Influence of point defects on the leakage current properties in $PbTiO_3$ single crystals

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Single crystals of $PbTiO_3$ (PT) were grown by a self-flux method, and the influence of lattice defects on the leakage current properties at 25°C of the PT crystals was investigated. While PT crystals annealed in air at 700 °C showed a leakage current density of the order of 10^{-5} A/cm^2, annealing under a high oxygen partial pressure of 35 MPa at 700 °C increased the leakage current density to 10^{-4} A/cm^2. This increase in leakage current by the oxidation treatment provides direct evidence that electron hole plays a dominant carrier for the leakage current property in the PT system. The conductivity at 800 °C of the PT crystals proportionally increased with an increase in oxygen partial pressure, and electron hole is revealed to be a detrimental carrier even at 800 °C. Thermogravimetric analysis showed that a larger weight loss due to PbO vaporization was observed under a higher oxygen partial pressure at high temperatures above 1000 °C. The enhanced vacancy formation of Pb under a higher oxygen partial pressure demonstrates that the surface reaction between Pb atoms and O atoms adsorbed onto the PT surface, which leads to PbO (g), is the limiting factor for the vacancy formation in the PT system. It is suggested that Pb vacancies act as an electron acceptor for generating electron holes, leading to a higher leakage current.
Key words: lead titanate, perovskite oxide, ferroelectric, defect control, single crystal

1. INTRODUCTION

Ferroelectric oxides with perovskite structure (ABO_3) are characterized by the displacements of A and B cations with respect to BO_6 octahedral cage, and the resultant dipole moments due to the cooperative ionic displacements induce a spontaneous polarization (P_s) along the one specific crystallographic direction. Lead titanate ($PbTiO_3$; PT) is one of the simplest members in the perovskite ferroelectrics. PT has attracted much attention for last several decades as a ferroelectric tetragonal end member forming morphotropic phase boundary with other rhombohedral perovskites [1, 2]. At room temperature, PT has a strong structural anisotropy which is developed during cooling through the cubic-tetragonal phase transition at 490 °C [3]. The structural anisotropy defied by the tetragonality of the unit cell, c/a, is as high as ~ 1.06 for PT [4]. The large c/a is closely related to the structural origin of a large P_s in the PT system. The large P_s provides a great deal of potential in piezoelectric and ferroelectric applications. Although PT single crystals can easily be grown and PT have been investigated for long years, there are few reports on the polarization switching of bulk PT by applying an electric field. It is widely recognized that the large spontaneous strain of PT crystals prevents their switching of P_s. Additionally, a sufficiently high electric field cannot be applied to PT crystals due to their poor insulating properties resulting from abundant defects in the crystals [5, 6]. The poor insulating properties attributed to defects are common to the perovskite oxides containing volatile elements such as bismuth, e.g., Bi layer-structured ferroelectrics and Bi-based perovskite oxides [7, 8]. It is required to establish the guiding principle of defect control for achieving the switching of P_s as well as high insulating properties. In this study, the influences of the vacancies of Pb and oxide ions on the leakage current are investigated on PT crystals grown by a self-flux method, and the mechanism of the leakage current is discussed.

2. EXPERIMENTAL

PT single crystals were grown by a self-flux method. Powders of PbO and TiO_2 (purity > 99.99%) were used as starting materials. The raw materials were thoroughly mixed by ball milling for 1 h (200 rounds / min) using ethanol as a medium. The dried mixture was soaked in platinum crucible at 1100 °C for 24 h and then slowly cooled (4 °C / hour) [9, 10]. Single crystals with cubic $(001)_{Cubic}$ major surface were obtained. The PT crystals were washed in dilute nitric acid to remove the excess PbO flux. X-ray diffraction (XRD) analysis using Cu-Kα radiation was performed for phase identification. Thermogravimetric (TG) measurements at 1000 °C were conducted to investigate the influence of oxygen partial pressure (Po_2) on the defect formation in the PT crystals.

The PT crystals were annealed in air at 700 °C for 10 h to remove the stress introduced in PT crystals during crystal growth. Some of the PT crystals were annealed under a high Po_2 (35 MPa) at 700 °C for 10 h to reduce oxygen vacancies. These crystals were cut into thin plate (thickness $\sim$ 150 μm), and then Au electrodes were sputtered onto the both surfaces of the crystals. The polarization and leakage current properties along the $[100]_{Cubic}$ axis were evaluated. The conductivity of PT single crystals was measured by electrochemical impedance spectroscopy (EIS) at a high temperature of 800 °C.

