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Electrical properties of La-doped $SrTiO_3$ (La: 0.1 to 2.0 at %) single crystals grown by xenon-arc image floating zone method

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Lanthanum-doped semiconducting strontium titanate single crystals having various lanthanum contents were grown in an air atmosphere by the xenon-arc image floating zone method. The crystals were characterized by X-ray powder diffraction, EPMA analysis and chemical analysis. Each lanthanum was accompanied by a trivalent titanium ion in the grown crystal. The electrical conductivity of these crystals was measured at 20 to 1150° C, and it was found to increase linearly with increasing lanthanum content. The mobility of the charge carrier was estimated from the concentration of trivalent titanium and the conductivities of the crystals. The mobility in the low temperature region agreed with previous studies. However, a significant difference was found at high temperatures. An error in the temperature dependence in the previous study is responsible for this difference. It is stressed that care is necessary in applying the results of single crystalline studies when discussing high-temperature bulk defect chemistry.

1. Introduction

Donor-doped semiconducting strontium titanate is an important material for the production of electronic components [1, 2] and is also a promising electrode material for the photoelectrolysis of water [3–5]. Its properties have often been studied very carefully on single crystalline specimens [6–21]. However, these detailed studies were confined to the lightly doped and/or reduced crystals in the low temperature region. There have been no reports on the electrical properties above room temperature for material containing more than $2 \times 10^{19}\,cm^{-3}$ (0.1 at %) donor, which is a very important range for practical application. Furthermore, the growth conditions and dopant concentrations of the crystals are not given in most studies. All the crystals were apparently grown by the Verneuil method in N. L. Industry, except for that grown by Gerthsen *et al.* [15]. No report is available on the properties of crystals grown by any other method.

Semiconducting strontium titanate is formed by reducing a pure or donor-doped material [21]. Each donor ion creates one trivalent titanium ion in the doped material, $La_xSr_{1-x}Ti^{3+}_xTi^{4+}_{1-x}O_3$. In an undoped material, oxygen vacancies which are formed by the loss of oxygen, again create trivalent titanium ions [13, 22, 23]. These trivalent titanium ions cause n-type conduction. In an oxidizing atmosphere, donor dopants are compensated by strontium vacancies, and an insulator is formed, $La_xSr_{1-3x/2}V_{Sr_{x/2}}TiO_3$ [24–28]. The shift from semiconductor to insulator depends on the temperature and oxygen pressure [29, 30]. In an air atmosphere only reports on insulating material exist for donor-doped strontium titanate heated under 1450° C.

In this paper, the electrical conductivity of lanthanum-doped semiconducting strontium titanate single crystals is reported over a wide concentration (0.1 to 2 at %) and a wide temperature region (20 to 1150° C). The crystals used for this study were grown in our laboratory by the xenon-arc image floating zone method [31] in an air

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atmosphere. With this method, the dopant concentration in the crystal is essentially same as that in the starting material [32]. This is in clear contrast to previous single crystalline studies in which uncertainty is present about the concentration of donor dopant. In this study, the dopant concentration was determined directly by chemical analysis. Trivalent titanium ions, which were created by the donor dopants, were also determined by chemical analysis.

The present results show that each lanthanum ion creates one trivalent titanium ion at the growth temperature and that the defect structure at this temperature was frozen in the grown crystals. The results are basically an extension of previous single crystalline studies in the low temperature region. At high temperatures, however, the conductivity extrapolated from the low temperature region differs significantly from the present results. This was ascribed to the wrong temperature dependence of assumed mobility in the high temperature region in previous studies. The result was also applied to discuss some previous results of polycrystalline studies. The problems of using polycrystalline specimens in studying bulk defect chemistry are discussed.

2. Experiments

Polycrystalline feed rods for crystal growth were prepared from titanium dioxide (Toho Titanium Co Ltd), reagent grade strontium carbonate and lanthanum oxide (both from Soekawa Kagaku) as starting materials. They were weighed to give the composition $La_xSr_{1-x}TiO_3$ ($x = 0$ to 0.02), added with a small amount of distilled water and mixed in a plastic ball mill for 5 h. The dried slurry was calcined at 1050° C for 10 h. The powder was added to PVA as a binder and was formed into rods (5 mm diameter by 60 nm) isostatically (1000 kg cm^{-2}), and sintered at 1050° C for 10 h. Similarly, rods of composition $La_xSr_{1-3x/2}TiO_3$ were prepared to examine the effect of starting composition on the growth behaviour.

