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Nd첨가가 Barium-Lead Titanate의 전기전도도와 격자상수에 미치는 영향

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Effect of Nd Doping on the Electrical Conductivity and Lattice Parameters of Barium-Lead Titanate

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초 록

$(Ba_{0.5}\ Pb_{0.5})_{1-x}\ Nd_x\ TiO_3$중의 x(Nd의 양)를 변화시키면서 격자상수와 전기전도도를 측정하였다. c축과 a축의 비(c/a)의 극대값은 실온에 있어서 전기전도도의 극대값과 일치하였다. 이것은 Nd원자의 치환위치와 강유전성의 변화에 의한 것으로 고찰되었다. Curie 온도이하에서는 Nd첨가량의 증가에 따라 전기전도도의 활성화에너지가 증가하는 경향을 나타내었다. 이것은 입경의 감소에 따른 Spontaneous polarization의 저하가 원인으로 고찰되었다. 첨가량의 역할을 입계의 potential barrier의 높이와 관련지어 논하였다.

I. Introduction

Rare earth-doped barium titanate ceramics show very large positive temperature coefficients of resistivity above ferroelectric Curie temperature(Tc), which is called PTC or PTCR effect.[1] This phenomenon has been observed in only sintered polycrystalline ceramics. A single crystal specimen shows low resistivity but its temperature coefficient is negative in all ranges of temperature.[2] That is, the semiconducting property is intrinsic to doped-barium titanate, while PTC effect is due to grain boundaries. The mechanism of the PTC effect was argued first by Heywang.[3] He assumed the potential barrier originated from surface acceptor levels at a grain boundary, the height of which is proportional to the reciprocal of the electric permittivity of high field biased barium titanate. According to his theory, the potential barrier is much lower below Tc than above Tc, which gives rise to a drastic change in the resistivity of the grain boundary region in the temperature range near Tc. Existence of the barrier has been confirmed by many workers,[4-6] but some other experimental facts still remain to be theoretically explained.[7,8] To supplement his theory, orientation of ferroelectric domains or the existence of thin intergranular insulating layers have been proposed.[7,9] However, there seems to be no decisive model to fully explain the PTC effect.

The Curie temperature of lead titanate($PbTiO_3$) is higher than that of barium titanate.[10,11] The solid solution system of barium-lead titanate($Ba_{1-x}Pb_xTiO_3$) shows higher Curie temperature varying proportionally to its lead content, x, and can also be made into a PTC semiconductor by rare earth oxide doping.[13] It

is empirically known that the commencement temperature of PTC effect is closely related to the ferroelectric Curie temperature or phase transition temperature of the bulk material.[13] Consequently, lead-substituted semiconducting barium titanate shows higher PTC commencing temperature. This property is applied to making a high temperature PTC heater and thermistor.

There is a suitable region of dopant concentration for making a semiconductor.[14] The conductivity reaches the minimum when the dopant concentration is between 0.1 and 0.3 at%. If the concentration is outside this optimum range, the material would become an insulator. This semiconducting-insulating behavior has not been clarified yet.

In the present study, the influence of dopant concentration upon the lattice parameters, and its relationship to electrical conductivity or temperature characheristics were investigated for the barium-lead titanate.

We used neodymium as a dopant because neodymium is one of the light rare-earth elements that are good for making a highly conducting semiconductor, and also because neodymium has high stability of trivalent state while the other elements have a tendency to change their valency states.

II. Experimental Procedure

(1) Specimen Preparation

Starting materials were barium carbonate, lead monoxide, titanium dioxide, and neodymium oxide which were of 99.99% purity, respectively. They were mixed with ethanol in an agate mortar and dried simultaneously. The mixture was calcined at 900°C for 1 h in an alumina crucible to proceed solid-state reaction. The resulting powder was then mixed meth anol and distilled water in a mill with resin-coated balls for 24 h.

After drying, the powder was mixed again in the same agate mortar and calcined for 12 h in order to give further uniformity in composition. Then the powder was pressed into rectangular bars (3×3×10 mm) under the pressure of ca. 100MPa. The molded bars were sintered at 1330 °C for several seconds. The cooling rate was carefully controlled to be 5° C/min. Sintering temperature was critical to the nature of the final product. Below 1330°C, the specimen did not show low enough resistivity, and when temperature was above 1330°C or the soaking time was longer, the specimens were melted.

The dopant concentration(x) was varied from 0.000 375 to 0.012 in$(Ba_{0.5}Pb_{0.5})_{1-x}Nd_xTiO_3$, while the Ba/Pb ratio was fixed as unity.

