Carrier generation and compensation in Y- and Nb-doped CaTiO₃ single crystals

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Electrical and optical properties of $Ca_{1-x}Y_xTiO_3$ and $CaTi_{1-x}Nb_xO_3$ ($x=0, 10^{-4}, 10^{-3}$, and 10^{-2}) single crystals were studied to understand the mechanisms of carrier generation and compensation by donor doping. Single crystals were grown by the floating-zone method in O₂ flow using an infrared radiation furnace. In both Y- and Nb-doped cases, the crystals of x = 0, 10^{-4} , and 10^{-3} are almost insulating, and show a pale yellowish color. On the other hand, the crystals of $x=10^{-2}$ are conductive and show a blue color. The conductivity measurement under air at high temperatures, from 500 to 1700 K, showed that the conductivity first decreases with an increase in dopant concentration from x=0 to 10^{-3} , and remarkably increases with a further increase in the concentration to $x = 10^{-2}$. Moreover, the Seebeck measurement at high temperature showed p-type conduction in the samples with a dopant concentration up to $x=10^{-3}$, which indicates the existence of unintentional acceptors. The origins of acceptors are suggested to be Al impurity and oxygen excess. All of the doped samples ($x = 10^{-4}$, 10^{-3} , and 10^{-2}) become conductive after H₂ reduction at 1000 °C, and metallic behavior is observed at low temperature. Simultaneously with the remarkable increase in the conductivity after H₂ reduction treatments, an optical-absorption band due to carriers appears in the near-infrared region. Carrier concentrations in the metallic samples are $10^{13}-10^{15}$ cm⁻³ for $x=10^{-4}$, $(5-6)\times10^{18}$ cm⁻³ for $x=10^{-3}$, and $(2-3) \times 10^{19}$ cm⁻³ for $x = 10^{-2}$, and Hall mobilities are found to be 2-4 cm²/V s for all conductive samples. The change in the electronic state of carriers from small polarons to delocalized electrons is observed in the samples of $x = 10^{-3}$ with increasing temperature during H₂ reduction. [S0163-1829(97)04943-6]

I. INTRODUCTION

Electrical conductivity of wide-band-gap titanates has been successfully controlled by substitutional doping similar to that in semiconductors, and they have been used in practical applications such as electrodes, gas sensors, and resistors. In science and technology of materials, understanding the chemical state of dopants and the reactions induced by doping is one of the most important subjects. The electronic state of dopants in oxide semiconductors is considerably more complicated than those in silicon and III-V semiconductors. The complex behavior originates from a wide variety of crystal structures, miscellaneous chemical reactions including nonstoichiometry, and various charged dopants in oxides, which easily cause polarization due to lattice distortion. Considerable efforts have been contributed to the titanates with perovskite and perovskite-related structures such as CaTiO₃,¹⁻⁷ SrTiO₃,⁸⁻¹⁶ and BaTiO₃.¹⁷⁻²² In spite of these studies, carrier generation mechanisms by doping in the oxide semiconductors have not been definitely elucidated so far.

In the present study, carrier-generation mechanisms by substitutional donor doping and transport properties of generated carriers in CaTiO₃ single crystals are investigated. CaTiO₃, which is a prototype of double oxides, has a distorted perovskite structure,²³ and this enables one to compare the physical properties with other perovskite-type oxides. A few studies have been carried out about carrier-generation mechanisms by doping in CaTiO₃.^{5,6} However, polycrystal-line samples were used in these studies, and some problems such as the segregation of dopants at the grain boundary were not perfectly eliminated. On the other hand, there have been some studies on the electrical conductivity of CaTiO₃.

single crystals. George and Grace² examined the conductivity at high temperature under a reducing atmosphere and Cox and Tredgold³ measured it simply using some kinds of metals as electrodes. Therefore, these studies do not give much information about carrier-generation mechanisms. However, Cox and Tredgold reported, from the observation of relation between the conductivity and the working function of electrodes, that their single crystals show *p*-type conduction. Such *p*-type conduction of nominally undoped crystals is also observed in SrTiO₃ and BaTiO₃ single crystals, and some models like impurity defects and cation excess have been proposed to explain the *p*-type conduction. Since information about *p*-type conduction is very important for understanding carrier-generation mechanisms by doping, it will be referred to and discussed in comparison with our results. In the present paper, we will report the preparation of single crystals doped with Y or Nb and their electrical and optical properties, and discuss the chemical competition between the generation of conductive electrons and the compensation due to unexpected positive holes.