Crystals were grown on a sintered rod of the same composition by the xenon-arc image floating zone method in a flowing air atmosphere at a growth rate of 20 to 30 mm h^{-1}. The lanthanum content and major impurities in the crystals were determined on two crystals. The compositional fluctuation of the crystal was examined by EPMA on a cut and polished surface of a crystal containing 2 at % lanthanum.

A rectangular bar (typically 1.5 mm x 1.5 mm x 15 mm) was cut from the crystal for electrical conductivity measurement. Fine platinum electrodes (0.1 mm diameter) for the four-point d.c. method were attached with a small amount of platinum paste (for high temperature measurement) and indium–gallium alloy (for room temperature measurements). A constant voltage d.c. power supply was used as a current source, and a strip chart recorder (internal impedance 10 MΩ) was used to measure the potential drops across the inner electrodes and the standard resistor which was connected in series to the specimen. The measurements were repeated by changing the polarity of the current, and the reading was averaged to cancel the potential generated by the thermal effect. The specimen was heated with a piromax-wound electric furnace. The temperature was controlled with a Pt13Rh–Pt thermocouple and an ON–OFF type temperature regulator. The temperature of specimen was measured using a second Pt13Rh–Pt thermocouple placed within 5 mm of the specimen. The atmosphere was flowing oxygen, argon or hydrogen.

The concentration of trivalent titanium ions, Ti^{3+}, in the crystal was measured using the method reported by Bois *et al.* [33]. Finely ground crystal was dissolved in a concentrated HCl solution containing ferrous ions, Fe^{3+}, in a flowing argon atmosphere. The total amount of Ti^{3+} ions was calculated from the concentration of Fe^{2+} ions which were formed by Reaction 1.

$$Ti^{3+} + Fe^{3+} \rightarrow Ti^{4+} + Fe^{2+} \qquad (1)$$

3. Results

3.1. Crystal growth and characterization

The starting composition has a significant effect on the growth behaviour. With the composition $La_xSr_{1-x}TiO_3$, the floating zone was very stable and the crystals were grown in the stationary condition. The melting temperature of the melt in the floating zone is constant with time and so is the output power of the xenon lamp required to maintain the zone. This occurs as expected when the cationic compositions are the same in starting feed rod and the grown crystal. If the anion sublattice is complete in the grown crystal, this growth behaviour suggests that the composition of the crystal can be expressed as $La_xSr_{1-x}Ti^{3+}_xTi^{4+}_{1-x}O_3$. With the starting composition, $La_xSr_{1-3x/2}TiO_3$, however, the floating

TABLE I Chemical analysis of crystals. (a) Comparison of lanthanum content in the starting feed rods and in the as-grown crystals.

Crystal number	La added to starting powder (wt %)	La found in crystal (wt %)
0.4La–$SrTiO_3$	0.30	0.29
2.0La–$SrTiO_3$	1.51	1.56

(b) Elements determined spectroscopically

Elements	0.4La–$SrTiO_3$	2.0 La–$SrTiO_3$
Ag	+ – ++	+ – ++
Al	+ – ++	+ – ++
Ba	*	*
Ca	++	
Cr	–	± – +
Cu	– – ±	–
Fe	+	+
La	++ – +++	+++
Mg	++ – +++	++ – +++
Mn	± – +	± – +
Si	+ – ++	+ – ++
Sn	±	±
Sr	strong	strong
Ti	strong	strong

No other elements found.
*Cannot be determined owing to interference.

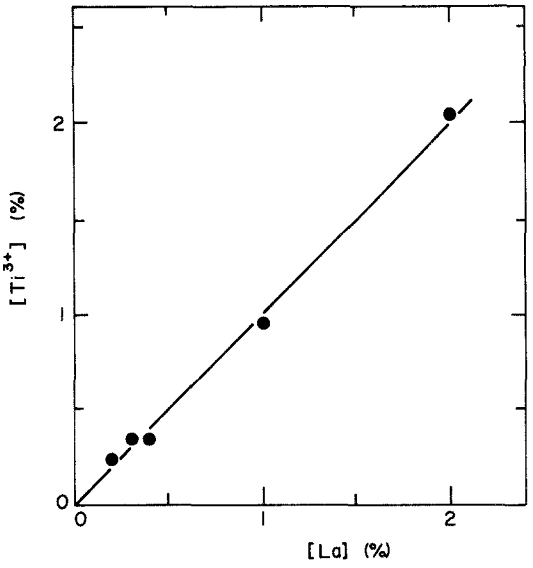

Figure 1 Relationship between the lanthanum content in the feed rod and the content of trivalent titanium in the as-grown crystal. The linear line shows the relationship expected from $La_xSr_{1-x}Ti_x^{3+}Ti_{1-x}^{4+}O_3$.