3. RESULTS AND DISCUSSION

Figure 1 shows the photograph of the PT crystals. Cubic-shaped yellow crystals with dimensions up to 3 mm × 3 mm × 3 mm were obtained in our study. These crystals looked homogeneous and no inclusion appeared.
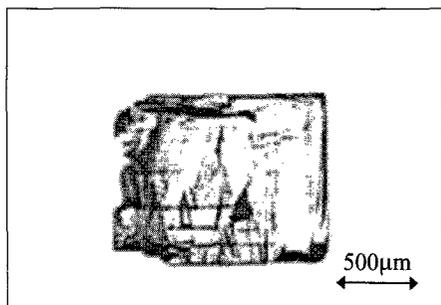
Fig. 1 PbTiO₃ single crystals
grown in this study.

Figure 2 exhibits the XRD pattern of the crushed powder of PT crystals. No impurity phase ascribed to inclusions etc. was detected. The crystal structure was determined to be tetragonal with the lattice parameters of $a = 0.3892$ nm and $c = 0.4145$ nm, which was in good agreement with the previous report [11].
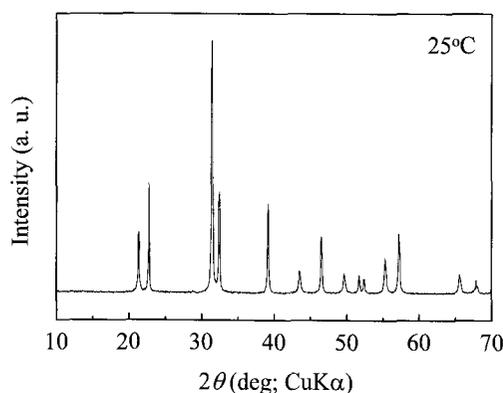
Fig. 2 XRD pattern of the crushed powder
of PT crystals.
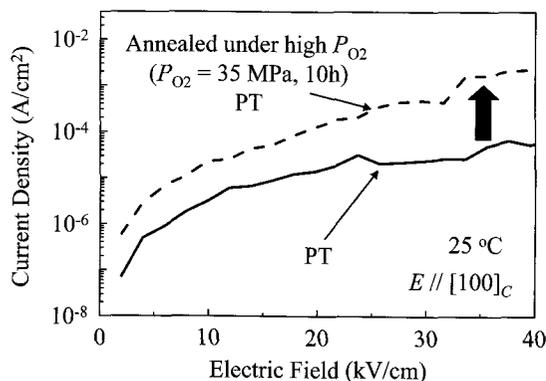
Fig. 3 Leakage current properties of
PT single crystals.

Figure 3 indicates the leakage current properties of PT crystals. The crystals annealed in air at 700 °C showed a leakage current density of the order of 10^{-5} A/cm². Note that the annealing under a Po_2 at 700 °C led to a marked increase in leakage current density by about one order of magnitude. This increase in leakage current density by the oxidation treatment is attributed to the following reaction:

$$V_O^{\cdot\cdot} + 1/2\,O_2 \rightarrow O_O^* + 2\,h^{\cdot} \qquad (1)$$
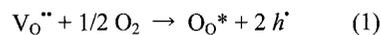
where $V_O^{\cdot\cdot}$ denotes the oxygen vacancy with two positive charges, O_O^* is the oxide ion at the oxygen site and $h^{\cdot}$ is electron hole. These results lead to a conclusion that oxygen vacancies exist in PT lattice and that $h^{\cdot}$ acts as a detrimental carrier of the leakage current at room temperature in the PT system. The leakage current properties of PT crystals are demonstrated to be dominated by $h^{\cdot}$ [12].
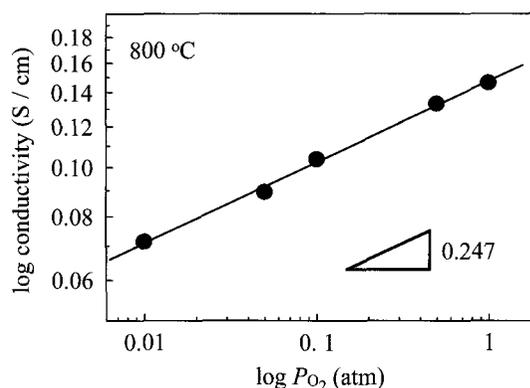
Fig. 4 Oxygen partial pressure dependence
of conductivity of PT single crystals.

