

산화된 SrTiO₃ 및 니켈도핑된 SrTiO₃ 단결정의 전기전도도

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Electrical Conductivity of Oxidized Pure and Ni-Doped SrTiO₃ Single Crystals

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요 약. 순수한 SrTiO₃ 및 Ni 도핑된 SrTiO₃ 단결정을 산화하여 700~1200°C 및 10⁻⁸~10⁻¹ atm의 온도 및 산소압력에서 산소압력의 함수로서 전기전도도를 측정하였다. 일정한 산소압력에서 전기전도도 값을 온도의 역수에 대하여 도시한 결과 직선관계를 나타내었으며 그 기울기로 부터 구한 활성화 에너지 값들은 순수한 SrTiO₃에 대하여 1.34 eV 이며 Ni-doped SrTiO₃에 대하여 1.06 eV 이다. 일정한 온도에서 전기전도도 값을 산소분압에 대하여 도시한 결과 주어진 온도 범위에서 전기전도도의 산소압력 의존도가 -1/5.6~-1/6.2로 나타났다. 실험치와 이론적으로 해석한 전기전도도의 산소압력 의존성으로 부터 산소공위결함모델을 산화된 SrTiO₃와 Ni-doped SrTiO₃ 단결정에 이용할 수 있음을 알게 되었다. 주어진 온도 및 산소압력 범위에서 전기전도 메커니즘이 각각 제안되었다.

ABSTRACT. The electrical conductivities of oxidized pure and Ni-doped SrTiO₃ single crystals were measured as a function of the oxygen partial pressure (P_{O_2}) at temperature from 700 to 1200 °C and P_{O_2} of 10⁻⁸ to 10⁻¹ atm. Plots of $\log \sigma$ vs. $1/T$ at constant P_{O_2} were found to be linear, and the activation energies obtained from the slopes of these plots have an average value of 1.34 eV for oxidized pure and 1.06 eV for oxidized Ni-doped SrTiO₃ single crystals at P_{O_2} 's between 10⁻⁸ to 10⁻¹ atm. The $\log \sigma$ vs. $\log P_{O_2}$ curves at constant temperature were found to be linear with an average slope of $\frac{-1}{5.6} \sim \frac{-1}{6.2}$ in the P_{O_2} ranges. From the agreement between experimental and theoretically predicted values for the electrical conductivity dependences on P_{O_2} , an oxygen vacancy defect model was found applicable to oxidized pure and Ni-doped SrTiO₃ single crystals over the temperature range, 700~1200 °C. Conduction mechanisms were proposed to explain the dependences of electrical conductivity on temperature and P_{O_2} .

INTRODUCTION

Both optical and transport properties of strontium titanate have been known to depend greatly on the method of preparation of the samples. The electrical¹⁻⁶ and optical⁷⁻¹⁵ properties have been intensively investigated, and measurements

of its electronic energy bands¹⁶⁻²², dielectric constants²³⁻²⁷ and Hall mobility²⁸⁻³¹ have been reported.

Pure SrTiO₃ single crystal is a cubic perovskite structure³² at room temperature with an energy band gap of 3.15~3.40 eV^{7,9,12,33}. Elastic constants³⁴ and ESR³⁵ results indicate

that a transition to a tetragonal phase takes place at 108 °K. Details about the crystal structure have been provided by several EPR studies using transition-metal and rare-earth ions³⁶. The color centers introduced in SrTiO₃ were F centers formed by trapping electrons, released by light irradiation, by vacancies already present in the crystal^{37,38}.

SrTiO₃ has filled valence bands derived from oxygen 2p orbitals and empty conduction bands derived from Ti 3d orbitals with neglecting the change in ionization potentials of oxygen and Ti ions with the degree of ionicity¹⁶. It is thought that the change in the ionization potentials can be compensated by the effect of the polarizability of the oxygen ion, since the calculated energy value²⁶ is consistent with the experimental value. Electron transport of SrTiO₃ is thought to occur *via* a narrow band formed from Ti 3d orbitals³⁹. This conclusion is supported by a tight-binding calculation¹⁶.