zone was unstable. The quantity of melt in the floating zone increased as the zone moved during the growth operation. The melt tended to flow off when its quantity became excessively large. Reducing the input power to the xenon lamp with time had some effect in compensating this increasing melt. However, the occasional flow out of the melt could not be avoided even with this adjustment. The source of this trouble is the difference in the cationic composition between the starting material and the grown crystal: assuming that the composition of the grown crystal is essentially same as that grown above, titanium dioxide in the starting material is in excess, relative to strontium and lanthanum oxides in this case. Excessive titanium dioxide, which could not enter the crystal lattice of strontium titanate, accumulated in the melt, reducing its melting temperature. When the melt became too rich in titanium oxide, part of it flowed out. The crystals used in this study were consequently grown from the starting composition $La_xSr_{1-x}Ti^{4+}O_3$.

Single crystals having a lanthanum content, x, up to 0.02 were successfully grown in this study. Their typical size was 3 to 4 mm diameter × 40 mm. The colour of all crystals was blue and became darker with increasing lanthanum content. Powder X-ray diffraction of the pulverized crystals shows sharp diffraction peaks of perovskite phase only. The concentrations of lanthanum determined by chemical analysis are presented in Table I for two representative crystals, $x = 0.004$ and 0.02. Clearly the lanthanum contents were the same in the starting feed rods and the grown crystals, as expected. In the same table, major impurities determined spectroscopically are also presented. Impurities with the highest concentrations are calcium and magnesium.

Fig. 1 shows the relationship between the lanthanum content in the feed rod and the content of trivalent titanium in the grown crystals. The concentration of lanthanum ions is equal to that of trivalent titanium ions which is in agreement with that expected from the composition $La_xSr_{1-x}Ti_x^{3+}Ti_{1-x}^{4+}O_3$.

Thinned crystals show stripes of a weaker colour perpendicular to the growth direction, suggesting a non-uniform distribution of lanthanum ions in the crystals. Attempts to determine this non-uniformity were only partially successful. Fig. 2 shows the results of EPMA scans (48 μm min^{-1}) along and normal to the growth direction. In the figure, the intensities of lanthanum $L\alpha_1$, and strontium $L\alpha_2$ were normalized relative to that of titanium $K\alpha_1$. For the lanthanum, the