II. EXPERIMENT

Single crystals were grown by the floating-zone (FZ) method using an infrared radiation furnace. Y and Nb ions were selected as *n*-type dopants to substitute for Ca and Ti ions, respectively. The nominal compositions of single crystals are $Ca_{1-x}Y_xTiO_3$ and $CaTi_{1-x}Nb_xO_3$ (x=0, 10^{-4} , 10^{-3} , and 10^{-2}). Calcined powders of CaO (99.99%) and TiO₂ (99.99%) and aqueous solutions of Y(NO₃)₃ (99.99%) and NbCl₅ (99.99%) were used as starting materials. The appropriate amount of powders was mixed thoroughly in ethanol, and the aqueous solution of the dopant ion was prop-

12 998

erly added during the mixing process. After drying the mixed powder, it was calcined in air at 1250 °C for 48 h with intermediate grinding. The powder was reground and pressed by cold isostatic press (CIP) in a shape of rod, and the rods were sintered in air at 1450 °C for 6 h. The crystals were grown from the rods in O₂ flow at a growth rate of 4–10 mm/h. All as-grown crystals were once annealed in Ar flow at 1000 °C for 6 h to remove thermal stresses. The Arannealed crystals are called as-prepared crystals in this paper. Some pieces of these crystals were subjected to reducing treatment in H₂ flow at 600, 800, or 1000 °C for 6 h to observe changes in the electrical and optical properties.

In chemical analysis using the inductively coupled plasma (ICP) method, samples were dissolved into hot concentrated sulfuric acid, and the solution was properly diluted. The concentrations of dopants and cation ratio for each crystal were estimated, and the impurities of Al, Fe, and Cr in the x=0 sample were inspected.

Electrical conductivity measurements were performed by the dc four-probe method in a wide range of temperatures. The conductivity at high temperatures, from 500 to 1700 K, was measured under air using as-prepared samples, while the conductivity at low temperatures, from 10 to 300 K, was measured under a He atmosphere using H₂-reduced samples. Some electrodes were used in each temperature region to provide Ohmic contacts: Pt paste in the range from 1050 to 1700 K, Ag-Zn paste in the range from room temperature (RT) to 1150 K, and Ag-Zn or In-Ga paste in the range from about 10 K to RT. The thermoelectric power of as-prepared samples was also measured under air in the temperature range from 900 to 1600 K to estimate Seebeck coefficients at high temperatures.

The carrier density at RT of all conductive samples after H_2 reduction was estimated from the Hall measurement under a magnetic field of 1.5 T. The temperature dependence of the carrier density of the as-prepared sample with an $x = 10^{-2}$ Nb concentration was also measured by the Hall measurement.

Optical transmittance spectra were measured in the wavelength range from 200 nm to 25 μ m before and after H₂ reduction. The crystals used in the optical measurements were polished with 0.5- μ m diamond slurry and the thickness was adjusted to 200 μ m within 5% error. Two spectrometers were used for the optical measurements; the ultravioletvisible-near-infrared (UV-VIS-NIR) spectrometer (Hitachi) in the range from 200 to 3600 nm, and the Fourier transform infrared spectrometer (Perkin-Elmer) in the range from 1666 nm to 25 μ m (6000–400 cm⁻¹).

III. RESULTS

A. Chemical composition

Most of the single crystal rods grown by the FZ method are 4–6 mm in diameter, and 30–60 mm in length. In both Y- and Nb-doped cases, the as-prepared crystals of x=0, 10^{-4} , and 10^{-3} are insulating and show a pale yellowish color. On the other hand, the crystals of $x=10^{-2}$ are conductive and show a blue color.

Table I shows dopant concentrations analyzed by the ICP method. The analysis of $x = 10^{-4}$ samples was relatively difficult because of the small dopant concentration, especially

TABLE I. Dopant concentrations of $Ca_{1-x}Y_xTiO_3$ and $CaTi_{1-x}Nb_xO_3$ single crystals. (For n_{ideal} refer to Sec. III E).