The fundamental edge of rutile, a material with the same Ti-O coordination as SrTiO₃, is 4.0 eV at room temperature⁴⁰ and is close to that of SrTiO₃. This closeness of the absorption edge of these materials indicates that this edge is due to transitions between predominately 2p oxygen states and 3d Ti states, and due to transitions between states with lattice admixture of Sr wave functions.

The pure and lightly doped SrTiO₃ return to their almost clear insulating state when the crystal is cooled slowly to room temperature from any temperature above 850 °C⁶, the "freeze-in" temperature for the diffusing of oxygen in SrTiO₃⁷. Heavily doped SrTiO₃ in its oxidized state is a brown insulating crystal with a narrowed band gap of about 2.7~2.9 eV.⁶

Very recently, electrocoloration was studied in SrTiO₃ doped with transition metals by applying dc electric fields at 100~325 °C.⁵ For

this material containing more than $1 \times 10^{18} \text{ cm}^{-3}$ oxygen vacancies, ionic conductivity was suggested⁵ using the mobility data²⁸ and diffusion data². It is very interesting observation on the electrical behavior of doped SrTiO₃ that the conductivities were found to be ionic and not proportional to the impurity content in clear sample. However, chromic behavior has been observed in the thermally activated pure and doped SrTiO₃⁶. It was found that this chromic behavior depends markedly upon the impurity concentration, the annealing temperature, and the rapidity of the quench. This quenching effect was also found by other investigators⁴¹ who observed that oxygen vacancies in SrTiO₃ can be frozen in by rapid quench. Now we can find a continuous controversy concerning the carrier property in SrTiO₃, and there exists very little information available about the properties of oxygen pressure dependence on electrical conductivity at both low and high temperatures in this material. Furthermore, nearly all of the experimental works for SrTiO₃ have been carried out at temperature below 700 °C and oxygen pressure above 10⁻¹ atm. In order to provide above information, an extensive study has been made as a function of oxygen partial pressure at high temperature for oxidized pure and Ni-doped SrTiO₃ single crystals.

EXPERIMENTAL

Sample preparation. Single crystals of pure and Ni-doped SrTiO₃ grown by N. L. Industries were used for the measurements of electrical conductivities at temperatures of 700 to 1200 °C and P_{O_2} 's of 10⁻⁸ to 10⁻¹ atm. The pure and 0.12, 0.36 and 0.79 mol% Ni-doped samples were cut from boules into rectangular blocks with approximate dimensions of 0.83×0.58×0.17 cm and 0.79×0.61×0.15 cm, respectively. The samples were polished on a wet 600

-A paper, and then on an emery paper until all dimensions were uniform surface. The polished samples were etched in 80 % solution of H_3PO_4 at $90^\circ C$ for 30 min, washed with distilled water, and then dried at $160^\circ C$.

The pure $SrTiO_3$ samples were oxidized at about $900^\circ C$ under flowing oxygen for 4 hr. The Ni-doped samples were oxidized as the same condition as the pure $SrTiO_3$. All the samples were re-etched in $(NH_4)_2S_2O_8$ and dilute HCl, and washed with $d-H_2O$, dried, and then connected to the Pt probes.

Conductivity measurements. Measurements of electrical conductivity were carried out according to the Valdes technique⁴², and instruments and apparatus for conductivity measurement are similar to those used in the previous works⁴³⁻⁴⁷. The sample temperature was measured with a pyrometer connected to a Pt-13% Pt-Rh thermocouple placed in a few mm from the sample. The various P_{O_2} 's required were established using pure oxygen or a mixture of 0.002 % oxygen in nitrogen obtained from Matheson Co. The pressures of the evacuated quartz container, pure oxygen, and oxygen-nitrogen mixtures were read on an ultra high-vacuum ionization gauge, a manometer, and a thermocouple gauge, respectively.

Some thermal transpiration effect was checked at low P_{O_2} 's below 10^{-8} atm and above $1200^\circ C$. For measurements at high temperature and low P_{O_2} 's electrical contacts were made using liquid gold cured in air at $650^\circ C$. This contact on our samples supplied a linear current-voltage characteristics over a wide range of voltage and temperature.