(2) Lattice Parameter Measurement

Lattice parameters were measured by X-ray powder diffraction method. For each sample, more than 10 diffraction peaks at high angles were measured using high purity Si powder as an internal standard. Lattice parameters were computed by a least squares method.

(3) Electrical Measurement

The D.C. two probe method was used for the measurements of electrical conductivity at room temperature. For the measurements at higher temperatures, the A.C. two probe method was adopted because the resistivity was rather high and its range was so wide. The specimen bars were plated silver electrodes on both sides. Silver did not give an ohmic contact to semiconducting barium titanate, but was dared to be used due to its thermal and mechanical stability. In our practical measurements at room temperature, In-Ga liquid metal alloy and silver electrodes gave similar resistivity of the sample. There is no problem in this small difference because our attention is not to the absolute value but to the variation of resistivity.

The resistance and capacitance were measured in the temperature range from 20°C to 400°C by a universal bridge (ANDO LCR-10). The frequency and the applied voltage were kept at 1 kHz and about 3.5V, respectively.

III. Results and Discussion

The variations of lattice parameters, a and c of the tetragonal phase against the neodymium content are shown in Fig. 1. Both parameters a and c change with the dopant concentration, going through minimum values. According to the previous reported works on the rare-earth doped barium titanate,[15,16] lattice parameters increased monotonously but very slightly

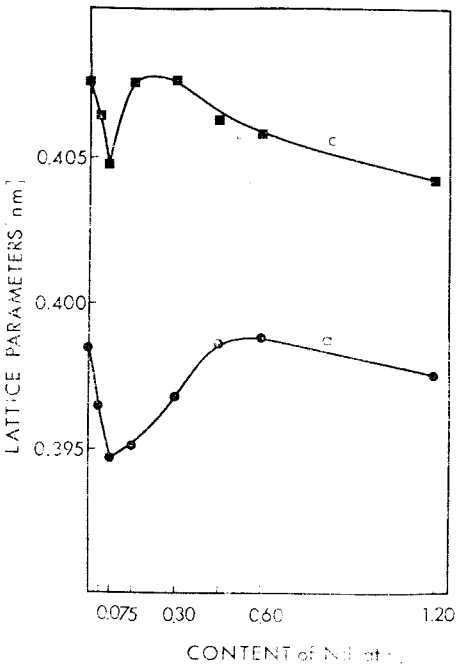

Fig. 1. Lattice parameters a and c of barium lead titanate plotted against doping concentration of neodymium.

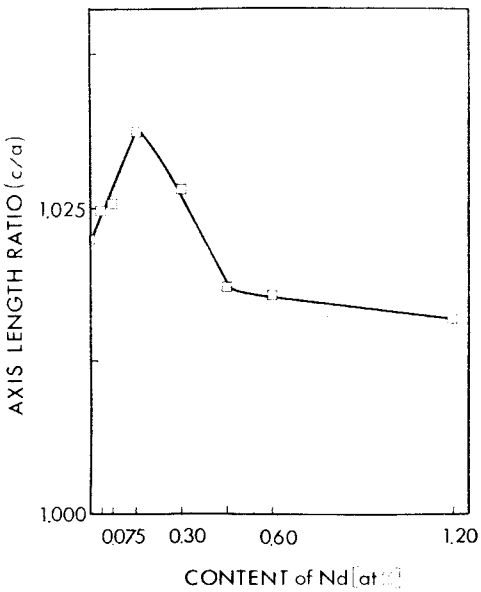

Fig. 2. Axis length ratios against the dopant content.

with increase in the dopant concentration. However, the aims of the previous investigation were to develop

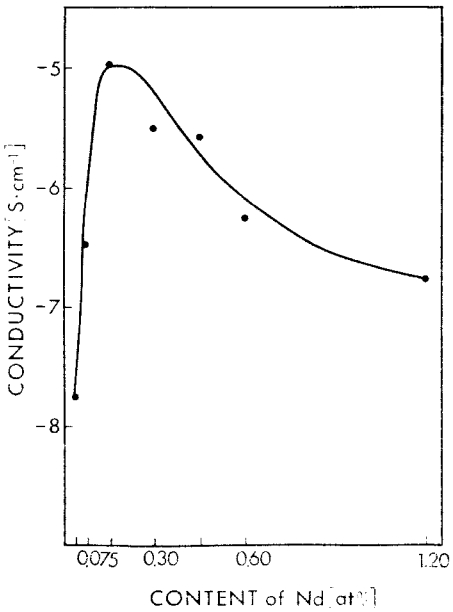

Fig. 3. Electrical conductivity at room temperature as a function of neodymium concentration.

a high permittivity caramic capacitor, measuring intervals of the dopant concentration were somewhat rough and the suitable range for making a semiconductor was neglected. Lattice parameters of gadolinium -doped barium titanate without lead were also measured in the course of this work, but their variations were too small to be related to a large resistivity change. It is thus thought that the substitutional addition of lead to barium titanate enhanced the variation of its lattice parameters.