Dopant	x (nominal)	x (analyzed)	$n_{\rm ideal}~({\rm cm}^{-3})$
Y	$ \begin{array}{r} 10^{-4} \\ 10^{-3} \\ 10^{-2} \end{array} $	6.6×10^{-5} 6.9×10^{-4} 5.6×10^{-3}	$\begin{array}{c} 1.1 \times 10^{18} \\ 1.2 \times 10^{19} \\ 1.1 \times 10^{20} \end{array}$
Nb	$ \begin{array}{r} 10^{-4} \\ 10^{-3} \\ 10^{-2} \end{array} $	$1.8 \times 10^{-4} \\ 1.0 \times 10^{-3} \\ 8.4 \times 10^{-3}$	$\begin{array}{c} 3.6 \times 10^{18} \\ 1.8 \times 10^{19} \\ 1.4 \times 10^{20} \end{array}$

for Nb ions which are not as sensitive as Y ions in the ICP method. The analyzed dopant concentrations are slightly different from the nominal ones for each concentration. However, the difference of the analyzed dopant concentrations between the samples of $x = 10^{-4}$, 10^{-3} , and 10^{-2} keeps almost one order of magnitude in each donor case. The deviation of cation ratio from nonstoichiometry is found to be less than 2% in the samples. However, the chemical analysis found an unintentional impurity in the sample of x=0. Fe and Cr impurities were not detected; therefore, their concentration are considered to be less than 100 ppm. (In this paper, ppm means a ratio by atom not weight.) On the other hand, an Al impurity was detected at a concentration of about 1000 ppm. Because starting materials do not include an Al impurity in such a high concentration, a grinding process using an alumina mortar is probably the origin of the contamination by Al ions. Therefore, we need to consider the influence of Al ions in the following discussions.

B. Temperature dependence of conductivity at high temperature

Figure 1 shows the temperature dependence of the electrical conductivity of as-prepared samples at high temperatures up to 1700 K. The measurement was carried out under air, and the elctrical conductivity was measured as temperature decreased in order to obtain reproducible results. Elec-



FIG. 1. Temperature dependence of the dc conductivity of asprepared single-crystal samples. $Ca_{1-x}Y_xTiO_3$: solid lines; $CaTi_{1-x}Nb_xO_3$: dotted lines; a dopant-free sample: dashed line.

Samples		Activation energies (eV) [Temperature ranges (K)]
	x = 0	2.01 (1580< <i>T</i> <1680), 0.60 (700< <i>T</i> <1300)
Y	$x = 10^{-4}$	2.03 (1580 $<$ T $<$ 1680), 0.92 (920 $<$ T $<$ 1110), 1.50 (760 $<$ T $<$ 870)
	$x = 10^{-3}$	2.44 (1580< <i>T</i> <1680), 1.80 (920< <i>T</i> <1470)
Nb	$x = 10^{-4}$	1.94 (1580 $<$ <i>T</i> $<$ 1680), 0.78 (930 $<$ <i>T</i> $<$ 1200), 1.12 (640 $<$ <i>T</i> $<$ 810)
	$x = 10^{-3}$	2.49 (1580< <i>T</i> <1680), 1.79 (950< <i>T</i> <1420)

TABLE II. Activation energies of dc conductivity of $Ca_{1-x}Y_xTiO_3$ and $CaTi_{1-x}Nb_xO_3$ single crystals at high temperatures.

tronic conduction, not ionic, is dominant in the whole temperature region, because no remarkable drop in the conductivity was observed after long-time polarization. However, dielectric effects prevented the dc measurements for the slightly conductive samples of x=0, 10^{-4} , and 10^{-3} at temperatures below about 500 K. The most notable observation in the figure is that the electrical conductivity first decreases with an increase in dopant concentration from x=0 to 10^{-3} , and remarkably increases with a further increase in the concentration up to $x=10^{-2}$.

The temperature dependence of conductivity is complicated and shows some thermal activation processes. The thermal activation energies of samples and corresponding temperature ranges are listed in Table II. For the samples of x=0, 10^{-4} , and 10^{-3} , the absolute values of the conductivity and slopes of the conductivity curves become almost the same between the samples in the region above about 1500 K, and this region can be interpreted as an intrinsic region. However, the origins of the other thermal activation processes from 600 to 1300 K are not elucidated only from the conductivity measurement.