In each measurement of conductivity, current and voltage readings applied to the sample were taken over a complete cycle to the temperature range for a given P_{O_2} starting from the low-temperature end, proceeding toward the high-

temperature end, and then back again to the lower end. From agreements between the calculated equilibrium values of the electrical conductivity taken at increasing and decreasing temperatures under constant P_{O_2} , it was found that an equilibrium existed between the specimen and the atmosphere. However, the data measured in the direction of increasing temperature did not agree with the data taken in the decreasing direction of temperature at P_{O_2} 's below 10^{-8} atm and temperatures above $1200^\circ C$.

Contamination of specimens. Spectrographic comparisons between the starting materials and the final specimens showed that no effective increase or decrease in the concentration of impurities appeared as a result of conductivity measurements within this temperature range, P_{O_2} 's and the experimental apparatus dimensions.

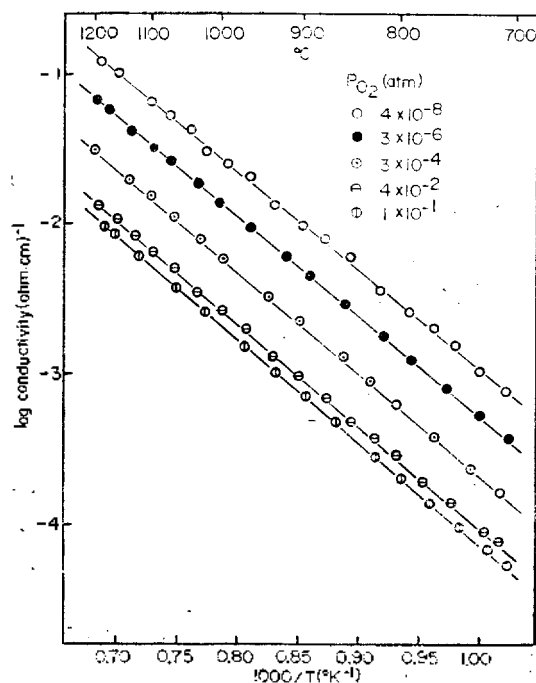


Fig. 1. Conductivities of oxidized pure $SrTiO_3$ single crystal as a function of reciprocal absolute temperature at a constant oxygen partial pressure.

RESULTS AND DISCUSSION

With a view to escaping from confusion, we shall level the samples as follows: The oxidized pure SrTiO_3 is OST and oxidized Ni-doped SrTiO_3 is OSTN; and in the case of 0.12 mol% -OSTN, 0.12 mol% shows the doping level.

The electrical conductivities as a function of reciprocal absolute temperature at a constant P_{O_2} are shown in Figs. 1, 3, 5 and 7 for four different samples of OST, 0.12 mol% -OSTN, 0.36 mol% -OSTN and 0.79 mol% -OSTN. Figs. 2, 4, 6 and 8 show the P_{O_2} dependences of electrical conductivities at a constant temperature. Isotherms of conductivity as a function of impurity content are presented in Figs. 6 and 10.

The Hall mobility does not depend on the degree of oxidation or on the particular doping agent at the conduction temperatures as high

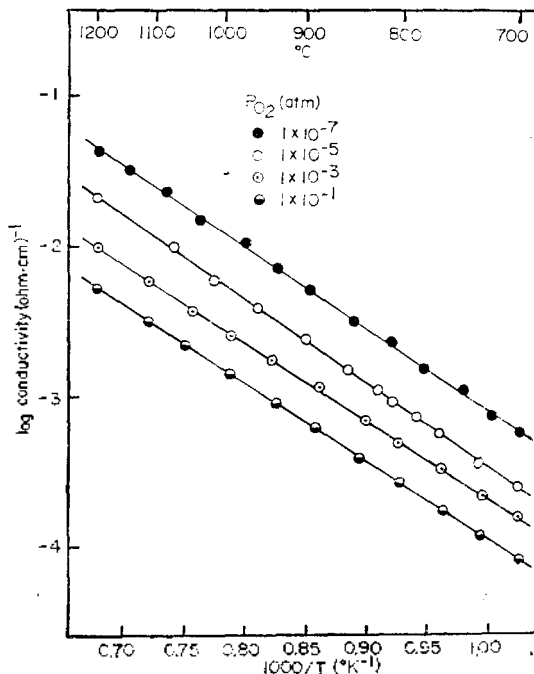


Fig. 3. Conductivities of oxidized 0.12 mol% Ni-doped SrTiO_3 single crystal as a function of reciprocal absolute temperature at constant oxygen partial pressure

