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Electrical Properties of $Sr_{1-x}La_xTiO_3 (0 \leqq x \leqq 0.10)$ Single Crystals Grown by the Floating Zone Method

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$Sr_{1-x}La_xTiO_3$ $(0 \leqq x \leqq 0.10)$ single crystals were grown by a floating zone method. We found that electrical resistivity decreased with increasing La content and was 10^{-3}–10^{-4} Ω cm at room temperature. The resistivity decreased with decreasing temperature but not linearly. The negative sign of the Hall coefficient indicated charge carriers to be electrons for all compositions. The linear relation between the reciprocal Hall coefficient and the electrical conductivity for the La-doped samples implied that the carrier mobility was constant and the conductivity depended only on the carrier concentration at room temperature. The resistivity of oxygen-deficient-type $SrTiO_{2.98}$ was 1 to 2 orders of magnitude larger than that of $Sr_{1-x}La_xTiO_3$ because of both low carrier concentration and low carrier mobility.

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Introduction

In recent years, conducting oxide materials have received great attention (*1–7*). The perovskite-type stoichiometric strontium titanate ($SrTiO_3$) is essentially an insulator, but reduced or donor-doped strontium titanate has an increased electrical conductivity (*8*). Conducting strontium titanate is a promising material for electronic applications, e.g., as an electrode for photoelectrolysis of water (*9*).

Pentavalent or trivalent ions have been used as dopants; Nb^{5+} (*10*), Y^{3+} (*11*), Nd^{3+} (*12*), and La^{3+} (*13*). However, there have been no reports on the electrical properties of strontium titanate doped with the above 2.0 at.% dopant. This could be due to the difficulty in preparation of a homogeneous specimen with high dopant level.

In this study we have successfully grown $Sr_{1-x}La_xTiO_3$ single crystals containing La^{3+} ion up to $X = 0.10$ by a floating zone (FZ) method, by which relatively large and homogeneous crystals can be grown. This report discusses some electrical properties of $Sr_{1-x}La_xTiO_3$ and oxygen-deficient-type $SrTiO_{2.98}$ in relation to the defect structure in these materials.

Experimental

$Sr(NO_3)_2$, La_2O_3, and TiO_2 powders were weighed to give $Sr_{1-x}La_xTiO_3$ $(0 \leqq x \leqq 0.10)$ and mixed in an agate mortar with ethanol. The powder was calcined at 1000°C for 10 hr in air. After grinding, the powder was molded in a cylindrical rubber tube under a hydrostatic pressure of 100 MPa to be a rod, typically 10 mm in diameter and 100 mm long. The molded specimen was introduced into a vertical tube furnace and sintered at 1300°C for 3 hr.

Crystal growth was effected by using an infrared radiation convergence-type apparatus with double ellipsoidal mirrors, in which

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FIG. 1. As-grown $SrTiO_{2.98}$ single crystal.

two halogen lamps were set as the infrared source, as for the other FZ growth of oxide materials (*14, 15*). The feed rod was suspended from the upper shaft with a platinum wire and a seed crystal, which was polycrystalline in this study, was fixed to the lower shaft. Rotation rate for both the feed rod and the seed crystal (counter rotation) was 30 rpm and the growth rate was 10 mm/hr. The growth run was carried out in a nitrogen flow of 2 liters/min to reduce some of titanium ions.

The lattice parameter was determined by the X-ray powder method using Si powder as an internal standard. Weight gain of the powdered specimen was measured by the oxidation in air at 1000°C for 24 hr in order to estimate Ti^{3+} content of the as-grown crystals from the reaction

$$Sr_{1-x}La_xTi^{3+}_xTi^{4+}_{1-x}O_3 + (x/4)O_2 \rightarrow (1-x)\,SrTi^{4+}O_3 + (x/2)La_2Ti^{4+}_2O_7.$$

Grown crystals were cut perpendicularly to the growth direction and were disk-shaped, 2 mm in thickness. A mechanically polished surface was etched with concentrated H_2SO_4 at 200°C. We determined whether the sample was a single crystal or polycrystalline from its etched pattern. A rectangular specimen was cut from the disk for electrical measurements. Temperature dependence of the resistivity was measured in the range of room temperature to 4.2 K by a four-probe method. The Hall coefficient was also measured at room temperature in a magnetic field of 10^4 G.

Results and Discussion

Figure 1 shows a representative grown crystal for $x = 0$, which was black in color with a lustrous surface. This indicates the as-grown crystal was nonstoichiometric, since the stoichiometric $SrTiO_3$ is colorless. Although the seed crystal was polycrystalline, the extremity of the grown crystal became a single crystal. This was determined by the etched pattern on the cross section, in which no grain boundary was found. When a solid–liquid interface of a growing crystal is convex toward the melt, grain boundaries are excluded perpendicularly to the interface, and a single crystal is, as a result, obtained at extremity (*16*). According to Kitamura *et al.*, the convex interface shape is usually observed during the growth of oxide materials which absorb the radiation from the heating lamp (*17*). In this study, all the grown crystals would readily absorb the radiation, because of their black color. Consequently, a convex interface shape would be realized during the crystal growth and single crystals were obtained.