Figure 2 shows the effect of the dopant concentration on a ratio of axis lengths or cell distortion from cubic system, c/a. The ratio has its maximum value at 0.15 at% Nd. In a highly doped region, c/a becomes closer to unity together with the broadened X-ray diffraction peaks. The peak broadening is considered to be caused by fining of the grains as shown later, but on the other hand, there is a possibility that the crystal system of barium lead titanate changes from tetragonal to pseudo-cubic in a highly doped region. Nonlinear changes in lattice parameters indicate that the type of a solid solution formed is not

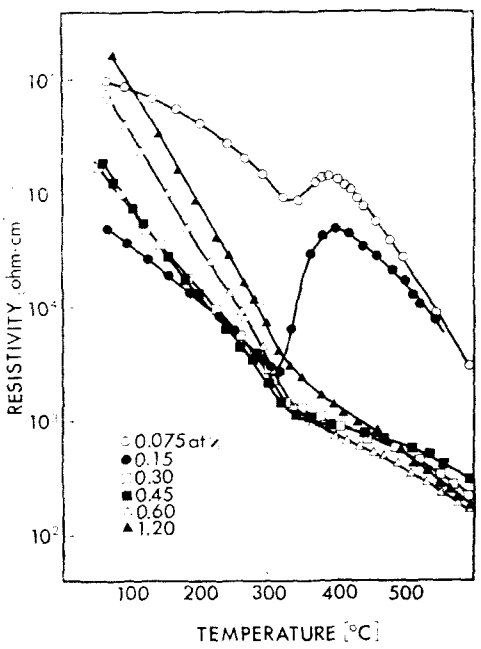

Fig. 4. Temperature dependence of electrical resistivity for Nd doped barium lead titanate.

necessarily the same in the whole composition range.

The result of electrical measurement at room temperature is shown in Fig. 3. The maximum of the conductivity was observed at 0.15 at% Nd. It is generally observed that an appropriate dopant concentration exists to make semiconducting $BaTiO_3$ and its range lies in between 0.2-0.4 at%,[9] which agrees well with the present results. The coincidence between the maximum of lattice distortion and the minimum of resistivity should be noted.

Figure 4 shows the dependence of the resistivity on temperature. Only the specimen doped with 0.15 at % Nd showed a significant PTC effect. A slight tendency of PTC could also be seen in the specimen containing 0.075 at% Nd. Highly doped specimens showed similar temperature dependence, common to a normal semiconductor(NTC), except that they all had points of inflection at the Curie temperature.

Since the ionic radius of neodymium(0.110 nm) is smaller than that of barium (0.143nm) or lead(0.120 nm) but larger than that of titanium(0.068nm), the contraction of lattice may be caused by substitution of neodymium for the barium-lead site. It is said to be possible that rare earth ions replace the Ba sites generating negatively charged barium vacancies to compensate their positive charge.[16,17] Therefore, it may be proper to consider for the present case that the replacement of barium-lead site with neodymium would have proceeded when the dopant concentration was lower than 0.075 at%, giving rise to a decrease in cell volume due to the difference in ionic radii. Simultaneously, the substitution of trivalent Nd ions for divalent Ba or Pb ions generated the conduction electrons, resulting in a decrease in resistivity.

When the dopant concentration is over 0.075 at%, the lattice parameters become larger. This phenomenon is inexplicable if only the substitution of Nd barium-lead site is taken into account. From the viewpoint of the difference in ionic radii, the variation of lattice parameters can only be explained on the assumption that the Nd ions would have replaced with Ti ions in a highly doped region. This was also pointed out by other workers[13,18] based on the analysis of elecrtical properties and NMR spectra. Replaced Nd ions for Ti sites would play a role as acceptors that compensate the donors, and hence decrease the concentration of conduction electrons leading to an increase in resistivity. This concept is in accordance with the observed resistivity change.