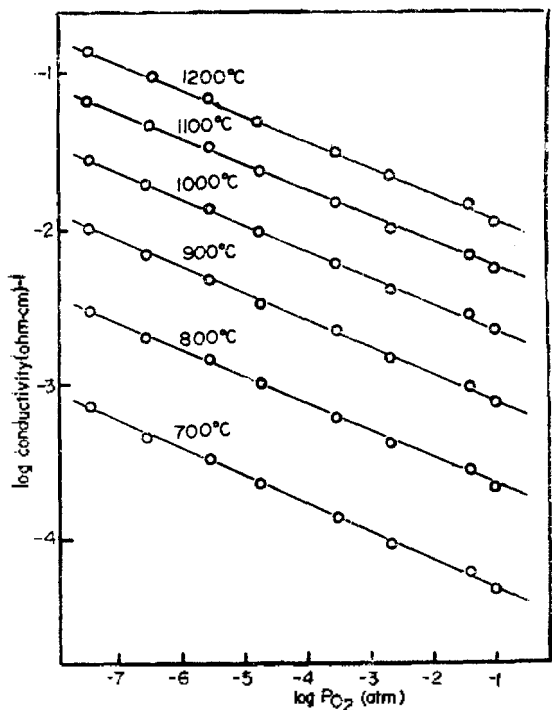


Fig. 2. Isotherms of conductivity of oxidized pure SrTiO_3 single crystal as a function of the oxygen partial pressure.

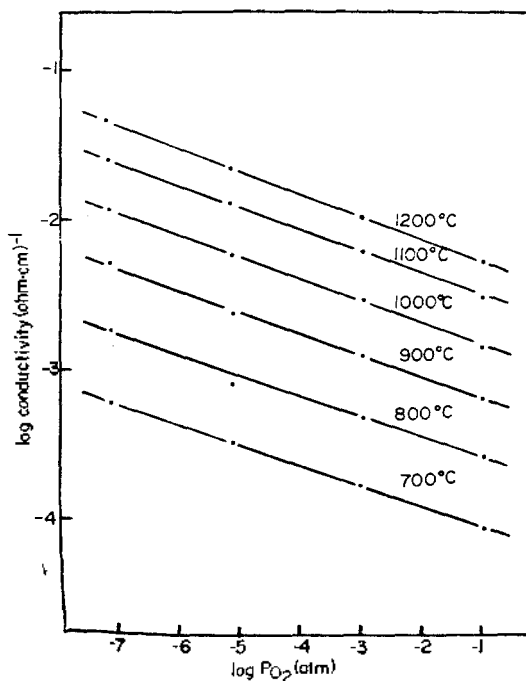


Fig. 4. Isotherms of conductivity of oxidized 0.12 mol% Ni-doped SrTiO_3 single crystal as a function of the oxygen partial pressure.

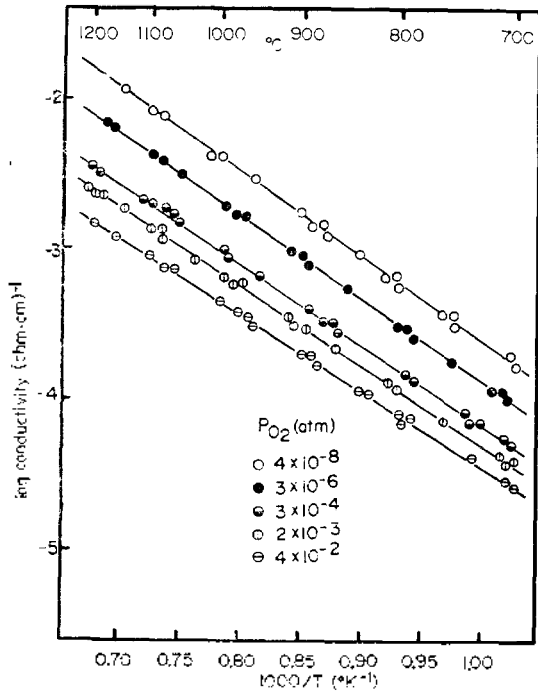


Fig. 5. Conductivities of oxidized 0.36 mol% Ni-doped SrTiO₃ single crystal as a function of reciprocal absolute temperature at constant oxygen partial pressure.