Figure 4 indicates the conductivity as a function of Po_2 at 800 °C. A proportional relation between log(conductivity) and log(Po_2) was obtained. The slope calculated in the relation log(conductivity)-log(Po_2) by a least-square method was 0.247, and this value is very close to 1/4, which is predicted by the vacancy formation formalism as discussed below [13, 16].

The equilibrium constant (K) of the Eq. (1) is given by:

$$K = [h^{\cdot}]^2 / [V_O^{\cdot\cdot}]\,Po_2^{1/2} \qquad (2)$$

where $[h^{\cdot}]$ denotes the concentration of $h^{\cdot}$ and $[V_O^{\cdot\cdot}]$ is the concentration of $V_O^{\cdot\cdot}$. In the case of a sufficiently high $[V_O^{\cdot\cdot}]$, which is determined by other defect such as Pb vacancies (as in the case for PT crystals), Eq. (2) can be rewritten as follows:

$$K' = [h^{\cdot}]^2 / Po_2^{1/2} \qquad (3)$$

where K' is a constant. In Eq. (3), $[h^{\cdot}]$ is proportional to $Po_2^{1/4}$. When $h^{\cdot}$ plays a dominant carrier in conductivity, log(conductivity) is also proportional to log Po_2, which gives the slope of 1/4 in the log(conductivity)-log Po_2 plot. This value of the slope (0.25) agrees well with the result determined by the EIS measurements (0.247). The conductivity measurements demonstrate that the charge carrier of the conductivity of the PT crystals at 800 °C as well as room temperature is $h^{\cdot}$. It is shown that $h^{\cdot}$ is

dominant carrier for electron conduction at temperatures from 25 °C to 800 °C [17].
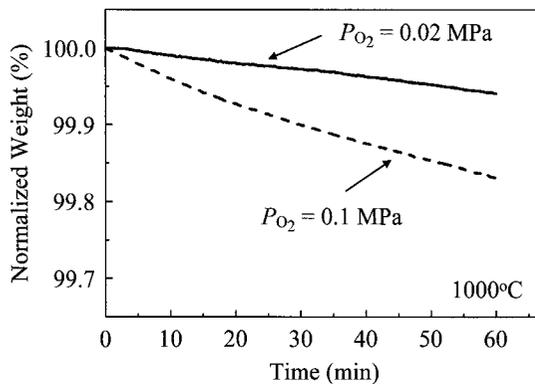
Fig. 5 Weight loss at 1000 °C
as a function of time for PT crystals

Figure 5 indicates the results of TG for the PT crystals at 1000 °C. While PT crystals did not show any weight loss below 950 °C, a marked loss of weight appeared at 1000 °C. The weight loss seems to be caused by the vaporization of Pb from PT crystals. A larger weight loss was observed under a higher P_{O_2}. The P_{O_2} dependence of weight loss enables us to consider the rate-determining process during defect formation for the PT crystals [18]. The enhanced vacancy formation of Pb under a higher oxygen partial pressure demonstrates that the surface reaction between Pb atoms and O atoms adsorbed onto the PT surface, which leads to PbO (g), is the limiting factor for the vacancy formation in the PT system. Pb ions in the lattice move to the surface of the crystals, react with oxygen adsorbed on the surface, and then PbO vaporize as gas phase, i.e., PbO (g) [19, 20]. The reactions of the Pb vacancy formation can be described as follows:

$$Pb_{Pb}^* \rightarrow V_{Pb}^{''} + 2\,h^{.} + Pb_{ad} \quad (4)$$

$$Pb_{ad} + 1/2\,O_2 \rightarrow PbO\,(g) \quad (5)$$
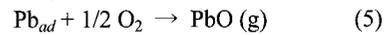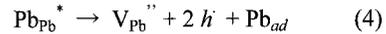
where Pb_{ad} denotes the lead atom adsorbed on the crystal surface, Pb_{Pb}^* is the lead ion at the Pb site and $V_{Pb}^{''}$ is the lead vacancy at the Pb site. A higher P_{O_2} is found to promote the reaction of Eq. (5), as can be seen in Fig. 5. Thus, the formation of Pb vacancies is accompanied with the generation of $h^{.}$ (see Eq. (4)). In the cooling process after the crystal growth, PT crystals absorb oxygen from the atmosphere, as expressed by Eq. (1) and therefore these reactions increase $[h^{.}]$.