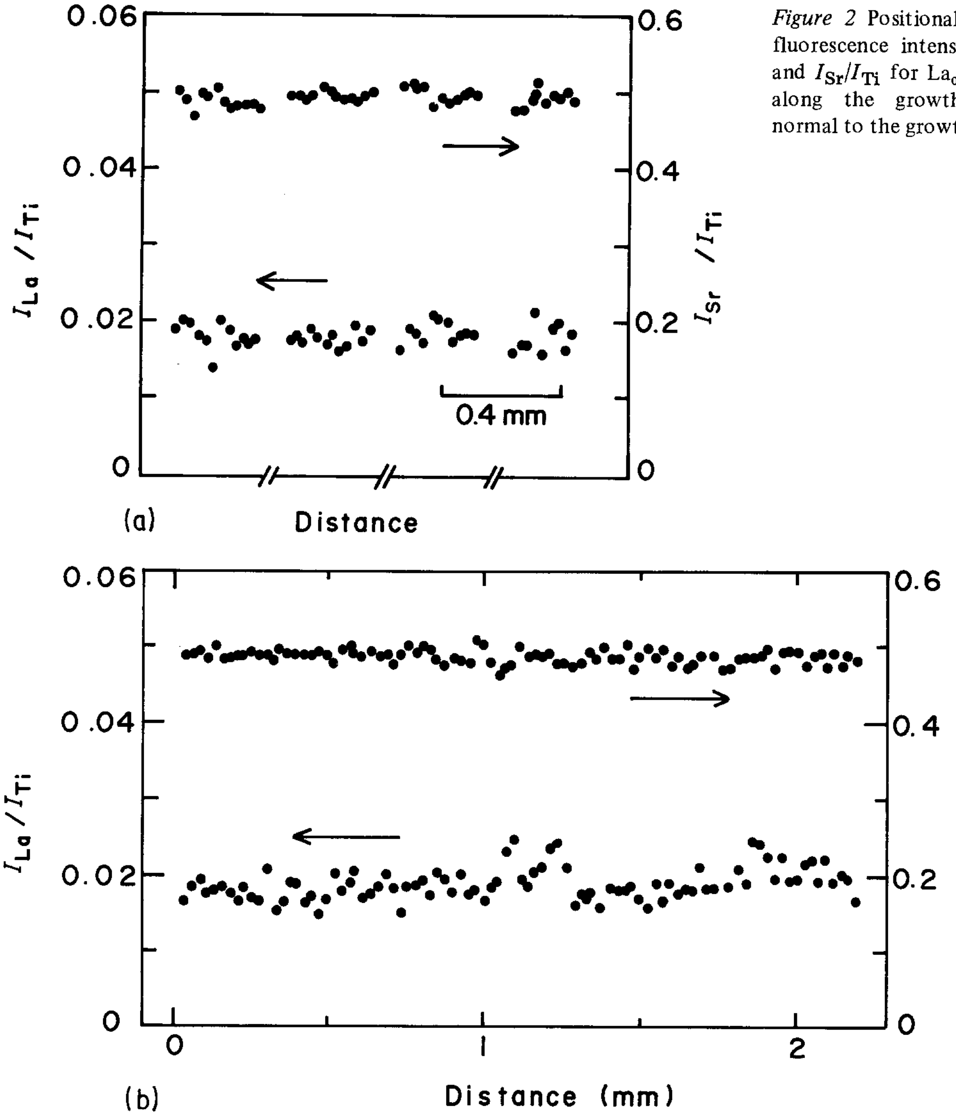

Figure 2 Positional change of X-ray fluorescence intensity ratios I_{La}/I_{Ti} and I_{Sr}/I_{Ti} for $La_{0.02}Sr_{0.98}TiO_3$: (a) along the growth direction; (b) normal to the growth direction.

scatter of this normalized intensity was comparable to that recorded at a fixed position without scanning. No definitive conclusion could be drawn on the non-uniform distribution of dopant. Only the range of non-uniformity could be estimated: by assuming the experimental accuracy (± 0.005 mol%), the local compositional change which may be present in the crystal was estimated to be 0.015 to 0.025 for $x = 0.02$.

3.2. Electrical conductivity

Fig. 3 shows the electrical conductivities of crystals with various lanthanum contents. The conductivity decreased with increasing temperature and with decreasing lanthanum content. For all crystals, the conductities were very reproducible and were affected less than a few percent by the atmosphere during measurement, except for that with $x = 0.001$. The major effect of atmosphere was the electrical noise occurring during the conductivity measurement, especially at lower temperatures (100 to 700° C). The noise increased in the order hydrogen, argon and oxygen atmosphere. This can be attributed to the formation of a very thin layer having a high electrical resistance on the crystal surface. Consequently, the results shown in Fig. 3 were made in a hydrogen atmosphere at 100 to 600° C and in an argon atmosphere at 600 to 1150° C except for that with $x = 0.001$. The high temperature conductivity extrapolated to room temperature essentially agreed with that of the as-grown crystals. For the crystal having