When the dopant concentration reached 0.15 at%, the lattice distortion c/a becomes the largest and the PTC effect was also the most remarkable. Jonker[9] pointed out first that the height of the potential barriers at grain boundaries which caused a PTC effect was lowered by a local internal field induced from an appropriate arrangement of 180° domains across the boundaries below the Curie temperature. If the temperature is higher than Tc, the height of barrier rises because the domain structure disappears. According to this theory, it can be postulated that a larger degree of spontaneous polarization and/or of suitable arrangement of 180° domains should cause a larger PTC effect. Since lattice distortion, c/a, is supposed to be a measure of the the degree of spontaneous polarization, smaller lattice distortion may be one of the reasons why the specimens of too high or too low doping levels did not show a PTC effect.

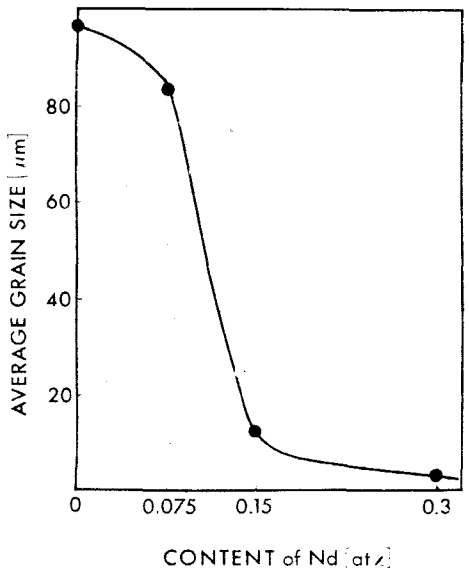

Fig. 5. Average grain size of the specimens as a function of dopant content.

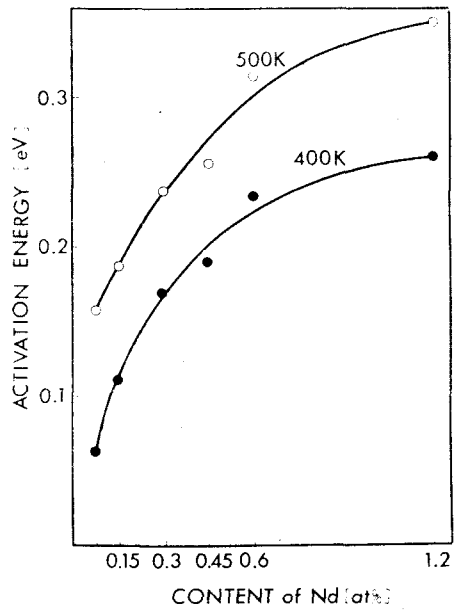

Fig. 6. Activation energy of electrical conductivity below the Curie tempetature against the dopant concentration.

As is generally known, rare-earth oxide acts as a grain growth inhibitor during sintering in the case of barium titanate.[19] To elucidate whether this was also the case for the present barium-lead titanate, grain size measurement was carried out. Figure 5 shows the result. The grain size decreased largely with an increasing content of the dopant. It has been reported that the ferroelectricity of barium titanate is suppressed by rare-earth doping due to a decrease in the grain size.[15,20] The domain structure cannot be constructed in the grains if they were too small, because each domain has a lower limit in its size. According to the Jonker's model, too small grains without domain structure would have depressed a PTC effect. It is also conceivable that when the average grain size decreases, the number of grain boundaries per unit length increases resulting in an increase in resistivity.

Apparent activation energy of conductivity below Tc is plotted against the dopant concentration in Fig. 6. The activation energy increased proportionally to the dopant concentration. This tendency is independent of the actual value of the resistivity nor PTC characteristics. The increase in activation energy indicates the increase in the height of potential barriers at grain boundaries. The dopant thus seems to play a role in raising the barrier below Curie temperature in proportion to its concentration. This may have been closely related to a decrease in grain size with increasing dopant concentration.

Based on the present results, we can summarize the roles of dopant in two different categories: (1) the dopant plays a significant role in valency control of the bulk behaving as either a donor or an acceptor depending on which site, Ba-Pb site or Ti site, it is incorporated into, (2) the dopant affects the height of grain boundary barriers which are associated with both grain size and the strength of local internal field.

IV. Conclusion

The following conclusions can be drawn from the present study;

(1) From the variation of the lattice parameters, it was found that Nd ions replaced the barium-lead sites at first generating conduction electrons, and then replaced the Ti sites at higher dopant concentration beh

aving as acceptors and compensating the electrons.

(2) Lattice distortion, c/a, reached its maximum value at 0.15 at% Nd. Maximum lattice distortion gave the largest PTC effect.

(3) The height of the grain boundary potential barrier increases as increasing the dopant concentration, for which the decrease in grain size accompanying degradation of the spontaneous polarization is responsible.

V. Acknowledgements

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