Figure 6 represents the schematic representation of the defect formation mechanism in PT crystals. Taking oxygen vacancies and lead vacancies into account, we can rewrite the composition of PT as $Pb_{1-x}TiO_{3-y}$. Perfect PT crystals ($x = y = 0$) are an insulator. At high temperatures, the formation of Pb vacancies is a dominant reaction (see Eq. (4)), and then the following defect condition; $x > y$ is established in PT crystals. At cooling process, absorption of oxygen from the atmosphere (the reaction shown in Eq. (1)) enlarges the difference between x and y, i.e., the defect condition $x \gg y$ is set in the PT lattice. A high p-type conduction observed in the PT crystals at room temperature in addition to 800°C can be explained by the defect structure that excess Pb vacancies (x) compared with oxygen vacancies (y) act as an electron-hole donor.

To obtain PT single crystals with a low leakage current (high resistance), both oxygen vacancies and lead vacancies must be reduced. It is revealed that heat treatment conditions strongly affect the creation of these vacancies, and adjusting these conditions is suggested for improving the insulating properties in the PT system.

4. CONCLUSION

PT single crystals were grown by a self-flux method, and the leakage current properties and polarization properties were investigated along the [100] cubic
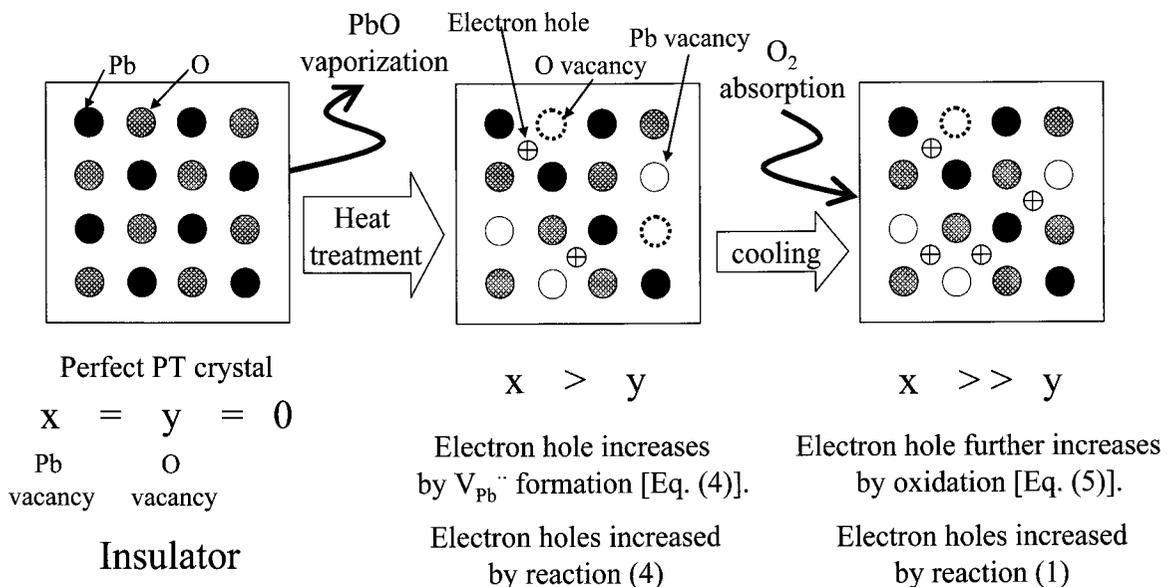
Fig. 6 Schematic representation of the defect formation
in the PT system at high temperatures.

direction. Annealing under a high oxygen partial pressure increased leakage current density by about one order of magnitude. At 800 °C, the conductivity of PT crystals increased in proportion to $Po_2^{1/4}$. These results provide direct evidence that electrical properties of PT crystals from room temperature to 800 °C are governed by p-type conduction. It is shown that the charge carrier in the PT crystals is electron-hole. The formation of Pb vacancies in high-temperature heat treatments is shown to increase electron hole, and furthermore oxygen absorption in cooling process leads to a further increase in electron hole, resulting in a higher leakage current at room temperature.

5. ACKNOWLEDGEMENT

6. REFERENCES

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