C. Seebeck coefficients

Figure 2 shows the Seebeck coefficients of as-prepared samples measured at high temperatures. Referring to the con-



FIG. 2. Seebeck coefficients of $Ca_{1-x}Y_xTiO_3$ (solid lines), $CaTi_{1-x}Nb_xO_3$ (dotted lines), and dopant-free (dashed lines) single-crystal samples.

ductivity shown in Fig. 1, the Seebeck measurement was successful in a conductivity range higher than about 10^{-4} S cm⁻¹ in the present experiment.

The Seebeck coefficients for the samples of x=0, 10^{-4} , and 10^{-3} are positive and almost constant below 1300 K, with values between 1.0 and 1.5 mV/K, and gradually decreases above 1300 K, with an increase in temperature up to 1600 K. In the case of $x=10^{-3}$, the sign of the Seebeck coefficient changes from positive to negative at about 1500 K, indicating a change in the type of major carriers. The temperature region above 1300 K, where the Seebeck coefficients decreases, can be regarded as both a preintrinsic region and an intrinsic region, which is consistent with the result of the conductivity measurement at high temperatures. The Seebeck coefficients of $x=10^{-2}$ samples are negative and almost constant in the whole temperature range, with a slight increase from -1.0 and -0.7 mV/K.

From the result of the Seebeck measurement, it is clearly understood that the conduction in the highly conductive samples with $x=10^{-2}$ is *n* type, while that in the slightly conductive samples with x=0, 10^{-4} , and 10^{-3} is *p* type.

D. Conductivity at low temperature

Figure 3 shows the electrical conductivity of H_2 -reduced samples measured at low temperature. Since the measurement was carried out continuously for each sample, the symbols in the figure do not indicate respective measured points, but signs to distinguish each curve. Sample numbers, nominal dopant concentrations, and conditions of H_2 reduction treatments are listed in Table III.

The x=0 sample keeps a rather low conductivity even after H₂ reduction at 1000 °C, and its conductivity measurement is impossible. Changes in conductivity upon H₂ reduction are similar between Y- and Nb-doped samples. The conductivity of the samples of $x=10^{-4}$ remains quite low even after H₂ reduction at 600 or 800 °C, but increases after H₂ reduction at 1000 °C. The samples of $x=10^{-3}$ show drastic changes in the conductivity, ranging several orders of magnitude with the transition from insulator to metal. The asprepared samples of $x=10^{-2}$ have already shown high conductivity with a metallic behavior above about 20 K, and the conductivity increases in the whole temperature range with increasing temperature during H₂ reduction. It should be noted that the conductivity of doped samples increases in



FIG. 3. Temperature dependence of the dc conductivity of H₂-reduced single-crystal samples. (a) $Ca_{1-x}Y_xTiO_3$, (b) $CaTi_{1-x}Nb_xO_3$. Symbols show the sample numbers in Table III. $\blacksquare:1, \square:2, \bullet:3, \bigcirc:4, A:5, \triangle:6, \bullet:7, \diamond:8.$

some orders of magnitude after H_2 reduction, and the absolute values evidently correlate with the dopant concentrations in their order.

E. Carrier densities and Hall mobilities

Table III shows the result of the Hall measurement at RT. The Hall coefficients of all conductive samples after H_2 reduction are negative, indicating that electrons contribute to the conduction as major carriers. Carrier densities increase with an increase in dopant concentration and in temperature

during the H_2 reduction. On the other hand, mobilities are not remarkably different between the samples in spite of the differences in dopant concentration or H_2 -reduction temperature. Therefore, the result indicates that the differences in the conductivity at RT are mainly derived from the difference in the carrier density.

The carrier generation efficiency η is defined as the ratio of the experimentally evaluated carrier density to the ideal carrier density (n_{ideal}), which can be calculated from the analyzed dopant concentration on the assumption that each donor ion, Y or Nb, generates a single electron. The efficiency is listed in the last column of the table. Since the maximum in the efficiencies is about 50% among the samples, it may be deduced that there are still a number of inactive donors even after H₂ reduction at 1000 °C.

Figure 4 shows the temperature dependence of carrier density and mobility of the as-prepared sample with $x = 10^{-2}$ Nb concentration. The carrier density is almost constant in the temperature range from 10 to 300 K, while the mobility increases more than an order of magnitude with decreasing temperature. Accordingly, it is understood that the temperature dependence of the conductivity for the Nb-doped sample deeply depends on that of the mobility.