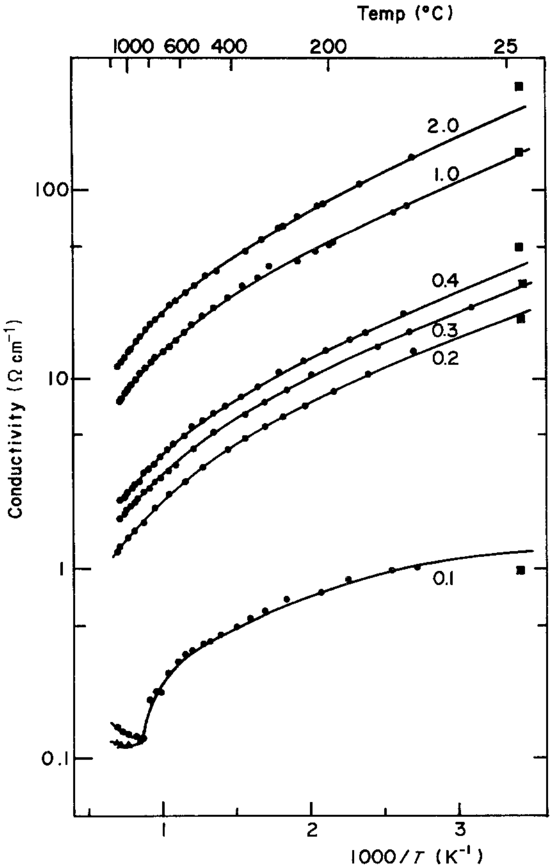

Figure 3 Electrical conductivites of semiconducting strontium titanate single crystals having various lanthanum contents: •, in argon or hydrogen; ▲, in oxygen; ■, as-grown crystal. The numbers on the curves show the lanthanum content (at %).

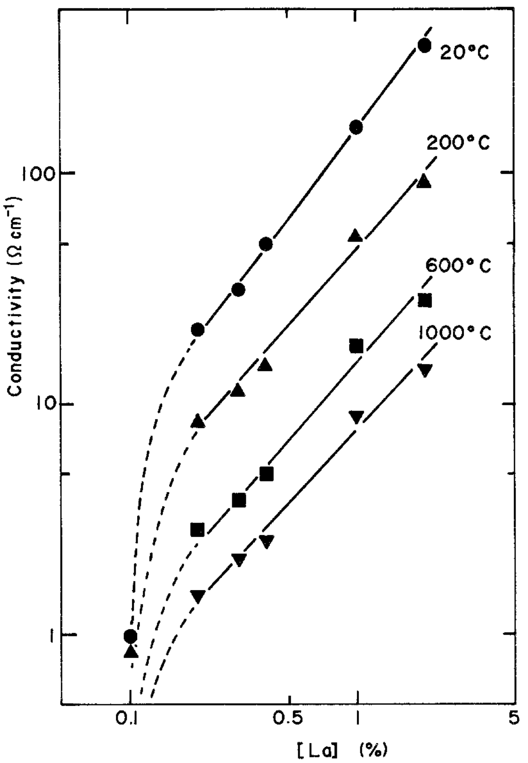

Figure 4 The relationship between the lanthanum content and conductivity at various temperatures.

$x = 0.001$, conductivity was higher in the argon atmosphere than in the oxygen atmosphere at temperatures above 900° C.

Fig. 4 shows the relationship between lanthanum concentration and conductivity at various temperatures. At all temperatures, the conductivity increases linearly with the concentration of lanthanum, except for that with $x = 0.001$.

4. Discussion

The above results can be understood assuming:

1. the composition of the crystal is expressed as $La_xSr_{1-x}Ti^{3+}_xTi^{4+}_{1-x}O_3$ at the growth condition; and
2. the high temperature defect equilibrium during the crystal growth is frozen into the grown crystals except for that with $x = 0.001$. The first assumption is supported by the results shown in Fig. 1. The second assumption is supported by the results on bulk conductivity, which is not affected by the atmosphere of measurement over a reasonable time period (100 h). If the defect structure is not frozen, the concentration of defects is governed by the temperature and oxygen pressure as found for the crystal with $x = 0.001$. A gradual change of conductivity should occur after a stepped change in temperature or atmosphere [34, 35], neither of which was found in Fig. 3 for the crystals having $x \geqslant 0.002$. For these crystals, only the conductivity near the surface was affected, as indicated from the noise experienced during conductivity measurements. The difficulty of oxidizing a fully reduced semiconductor to form a less conductive material is also reported for single crystalline strontium titanate [17] and also for polycrystalline barium titanate [36].