$Sr_{1-x}La_xTiO_3$ had cubic structure for La content of up to 10 at.%. Figure 2 shows the relationship between La content and lattice parameters of $Sr_{1-x}La_xTiO_3$ calculated from the diffraction on the (310) face. The lattice parameters increased linearly with increasing La content. The ionic radius of La^{3+} is just less than that of Sr^{2+}, i.e., La^{3+} : 0.123 nm and Sr^{2+} : 0.125 nm for 12-fold coordination. On the other hand, the ionic radius of Ti^{3+}, which formed for the charge compensation, is larger than that of Ti^{4+}, i.e., Ti^{3+} : 0.076 nm and Ti^{4+} : 0.068 nm for 6-fold coordination. Ti^{3+} constant was approximately equal to nominal La content for any composition from the weight gain after the oxidation. Accordingly, the increase in lattice parameters is attributable to the increase in Ti^{3+} content of the crystals.

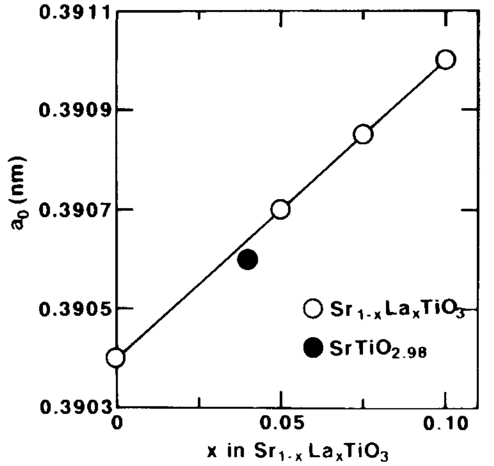

FIG. 2. The relation between La content and lattice parameters of $Sr_{1-x}La_xTiO_3$.

In Fig. 2, a solid circle indicates the lattice parameter of reduced $SrTiO_{2.98}$, in which Ti^{3+} content corresponds to that of $x = 0.04$ in $Sr_{1-x}La_xTiO_3$. The lattice parameter is larger than that of $SrTiO_3$ (0.3904 nm). In this case, the formation of the Ti^{3+} ion is again responsible for the increase in the lattice parameter.

Figure 3 shows the temperature dependence of electrical resistivity for $Sr_{1-x}La_xTiO_3$. The resistivity decreased with increasing La content and 10^{-3}–10^{-4} Ω cm at room temperature. For any composition, the resistivity decreased with decreasing temperatures but not linearly. This result agrees with previous study by Uematsu *et al.* (*13*), though, in their study, the La content was only up to 2 at.% and the temperature range for the resistivity measurements was only that above room temperature. We found that the temperature dependence of resistivity for $SrTiO_{2.98}$ was very similar to that for $Sr_{1-x}La_xTiO_3$. This result indicates that the dominant scattering process for charge carrier in both $Sr_{1-x}La_xTiO_3$ and $SrTiO_{2.98}$ is essentially identical. The nonlinear dependence of resistivity for temperature is also found in Na_xWO_3 (*4*) and ReO_3 (*5*), in which optical mode phonon scattering is recognized as the dominant scattering processes for electrical resistance. However, the behavior of resistivity we observe for $Sr_{1-x}La_xTiO_3$ is not readily attributed to optical phonon scattering at this stage.

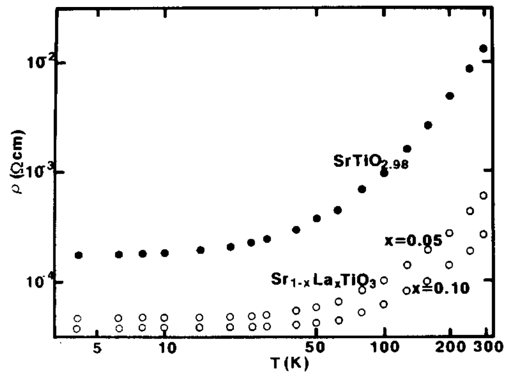

FIG. 3. Temperature dependence of resistivity for $Sr_{1-x}La_xTiO_3$ and $SrTiO_{2.98}$.

At room temperature, the resistivity for $SrTiO_{2.98}$ was about 10^2 Ω cm, which was 1 to 2 orders of magnitude larger than that of $Sr_{1-x}La_xTiO_3$, although the Ti^{3+} content of about 4 at.% was comparable to that for $Sr_{1-x}La_xTiO_3$.

The electrical conductivity (σ), namely the reciprocal of resistivity, is generally expressed as

$$\sigma = n e \mu, \tag{1}$$

where n is carrier concentration, e is elementary electric charge, and μ is carrier mobility. If n and μ are determined for each composition, the difference in the resistivity between $Sr_{1-x}La_xTiO_3$ and $SrTiO_{2.98}$ might be clarified. The reciprocal of the Hall coefficient, $1/R_H$, is proportional to the carrier concentration, that is,

$$1/R_H = n e. \tag{2}$$

On the basis of Eq. (1) and Eq. (2), the carrier concentration and mobility are readily calculated. Thus, we investigated the Hall coefficient for each composition.