F. Optical transmission spectra

Figure 5 shows the optical transmittance spectra of Ydoped samples before and after H₂ reduction. Changes in the spectra are almost the same in both Y- and Nb-doped cases. Before H₂ reduction, $x=10^{-4}$ and 10^{-3} samples have no detectable absorption band in the range between the fundamental absorption (~350 nm) and the lattice vibration absorption (~7000 nm). On the other hand, the conductive samples with $x=10^{-2}$, which show a blue color, have an absorption edge due to conductive electrons in the NIR region. After H₂ reduction at 1000 °C, the samples of x $=10^{-4}$ show a pale gray color and the other samples of x $=10^{-3}$ and 10^{-2} show a blue color.

Figure 6 shows systematic changes in the optical transmittance spectra of a Y-doped sample with $x=10^{-3}$ with increasing H₂-reduction temperature. A broad absorption band is induced at 3750 nm (~0.33 eV) by H₂ reduction at 600 and 800 °C, and grows further after H₂ reduction at 1000 °C. The change in the optical spectra is systematically related to the change in the carrier densities at RT or that in the conductivities at low temperature. Therefore, it is indicated that the conductive electrons generated by H₂ reduction are responsible for the IR-absorption band and edge.

IV. DISCUSSION

A. Possible origins of acceptors

The most remarkable observation in the conductivity measurement at high temperature is that the conductivity does not simply increase with the dopant concentration: the electrical conductivity first decreases with an increase in the dopant concentration up to $x=10^{-3}$. Moreover, the Seebeck measurement revealed that the slightly conductive samples with x=0, 10^{-4} , and 10^{-3} evidently show *p*-type conduction, which is quite similar to SrTiO₃ (Refs. 9 and 10) and BaTiO₃ (Ref. 17) single crystals. Since all samples are single

No.	Dopant	Treatment	$\sigma_{\rm RT}~({\rm S~cm^{-1}})$	$n_{\rm expt}~({\rm cm}^{-3})$	$\mu_H ~(\mathrm{cm}^2/\mathrm{V~s})$	$\eta\left(\% ight)$
1 <i>a</i>	Y $x = 10^{-4}$	H ₂ 1000 °C	9.09×10^{-4}	1.3×10^{15}	4.3	0.12
2a	Y $x = 10^{-3}$	H ₂ 600 °C	5.98×10^{-4}	4.6×10^{14}	8.2	3.7×10^{-3}
3 <i>a</i>	Y $x = 10^{-3}$	H ₂ 800 °C	1.03×10^{-1}	4.8×10^{17}	1.3	3.8
4a	Y $x = 10^{-3}$	H ₂ 1000 °C	2.82×10^{0}	$6.0 imes 10^{18}$	2.9	48.
5 <i>a</i>	Y $x = 10^{-2}$	as-prepared	1.24×10^{0}	2.4×10^{18}	3.3	2.2
6 <i>a</i>	Y $x = 10^{-2}$	H ₂ 600 °C	2.41×10^{0}	3.9×10^{18}	3.9	3.6
7 <i>a</i>	Y $x = 10^{-2}$	H ₂ 800 °C	4.43×10^{0}	$8.7 imes 10^{18}$	3.2	8.1
8 <i>a</i>	Y $x = 10^{-2}$	H ₂ 1000 °C	1.70×10^{1}	3.2×10^{19}	3.4	30.
1 <i>b</i>	Nb $x = 10^{-4}$	H ₂ 1000 °C	3.05×10^{-5}	5.0×10 ¹³	3.8	2.8×10^{-3}
2b	Nb $x = 10^{-3}$	H ₂ 600 °C	2.77×10^{-5}	5.0×10^{13}	3.5	2.8×10^{-4}
3 <i>b</i>	Nb $x = 10^{-3}$	H ₂ 800 °C	5.89×10^{-2}	1.1×10^{17}	3.5	0.59
4b	Nb $x = 10^{-3}$	H ₂ 1000 °C	2.07×10^{0}	5.8×10^{18}	2.2	33.
5 <i>b</i>	Nb $x = 10^{-2}$	as-prepared	1.91×10^{0}	4.4×10^{18}	2.7	2.4
6 <i>b</i>	Nb $x = 10^{-2}$	H ₂ 600 °C	2.45×10^{0}	5.1×10^{18}	3.0	2.8
7 <i>b</i>	Nb $x = 10^{-2}$	H ₂ 800 °C	4.73×10^{0}	9.7×10^{18}	3.1	5.4
8 <i>b</i>	Nb $x = 10^{-2}$	H ₂ 1000 °C	1.50×10^{1}	2.4×10^{19}	3.9	14.