The formation of semiconducting crystals in an oxidizing condition can be attributed to the high growth temperature. In donor-doped strontium titanate and also in barium titanate, the structural analogue, the defect structure tended to favour the formation of semiconducting material with increasing temperature and/or with decreasing oxygen pressure [24, 30, 37, 38]. The oxygen pressure

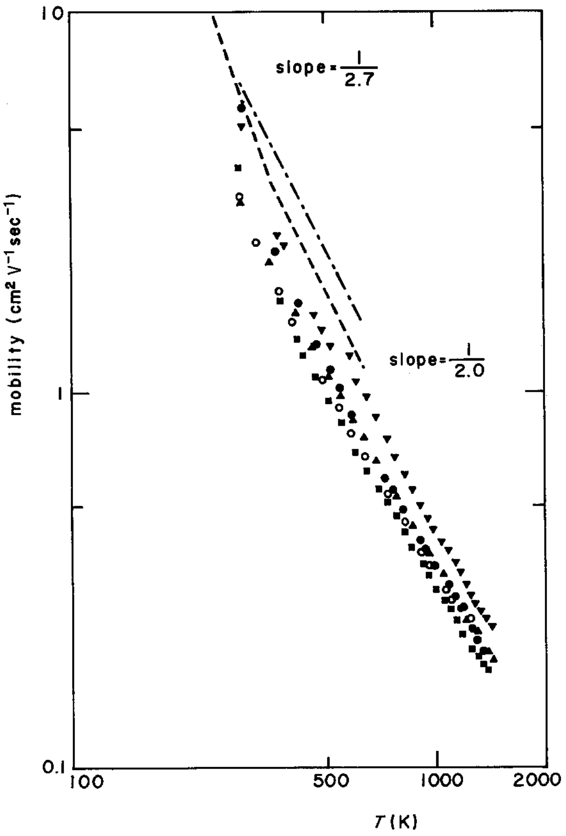

Figure 5 Charge carrier mobilities in semiconducting strontium titanate single crystals having various lanthanum concentrations: ▲, $x = 0.002$; ○, 0.003; ■, 0.004; ▼, 0.01; ●, 0.02. ---, Tufte and Chapman [11]; —·—·—, Perluzzo and Destry [17].

allowing the formation of semiconducting materials increases with increasing temperature. In the donor-doped barium titanate system, the defect type of $La_xBa_{1-x}TiO_3$ is, in fact, formed even under oxidizing conditions above 1300° C [38]. At a given temperature, a much stronger reduction is required to form semiconducting material in lanthanum-doped strontium titanate [13, 21]. At 1450° C, which is the highest temperature previously studied in detail for the material, sintering in air reportedly resulted in an insulating material [24]. A still higher temperature is apparently necessary to shift the defect structure from that forming insulating material to that forming semiconducting material in air [39]. The present results show that such a formation of semiconducting strontium titanate is, in fact, possible at the melting point, 1900° C [40] in an air atmosphere.

Fig. 5 shows the mobility of the charge carrier, electrons, for various crystals. For the calculation of mobility, the carrier concentration was assumed to be equal to the lanthanum concentration (assumption 1). Complete ionization of the donor was reported down to liquid helium temperature [11, 14]. In the figure, the mobility decreased with increasing temperature (approximately T^{-2}), but was affected only slightly by lanthanum concentration. The mobility found in this study was 3.2 to 5.6 cm^2 V^{-1} sec^{-1} at room temperature. Table II summarizes the reported mobilities of the carriers. The mobility does not change significantly with carrier concentration, which agrees well with the present results. At room temperature, the magnitude of mobility in the present study is slightly smaller than those reported in the Hall studies, weight change [15] and density measurements [21]. The mobility determined in this study represents the drift mobility. In a non-degenerate semiconductor, this is characteristically different from the Hall mobility by a factor of $1/r$, where r is an assumed constant which varies with the scattering mechanism of carriers (1.18 for acoustic phonon scattering, 1.10 for optical phonon scattering, and 1.93 for impurity scattering) [41]. The optical phonon scattering is likely to be dominant in strontium titanate above room temperature [9, 11, 14, 16–19]. In addition, the characteristics of defects are expected to be different in the present crystal grown by the FZ method and those grown by the Verneuil method. With these slight uncertainties taken into account, the agreement of mobilities determined in this study and in the previous Hall studies was excellent around room temperature. However, mobilities determined by other methods were less accurate. Changes in weight and density associated with the semiconductor formation are very small [15], and have a high uncertainty. Defects generated extrinsically by impurities are neglected in the weight change measurements. The measured densities are reported to change from boule to boule [21].