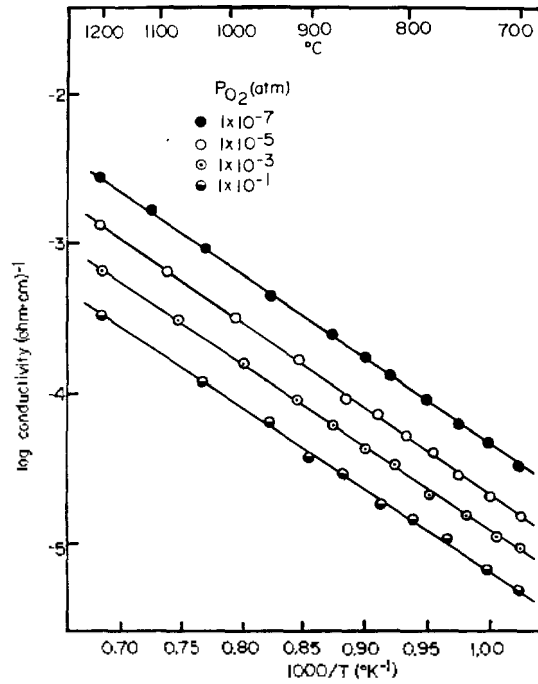


Fig. 7. Conductivities of oxidized 0.79 mol% Ni-doped SrTiO₃ single crystal as a function of reciprocal absolute temperature at constant oxygen partial pressure.

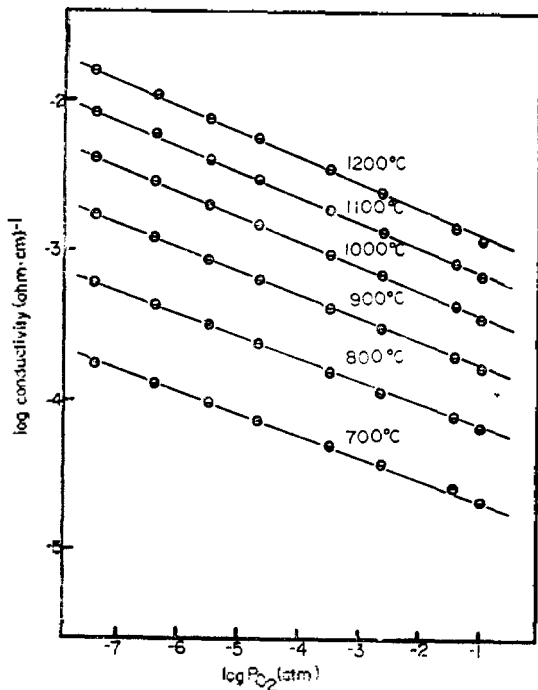


Fig. 6. Isotherms of conductivity of oxidized 0.36 mol% Ni-doped SrTiO₃ single crystal as a function of the oxygen partial pressure.

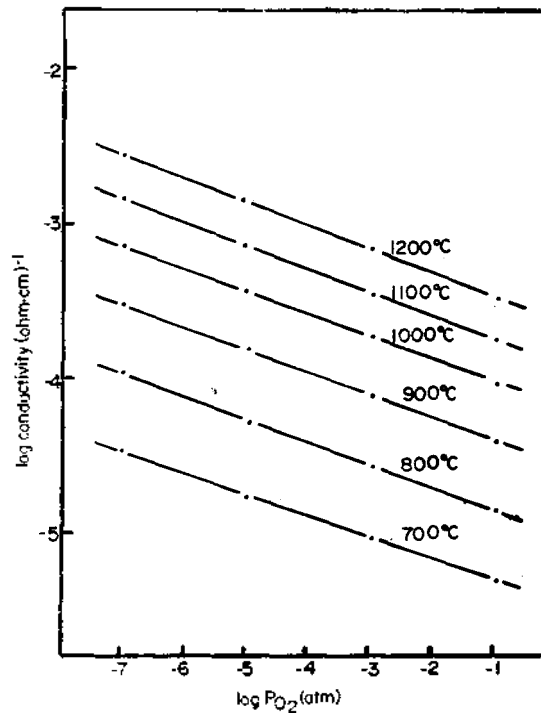


Fig. 8. Isotherms of conductivity of oxidized 0.79 mol% Ni-doped SrTiO₃ single crystal as a function of the oxygen partial pressure.