TABLE III. Carrier density and Hall mobility of $Ca_{1-x}Y_xTiO_3$ and $CaTi_{1-x}Nb_xO_3$ single crystals.

crystals, it is impossible to speculate that the dopants Y or Nb segregate at the grain boundary, which is often proposed in the case of polycrystalline samples to explain inactive donors. Taking these results into account, the existence of some acceptors in the crystals is strongly suggested. Then, the observation of the conductivity at high temperature will be explained in the way that x=0 sample has already contained some defects as acceptors up to $x=10^{-3}$. The carrier compensated for by acceptors up to $x=10^{-3}$. The carrier samples would be the same in both Y- and Nb-doped cases, because the unexpected behaviors in the conductivity at high temperature are similar in both cases.

Two possible origins of the acceptors are proposed to explain the results. (Interstitial ions are neglected here at the first approximation, owing to their large formation energy.) One is an impurity defect, Al^{3+} substituted for Ti^{4+} , and the other is an oxygen excess related to the deviation of the cation ratio. We speculate at present that the first one is



FIG. 4. Temperature dependence of the carrier density and Hall mobility of the as-prepared sample with $x = 10^{-2}$ Nb concentration. Solid and open circles show the carrier density and Hall mobility, respectively.

dominant, especially at dopant concentrations from x=0 to 10^{-3} . In the following, we will discuss these defects as the origins of acceptors.

1. Impurity defects

Most studies of the nonstoichiometry of alkaline-earth titanates attribute the origin of *p*-type conduction and the oxygen partial pressure dependence of conductivity ($\sigma \propto P_{O2}^{\pm 1/4}$) to an impurity acting as an acceptor such, as Al³⁺ substituted for Ti⁴⁺.^{3,11,19} Moreover, there was a report that Al³⁺ substituted for Ti⁴⁺ acts as an acceptor in CaTiO₃,⁵ and a similar behavior was observed in SrTiO₃, ¹⁵ BaTiO₃,²⁰ and TiO₂.²⁴

The following two reactions can be considered for an acceptor originated from the Al impurity (the Kröger-Vink notation²⁵ is used in the following equation):

$$Al_{Ti} \rightarrow Al'_{Ti} + h^{-} \tag{1}$$



FIG. 5. Optical-absorption spectra of Y-doped samples before (thin lines) and after (thick lines) H₂ reduction at 1000 °C. Solid, dashed, and dashed-dotted lines show the dopant concentration $x = 10^{-4}$, 10^{-3} , and 10^{-2} , respectively.



FIG. 6. Optical transmission spectra of $Ca_{1-x}Y_xTiO_3$ with $x = 10^{-3}$ after H₂ reduction at each temperature.

$$(Al_{2}O_{3})_{impurity} \rightarrow 3O_{O} + (2Al'_{Ti}V_{O}^{..}) + 2(V''_{Ca}V_{O}^{..}),$$
(2)
$$(2Al'_{Ti}V_{O}^{..}) + \frac{1}{2}O_{2} \rightarrow 2Al'_{Ti} + 2h^{.}.$$

Reaction (1) represents the simple substitution of Al^{3+} for Ti⁴⁺ followed by the ionization reaction of Al ions. Reaction (2) exhibits the incorporation of Al^{3+} into Ti^{4+} sites, and the generation of associated defects related oxygen vacancies, which are accompanied by the insertion of oxygens at the oxygen vacancies. In our experiments, an Al impurity was detected in x=0 sample at the concentration of about 1000 ppm, and it is probably included in other samples of x $=10^{-4}-10^{-2}$ at almost the same concentration. Since the concentration of an Al impurity is almost equal to the dopant concentration of $x = 10^{-3}$ samples, and the lowest conductivity at high temperature was observed for samples of x $=10^{-3}$, one of the origins of acceptors in our experiments can be deduced to be the Al impurity. The above two reactions are not distinguished from each other so far, because a deviation of a precise cation ratio on the order of 10^{-3} is not available. However, whichever reaction we consider, the substitution of Al³⁺ for Ti⁴⁺ is one of the most probable origins of acceptors in our samples.