Care is necessary in estimating the high temperature mobility (> 500 K) from the low temperature data by extrapolation. The extrapolated mobility at 1000° C is 2 to 3 times smaller than the true mobility. This error in estimation is ascribed to the wrong temperature dependence of mobility at high temperatures. Many previous studies [11, 12, 16, 20] report an approximately $T^{-2.7}$ dependence of mobility, which is considerably different from T^{-2} dependence determined in the present study. The temperature dependence

TABLE II Summary of reported carrier mobility

Authors	Dopant	Temperature (K)	Carrier concentration ($\mathrm{cm^{-3}}$)	Mobility ($\mathrm{cm^2\,V^{-1}\,sec^{-1}}$)	Remarks
Parker and Yahia [9]	–	190–500	4×10^{15}–1.6×10^{18}	4–13	
Tufte and Chapman [11]	–	1.6–550	2.7×10^{17}–2.4×10^{19}	5.2–8.0	
	Nb		1.4×10^{17}–2.8×10^{19}	4.8–6.7	
Frederikse *et al.* [12]	–	4.2–300	6.3×10^{17}–1.2×10^{19}	5–6.5	
	Nd: 0.05 wt %		4.8×10^{18}	6.5	
Frederikse and Hosler [14]	–	1–1000	3.5×10^{17}–5.3×10^{20} (4 K)		Mobility (> 300 K) not reported
	Nb: 0.01–1.0 wt %		5.7×10^{18}–3.8×10^{20} (4 K)	3.5–5	Mobility (> 300 K) reported only for Nb $\leqslant$ 0.05 wt %
	La: 0.025–0.1 wt %		3.1×10^{18}–1.6×10^{19} (4 K)	3.5–6	
Perluzzo and Destry [17]	–	300–700	6.8×10^{17}–1.2×10^{21}	5.9–7.1	
	Nb: 0.015–0.05 wt %		3.2×10^{18}–6.0×10^{20}	6.4	
Lee *et al.* [16]	–	2–300	7.7×10^{16}–3.3×10^{18}	3.3–4.7	
Gerthsen *et al.* [15]	–	room temp.	1×10^{19}–9×10^{19}	5.8 5.9 (gravimetric)	
Yamada and Miller [21]	–	77, 295	2.5×10^{18}–5.8×10^{19}	5.4–6.4	Density change consistent with Hall data

in previous studies was mostly determined in the low temperature region (⩽ 500 K) and is not directly applicable to higher temperatures. Careful re-examination of high temperature data in these reports shows that T^{-2} dependence does occur as shown in Fig. 5. Further support of the T^{-2} dependence is obtained by comparing the data of Walters and Grace [13] and Yamada and Miller [21]. Both authors use the single crystal grown by N. L. Industry. The former report the effect of oxygen pressure on the electrical conductivity and the latter the effect of oxygen pressure on carrier concentration. The mobility of the carrier calculated from these studies was $0.25\,\mathrm{cm^2\,V^{-1}\,sec^{-1}}$ at 1300° C, which agrees well with the present results but not with those extrapolated from low temperature data.

High temperature conductivity of donor-doped polycrystalline strontium titanate in a reducing condition (10^{-16} atm) [29] agrees apparently only with the present results. The linear increase in conductivity with increasing lanthanum content was the same as in the present study. However, the conductivity measured in that study was approximately one-fifth that obtained in the present study. A grain-boundary effect is the likely source of the difference. This strongly suggests that the conductivity of the polycrystalline specimen does not fully reflect the bulk property even at high temperature.

At low temperatures, the difference becomes even more serious. A significant difference is found between single and polycrystalline studies in the absolute magnitude of conductivity, in the temperature dependence and also in the dependence of conductivity on donor concentration [24, 30, 37]. In strongly reduced and quenched donor-doped polycrystals, the conductivities do not change linearly with the dopant concentration [30, 37]. At 300 K, the conductivity was maximum at $x = 0.002$ and decreased with both decreasing and increasing donor concentration. Their conductivities are one to three orders of magnitude lower than those of corresponding single crystals of this and previous studies. The temperature dependence of conductivity is reserved at low temperatures [24, 30, 37]: the conductivity of polycrystalline specimens increases with increasing temperature. The differences in low temperature electrical characteristics in polycrystalline and single crystalline specimens strongly suggest that the microstructure of polycrystalline materials is responsible. Re-equilibration of defects in the crystallite which forms the grains during quenching by oxidation and/or grain-boundary phenomena must be considered.

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