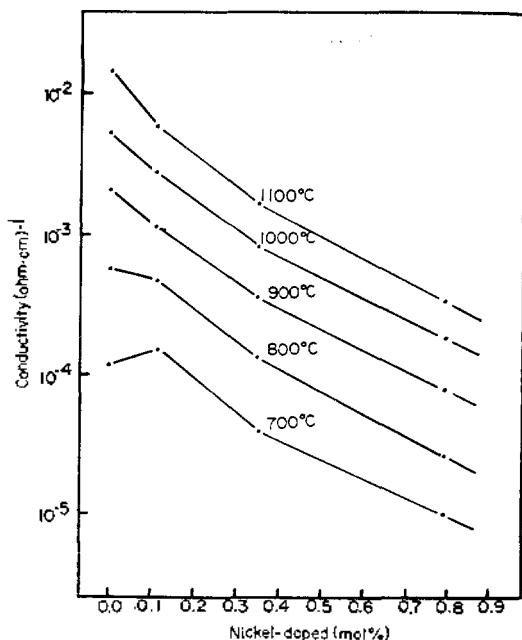


Fig. 9. Conductivities of oxidized pure and Ni-doped SrTiO₃ as a function of dopant concentration at 1×10^{-3} atm.

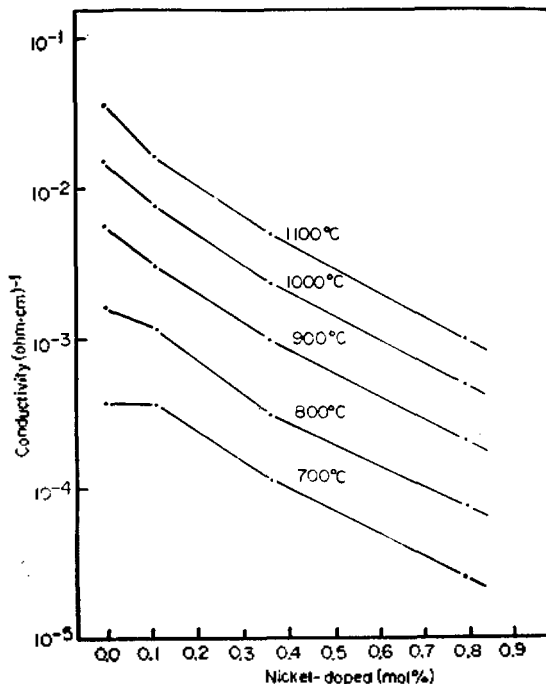


Fig. 10. Conductivities of oxidized pure and Ni-doped SrTiO₃ as a function of dopant concentration at 1×10^{-6} atm.

as 700~1200 °C. Under this assumption an analysis of present experimental results was made. Assuming that there are two kinds of carriers in SrTiO₃ doped with nickel, *i.e.*, one in the conduction band and the other in the impurity band, one is the electron excited from donor sites due to oxygen vacancy, and the other is the positively charged oxygen vacancy due to impurity doping. If positively charged oxygen vacancies in the impurity band are predominate carriers, then impurity-band conduction predominates in this material.

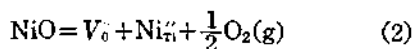
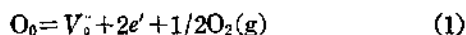
Our conductivity results of OSTN, however, indicate that the contribution to the conductivity by oxygen vacancies in the impurity band does not exceed that by electron carriers in the conduction band. In other words, since the increase in impurity concentration results in the decrease in conductivity as shown in Figs. 9 and 10, oxygen vacancies can not be the pred-