2. Oxygen excess

The estimated carrier-generation efficiency η is considerably low in the as-prepared samples of $x = 10^{-2}$; that is, more than 90% of donors are compensated for. This compensation cannot be explained only by the Al impurity, because its concentration is expected to be at most a few thousand ppm. Therefore, another origin of the acceptors is supposed for the compensation. Since no other impurity except Al was detected in the samples, and H₂ reduction removes the compensation effectively, oxygen excess is considered to be concerned with another origin of the acceptors. However, it should be noted that the acceptor originated from oxygen excess apparently become dominant only when the dopant concentrations increase more than that of the Al impurity. This is probably because reactions related to the oxygen excess need more energy than the generation of Al acceptors, that is, the substitution of Al^{3+} for Ti^{4+} .

The reaction for the generation of positive holes originated from oxygen excess can be described as follows:

$$O_2 + V_0^{\cdot \cdot} \leftrightarrow O_0^{\cdot \cdot} \leftrightarrow O_0 + 2h^{\cdot}$$
 (3)

Reaction (3) needs oxygen vacancies which already exist in samples. The origins of the oxygen vacancies may be expected as follows:

$$(CaO)_{excess} \rightarrow Ca_{Ca} + V_{Ti}^{\prime\prime\prime\prime} + O_O + 2V_O^{\prime\prime}, \qquad (4)$$

$$(\text{TiO}_2)_{\text{excess}} \rightarrow V_{\text{Ca}}'' + \text{Ti}_{\text{Ti}} + 2\text{O}_{\text{O}} + V_{\text{O}}'', \qquad (5)$$

$$\text{null} \to V_{\text{Ca}}'' + V_{\text{Ti}}''' + 3V_{\text{O}}^{\,\cdot\,}, \qquad (6)$$

$$CaTiO_{3} \rightarrow V_{Ca}^{\prime\prime} + Ti_{Ti} + 2O_{O} + V_{O}^{\prime\prime} + (CaO)_{layer}.$$
 (7)

Reactions (4) and (5) are originated from the deviation of cation ratio, and reaction (6) is derived from Schottky defects. Reaction (7) expresses structural defects induced by the insertion of CaO layers.^{5,13,14} If the oxygen vacancies derived from reactions (4)–(7) accommodate oxygens from the atmosphere following reaction (3), the incorporated oxygens act as acceptors and generate positive holes.

We consider that the model of the deviation in cation ratio is dominant among the reactions, because it is no wonder to speculate that the slight deviation occurred during the growth of crystals. Eror and Balachandran studied whether the deviation of cation ratio generates acceptors or not, using polycrystalline samples.⁴ According to this study, equilibrium electrical conductivity profiles do not change upon the deviation of the cation ratio, and the possibility of the formation of acceptors from the deviation of the cation ratio was denied. However, the samples in this study were polycrystalline, and the microscopic chemical characterization of the grain boundaries was not carried out. Therefore, it is an open question whether extra cation sites are formed by cation excess, and whether oxygen vacancies for oxygens from the atmosphere are generated simultaneously. Choi and co-workers reported that the acceptor which causes *p*-type conduction is attributed to TiO_2 excess in $Ba_{0.03}Sr_{0.97}TiO_3$ single crystals with 5% of deviation in cation ratio. 9,10 In our samples, the deviation of the cation ratio was found in a few percent of the magnitude, which suggests that most of the oxygen vacancies may be generated because of nonstoichiometry in the cation ratio.

The existence of the Schottky defects cannot be simply denied from the entropic point of view. However, it will be negligible at the first approximation because their concentration is supposed to be not as high as that of the cation excess, and the formation of the defects needs much energy owing to their large electrical charge.

The model of structural defects induced by the insertion of CaO layers is acceptable, because the existence of Ruddlesdon-Popper type compounds, n-CaTiO₃·CaO (n = 2and 3), are known in the CaO-TiO₂ system. However, unfortunately there is yet no experimental evidence of the generation of oxygen vacancies by this model. Whatever the origins of oxygen vacancies, the oxygen incorporated into crystals from the atmosphere is the only probable origin of the acceptor, except for the Al impurity in the present experiments. The discussions in Sec. IV A focused on the mechanism of hole generation and carrier compensation phenomena. Now, we focus our attention on the generation of electrons and their transport phenomena.

