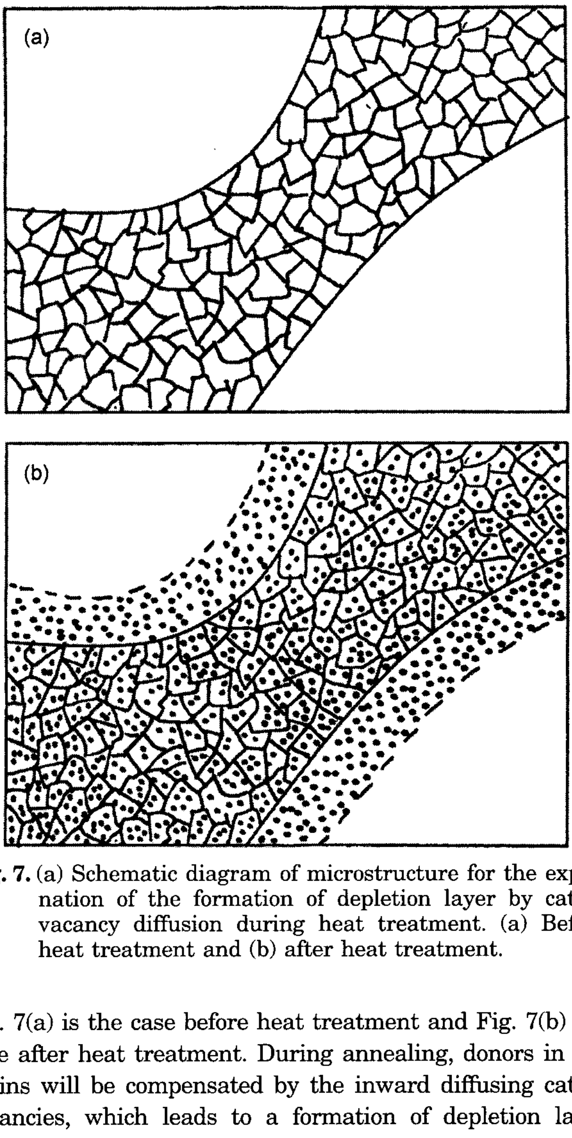

Fig. 7. (a) Schematic diagram of microstructure for the explanation of the formation of depletion layer by cation vacancy diffusion during heat treatment. (a) Before heat treatment and (b) after heat treatment.

Fig. 7(a) is the case before heat treatment and Fig. 7(b) the case after heat treatment. During annealing, donors in the grains will be compensated by the inward diffusing cation vacancies, which leads to a formation of depletion layer around grain boundaries. Prolonged annealing increases the width of the depletion layer. Therefore, small grains will be totally compensated by the cation vacancies in a short time, while the depletion layer stays at the edge of large grains. In this case, the small grains will lost the semiconducting characteristics but large grains are still semiconductive. Theoretically, if V_{Ba}'' are the only cation vacancies, the resistance of the sample will reach to a maximum in an hour. However, the resistance increased slowly with respect to the annealing time. This indirectly supports that there might be another cation vacancies of V_{Ti}'''', which has lower diffusion coefficient than V_{Ba}''. Consequently, the separation of complex impedance semicircle mentioned above seems to be caused by totally compensated small grains, which produced another capacitance and resistance components.

4. Conclusion

Abnormal grain growth has artificially introduced in semiconductive $BaTiO_3$ ceramics, which exhibit PTCR effect.

Samples with various volume fraction of the abnormal grains were prepared by controlling sintering time, and the effect of heat treatment time on the electrical properties of donor-doped semiconductive $BaTiO_3$ ceramics was examined. Room temperature resistivity (ρ_{min}) drastically decreased when the abnormal grains form a 3-3 conduction connectivity. Complex impedance patterns which are characterized by the grain and grain boundary properties were examined in La-doped $BaTiO_3$ ceramics in which abnormal grains are formed. The complex impedance patterns of samples were microstructure dependent since the depth of depletion layer formed by inward diffusion of cation vacancies is governed by annealing time. Only one semicircle of complex impedance pattern was appeared in the samples having homogeneous microstructure. However, in the case of duplex microstructure the separation of complex impedance pattern was observed. It was explained due to entire depletion of small grains.

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