ominate carriers at high temperatures of 700 to 1200 °C. Our conductivities are in good agreement with electron carriers produced by oxygen vacancies at P_{O_2} 's of 10^{-8} to 10^{-1} atm and temperatures from 700 to 1200 °C. These electron carriers in present conductivity were found as free-electron carriers by others^{4,6,10,41,48} in the infrared absorption studies. Furthermore, Wild *et al.*⁶ have described in their energy-level scheme for SrTiO₃ that oxygen vacancies in the reduced crystals form either a narrow impurity-type band or introduce several closely overlapping levels in the band gap about 0.80 eV above the valence band. Upon application of dc electric fields to transition-metal-doped SrTiO₃ samples, however, Blanc and Staebler⁵ have made a conclusion that essentially all the electrical conductivity occurs via motion of vacancies at 100~325 °C. With the values of 0.3~0.9 eV larger than 0.2~0.3 eV found by

Walters and Grace², Paradino et al⁴⁹ and Paradino⁵⁰ they interpreted their activation energies in terms of a strong interaction between positively charged vacancies and negatively charged impurities, even though the conductivities were not proportional to the impurity content.

Now the reason is to be noted why electrons produced by oxygen vacancies are predominant carriers in the electrical conduction for the present specimens. Assuming that the partial pressures of Ti, Sr, and Ni were very low over the sample, because none of the Ti, Sr or Ni was nearly evaporated from the single crystal specimens during the measurement², the variation of conductivity can be interpreted only in terms of P_{O_2} and temperature. On the other hand, the present results must be associated with oxygen vacancy, since our conductivity measurements were undertaken at low P_{O_2} 's. This results from the fact that oxygen vacancies can be formed at low P_{O_2} by the reduction process^{1, 2, 4, 5, 15, 28, 49, 50}.

The analysis of the variation of conductivity is based on the following two sets of chemical equilibrium that represents the formation of an oxygen vacancy and two electrons in the conduction band by the deduction of an oxygen ion from an axial site, and of an O-vacancy being necessary to charge compensate the Ni^{2+} , respectively.



Where $V_0^{\cdot\cdot}$ is positively charged O-vacancy, e' is negatively charged conduction electron. The eq. (1) is characterized by the deduction of an O-ion from a normal site, and eq. (2) is done by nickel doping which entered the cubic site substitutionally on Ti^{4+} sites according to the controlled valence. It is probable

that a reduction of the electron concentration would result according to the eq. (2).

Assuming that the very low concentration of defects does not introduce an interaction between defects, and that the sole charge carriers are electrons in the conduction band, the equilibrium constant in the eq. (1) is

$$K(T) = [V_0^{\cdot\cdot}][e']^2 P_{O_2}^{1/2} \quad (3)$$

Where it is assumed that the mole fraction of O-vacancies and mole fraction of conduction electrons are considered equal to their respective thermodynamic activities. $[e']$ is equal to $2[V_0^{\cdot\cdot}]$ in eq. (3) with this assumption and two conduction electrons originating from each oxygen vacancy. The equilibrium constant is then

$$K(T) = 1/2[e']^3 P_{O_2}^{1/2} \quad (4)$$

The electrical conductivity is $\sigma = [e']q\mu(t)$. Here σ is conductivity, $[e']$ is concentration of conduction electron, q is charge, and $\mu(t)$ is mobility. Since conductivity depends upon the concentration of conduction electron, it follows that

$$\sigma = [e']q\mu(t) \quad (5)$$

When $[e'] = 2K(T)P_{O_2}^{-1/6}$ in eq. (4) is substituted in eq. (5) the electrical conductivity becomes

$$\sigma = 2K(T)q\mu(t)P_{O_2}^{-1/6} \quad (6)$$

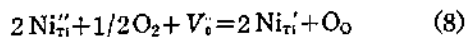
Where as was mentioned above, if $\mu(t)$ is constant, the dependence of electrical conductivity on P_{O_2} follows that

$$\sigma = K'(T)P_{O_2}^{-1/6} \quad (7)$$

This prediction is undertaken under the assumption that the electron mobility is independent of the change in concentration of charge carriers due to O-vacancy, and if it is true electrical conductivity dependences on P_{O_2} for various

samples are in good agreement with the above theoretically predicted average value of $-1/6$, the slopes shown in *Figs. 2, 4, 6* and *8*.