After H_2 reduction, all doped samples become conductive owing to reactions concerned with oxygens. Two reactions are considered for the carrier generation: one is the release of oxygens incorporated into crystals as acceptors, and the other is the generation of newly induced oxygen vacancies independent of acceptors. The former reaction can be described, in other words, as the activation of donors by the cancellation of compensation. Taking into consideration that the conductivity and carrier density of H_2 -reduced samples depend on the donor concentration, and that the carrier generation efficiency is less than 100%, the former reaction would be more favorable than the latter. Although it cannot be determined at present how the oxygen vacancies are related to acceptors in the microscopic point of view, H_2 reduction treatments effectively cancel the compensation by acceptors.

The conductivity of all doped samples shows metallic behavior in the temperature range from 20 to 300 K after H₂ reduction at 1000 °C. The behavior of the conductivity in these metallic samples is quite similar to that in the asprepared samples of $x = 10^{-2}$, which are metallic without H₂ reduction. Therefore, it may be deduced that the conduction of electrons occurs in the same manner among these metallic samples. From the temperature dependence of the carrier density and mobility in an as-prepared sample with $x = 10^{-2}$ Nb concentration (Fig. 4), the carrier density is almost independent of temperature, while the mobility strongly depends on temperature. This is a typical characteristic of degenerated semiconductors. Since the bottom part of the conduction band in CaTiO₃ mainly consists of Ti 3d orbitals like $SrTiO_3$ ²⁶ the conduction electrons move on the Ti 3d orbitals as delocalized electrons in the metallic samples.

The conductivity of $x = 10^{-3}$ samples drastically changes by H₂ reduction treatment. In the semiconducting state obtained after H₂ reduction at 600 °C, the conductive electrons move on the Ti 3*d* orbitals with a help of thermal energy as small polarons. The thermal activation energy for the small polarons can be estimated to be 0.086 eV for the Y-doped sample, and 0.082 eV for the Nb-doped sample, from the activation energies in the conductivity near the lowtemperature limit of the measurement (Fig. 3). An opticalabsorption band appears after H₂ reduction in the IR region (Fig. 6), at 0.33 eV for the Y-doped sample with $x = 10^{-3}$, and at 0.34 eV for the Nb-doped sample with $x = 10^{-3}$. If we assume that the origin of the absorption is the small polarons, the energies are regarded as optical energies for the excita-

tion of the small polarons. Then it is found that the thermal and optical energies almost satisfy the relation E_{opt} = $4 \times E_{\text{therm}}$, which can be applied to small polarons.²⁷ This agreement may support the assignment of the absorption band in the IR region to the small polarons. The mole absorption coefficient, which is estimated to be more than 10^5 l/ mol cm, assuming that the small polaron concentration is equal to the carrier density, seems far larger in comparison with Ti³⁺ absorption in aqueous solutions. Since there are some discussions and contradictions in the assignment of the IR-absorption band in SrTiO₃,^{28,29} BaTiO₃,^{30–32} TiO₂,^{33–35} or WO₃,³⁶ more direct and systematic experimental results are necessary to assign the absorption band. Because electrical and optical measurements are macroscopic observation of carriers, microscopic observations such as ESR will be needed for further investigations of carrier-generation mechanisms, clarifying the electronic state of carriers as well as the acceptors discussed above.

V. CONCLUSION

Single crystals of $Ca_{1-x}Y_xTiO_3$ and $CaTi_{1-x}Nb_xO_3$ (x=0, 10^{-4} , 10^{-3} , and 10^{-2}) were grown by the FZ method, and the electrical and optical properties were examined. In both Y- and Nb-doped cases, the crystals of x=0, 10^{-4} , and 10^{-3} are insulating, while the crystals of x= 10^{-2} are conductive. The electrical conductivity at high temperature shows a complicated behavior that first decreases with an increase in dopant concentration up to x= 10^{-3} . The result of Seebeck measurements demonstrates that the electrical conduction is p type for the samples of x= 0, 10^{-4} , and 10^{-3} , indicating the existence of acceptors. The origins of the acceptors are discussed and concluded to be Al impurity and oxygen excess. Al impurity is dominant until the dopant concentration exceeds the impurity concentration.

After H_2 reduction, all doped samples become conductive due to oxygen vacancies, with the cancellation of the compensation by oxygen-related acceptors. The carriers in semiconducting and metallic states are understood to be small polarons and delocalized electrons, respectively.

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