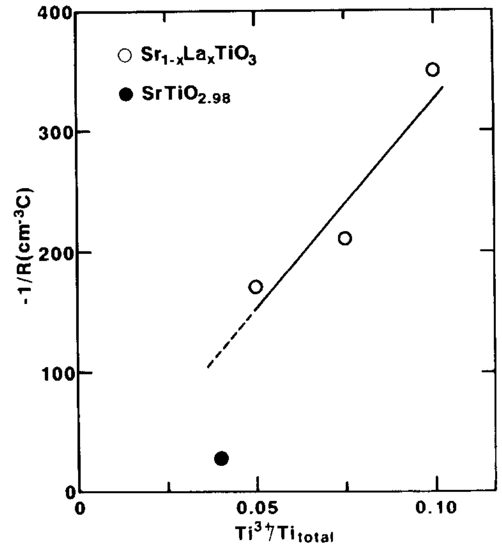

FIG. 4. The relation between the Ti^{3+} content and the reciprocal of the Hall coefficient for $Sr_{1-x}La_xTiO_3$ and $SrTiO_{2.98}$.

Figure 4 shows the relation between Ti^{3+} content and the reciprocal Hall coefficient. The sign of the Hall coefficient was negative for all compositions, and the dominant charge carrier was therefore electrons in this system. In $SrTiO_{2.98}$, the reciprocal of the Hall coefficient is very small compared with that of $Sr_{1-x}La_xTiO_3$. According to Eq. (2), the carrier concentration in $SrTiO_{2.98}$ would be considerably lower than in $Sr_{1-x}La_xTiO_3$. The oxygen vacancies formed in $SrTiO_{2.98}$ might trap some electrons.

Figure 5 shows the relation between the reciprocal Hall coefficient and the electrical conductivity for $Sr_{1-x}La_xTiO_3$ and $SrTiO_{2.98}$. For $Sr_{1-x}La_xTiO_3$, a linear relation holds within $0.05 \leqq x \leqq 0.10$, while a solid circle for $SrTiO_{2.98}$ indicates negative departure from the extrapolation of the linear relation. On the basis of Eq. (1), the carrier mobility is constant in $Sr_{1-x}La_xTiO_3$. The electrical resistivity therefore depends on only the carrier concentration. The negative departure of $SrTiO_{2.98}$ from the extrapolation of the linear relation in $Sr_{1-x}La_xTiO_3$ implies a lower carrier mobility than that of $Sr_{1-x}La_xTiO_3$. In $SrTiO_{2.98}$, the oxygen vacancies might behave as the dominant scattering processes at room temperature. Consequently, relatively larger resistivity of $SrTiO_{2.98}$ can be explained by both low carrier concentration and low carrier mobility.

Conclusion

$Sr_{1-x}La_xTiO_3$ single crystals were successfully grown by the floating zone method in the range of $0 \leqq x \leqq 0.10$. The lattice parameters of the crystals increased linearly with increasing La content because of the formation of Ti^{3+} in lattice positions. The resistivity for $Sr_{1-x}La_xTiO_3$ decreased with increasing La content and decreased with decreasing temperatures as it did for $SrTiO_{2.98}$. The charge carriers were electron, since the sign of the Hall coefficient

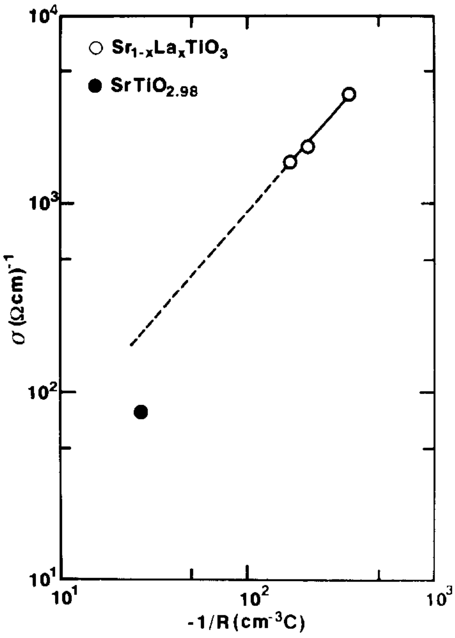

FIG. 5. The relation between the reciprocal of the Hall coefficient and conductivity for $Sr_{1-x}La_xTiO_{2.98}$ and $SrTiO_{2.98}$.

was negative. For $Sr_{1-x}La_xTiO_3$, the linear relation between the reciprocal of the Hall coefficient and electrical conductivity indicated that the carrier mobility was constant and the conductivity depended only on the carrier concentration at room temperature. For oxygen-deficient-type $SrTiO_{2.98}$, the relatively larger resistivity than for $Sr_{1-x}La_xTiO_3$ was attributable to both low carrier concentration and low carrier mobility.

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