Next, we turn to discussion of an interpretation of conductivity results for oxidized region of OSTN. It appears likely from the decrease in conductivity of OSTN for the oxidized region in comparison with that of OST that nickel entered the lattice substitutionally on Ti⁴⁺ sites can be oxidized at 900 °C and flowing O₂, however, it reduces conduction electrons successively from the O-vacancy. This reduction process of conduction electrons can be written as follows.



The decrease in electron concentration in eq. (8) is consistent with the lower conductivity of OSTN compared with that of OST even in the oxidized region of STN. Even though the practically doubly positive charged nickel oxidizes and then the oxidized nickel reduces the conduction electron, the concentration of reduced electron decreases only to $C/2$ not to zero in order to maintain the local charge neutrality through the crystal. Here we can estimate that the decreasing effect in electron concentration can nearly be compensated by controlled counter doping of nickel.

It is, however, somewhat surprising that the activation energy was decreased with decreasing conductivity for OSTN group in comparison with that for OST. We generally believe that the activation energy must increase with decrease in carrier concentration, since the activation energy decreases due to the increase in the overlap of the electronic wave functions as the electron carrier concentration increases. Our observed activation energy, therefore, can not be interpreted in terms of a carrier concentration and of a usual conduction band.

Under P_{O_2} 's of 10^{-8} to 10^{-1} atm, the activation energy of OST was found to be 1.34 eV. This observed value is assumed to be the sum of an energy for generation of a charge carrier plus that for formation of an O-vacancy.

As will be cited below, however, there are good reasons to believe that an energy for generation of a charge carriers from donor sites to the conduction band is very small in comparison with an energy of formation of an O-vacancy.

Tufte and Chapman²⁸ have found that an oxygen vacancy in SrTiO₃ forms a doubly charged donor center and the energy levels of the donor centers are in the conduction band due to overlap and screening effects in the heavily doped samples. They obtained an activation energy of 0.08 eV from the slope of the linear portion of the reciprocal Hall coefficient *vs.* $1/T$ in the most lightly doped samples, being consistent with an activation energy calculation from the data of Frederikse *et al.*¹¹ Lee *et al.*⁴ have observed the activation energy of 0.035~0.08 eV with pure SrTiO₃ samples reduced in vacuum at temperatures of 650~900 °C. More recently, Morin and Oliver²¹ have reported the oxygen-ion-vacancy donors to lie 0.085 eV below the conduction band with measurements of thermally stimulated current, electrical conductivity and thermo electric effect on insulating SrTiO₃ crystals. Very recently, Lee *et al.*¹⁵ have made an summary in their low-temperature transport measurements for reduced and doped SrTiO₃ that Nb donor levels are hydrogenic whereas oxygen vacancy donor levels produced by the reduction process may lie 0.10 eV below the conduction band depending on the sample preparation.

On the other hand, Walters and Grace² have measured the electrical conductivity of untreated pure SrTiO₃ at temperature range of 900 to

1300 °C under the H₂O-H₂ ambient with a range of $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratio from 4×10^{-2} to 2×10^{-4} . From conductivity vs. $1/T$ plot of them, we can find an approximate activation energy of 1.30 eV. Our activation energy of 1.34 eV is similar to the value observed by Walters and Grace². Additionally, we can find a spread in electron trap energy of 0.3 eV beginning some what from 0.08 eV below the conduction band in the thermally stimulated conductivity vs. $1/T$ plot for *n*-type pure SrTiO₃.²¹ With the observed values of ~ 0.1 eV^{4, 15, 21, 28} the donor sites in the vicinity of oxygen vacancy are believed to lie 0.1 eV below the bottom of the conduction band. The activation energy² and electron trap²¹ energies permit us to believe that about 1 eV contributes to the formation of an oxygen vacancy.

This interpretation of the present activation energy is consistent with the decrease in activation energy in the sequence OST(1.34 eV), OSTN(1.06 eV), STN(0.92 eV)⁵¹, since heavily doped SrTiO₃ has a charge transfer band associated with impurity⁶ and the binding energy for an axial oxygen ion decreases with increase in concentration of lower-valence cations. This result of the activation energy indicates indirectly that the higher the concentration of defect due to dopants the lower is the energy of formation of a defect.

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