Electrical Conductivity of Novel Tetragonal t'_{meta}-$(Ce_{0.5}Zr_{0.5})O_2$ Phase Prepared by Reduction and Successive Oxidation of t' Phase

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A tetragonal t'-$(Ce_{0.5}Zr_{0.5})O_2$, (t'), prepared from ceria and zirconia mixtures by a conventional ceramic method, was reduced at 1123 K and successively oxidized at 873 K to attain a novel tetragonal phase, t'_{meta}-$(Ce_{0.5}Zr_{0.5})O_2$ (t'_{meta}). The electrical conductivity σ_t of t'_{meta} was measured as a function of temperature and time and compared with that for t'. The conducting species were also discussed on the basis of the measurements for ionic transference number $\bar{t}_{ion}$. The σ_t for t'_{meta} was approximately an order of magnitude higher than that for t', and reproducible as a function of temperature between 973 and 1073 K. At increasing temperatures above 1173 K, the σ_t decreased gradually with time and became consistent with t'. The change in σ_t resulted from the fact that a phase transition, $t'_{meta} \rightarrow t'$, occurred above 1173 K. It was concluded that t'_{meta} is a metastable phase with lower thermodynamic stability than that of t'; however, it is virtually stable up to around 1143 K. t'_{meta} and t' are the predominant electronic conductors, possibly because of a hopping mechanism. © 2000 Academic Press

Key Words: ceria; zirconia; electrical conductivity; metastable phase; fluorite-related structure; phase transition.

1. INTRODUCTION

Metastable phases appearing in the $xCeO_2$–$(1-x)ZrO_2$ system maintain the distribution of cations in the respective precursors. In the range of $x = 0.3$–0.7, when the CaF_2-type cubic phase obtained at high temperatures is cooled in the furnace, despite its low cooling rate, a tetragonal t' form, $(Ce_xZr_{1-x})O_2$, could appear (1, 2). The t' phase possesses the random distribution of Ce and Zr ions observed in the precursor cubic CaF_2-type phase (1, 3, 4). κ-$CeZrO_4$ is a metastable phase possessing an ordered arrangement of cations (5); it was obtained by oxidation of a pyrochlore precursor (2, 6). The pyrochlore-type phase, $CeZrO_{3.5+\delta}$, obtained in a reducing atmosphere possesses arrays of Ce and Zr ions, respectively, in the $\langle 110 \rangle$ direction. Its oxidation at a low temperature, e.g., 873 K, leaves the ordered arrangement of Ce and Zr ions in the resulting κ-$CeZrO_4$ phase.

Very recently, the authors prepared the precursors, $CeZrO_{3.5+\delta}$, with various δ values from the t'-$(Ce_{0.5}Zr_{0.5})O_2$ phase by changing the reduction temperature and time (7); the mixing state, i.e., ordering level of Ce and Zr ions, may differ among the precursors. As the δ value was decreased, the precursor became a pyrochlore-type, and therefore the final phase obtained by reoxidation was the κ-$CeZrO_4$. When the δ value was large, the final phase was the t' phase, as expected. However, for an intermediate reduction rate, i.e., $\delta = 0.113$, the powder XRD and Raman spectrum analyses implied that the final phase obtained by reoxidation was a novel tetragonal $(Ce_{0.5}Zr_{0.5})O_2$ phase, which possessed a disordered arrangement similar to that of the t' phase but might have a slightly different coordinate of oxygen from the t' (7); the novel tetragonal phase was named t'_{meta}-$(Ce_{0.5}Zr_{0.5})O_2$ (or just t'_{meta}) in the present study. Any difference in the powder XRD patterns of t' and t'_{meta} could hardly be recognized; however, the Raman band around 524 cm^{-1} detected for t' was decreased or shifted toward a larger wavenumber for t'_{meta}.

Previous results imply that the difference in the structures of t' and t'_{meta} must be very small. One of the objectives of the present study is to measure the total electrical conductivity, σ_t, of the t'_{meta}-$(Ce_{0.5}Zr_{0.5})O_2$ phase, together with that of the t'-$(Ce_{0.5}Zr_{0.5})O_2$ phase, and to examine whether these electrical properties reflect the small but distinct difference in their structure. Another objective is to measure the change in the electrical conductivity of the t'_{meta}-$(Ce_{0.5}Zr_{0.5})O_2$ phase with time as a function of temperature. The results may give us information on the thermal stability of the t'_{meta}-$(Ce_{0.5}Zr_{0.5})O_2$ phase. The conducting species were also discussed on the basis of measurements for ionic transference number $\bar{t}_{ion}$.

2. EXPERIMENTAL

Preparation of t' and t'_{meta} Disks

Powdered raw materials of CeO_2 (Na, <100 ppm; Fe, <10 ppm) and ZrO_2 (HfO_2, 3.8 mass%; Na, <100 ppm;

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Fe, <100 ppm), which were supplied by Santoku Kinzoku Kogyo Co., Ltd., were first thoroughly mixed at a molar ratio of 1:1 using a ball mill, and pressed into 17-mm-diameter and 3-mm-thick disks under 100 MPa pressure. These were sintered in air at 1923 K for 50 h to attain a single phase with a cubic CaF_2-type structure. When these were cooled by cutting the electric power off in the furnace, the phase transformed to a single t'-$(Ce_{0.5}Zr_{0.5})O_2$ phase. One of the disks was used as a starting t' sample for the measurements of σ_t and $\bar{t}_{ion}$.

The preparation of t'_{meta} phase from t' powder was described in a previous report (7). In the present work, the t'_{meta}-$(Ce_{0.5}Zr_{0.5})O_2$ disk was prepared from the deoxidation and successive reoxidation of the t' disk in the same manner, except for the time spent on the deoxidation at 1123 K. The three disks of t' were loaded in the sample chamber of a closed-system oxygen analyzer employing an electrochemical oxygen pump (8, 9); each disk was approximately 13.5 mm in diameter, 2 mm thick, and 1.6 g. O_2 gas was introduced and then the sample was heated at 873 K for 10 h to control the oxygen content; its composition after the annealing was regarded as stoichiometric, $(Ce_{0.5}Zr_{0.5})O_2$. After being cooled to 373 K in O_2 gas, the system was evacuated, and then an Ar +1% H_2 gas mixture was introduced and circulated. Within 10 h of the potentiostatic operation with four leads being started by applying −1.3 V to the oxygen pump, the electrical current, $I_\infty(t)$, passing through the oxygen pump became sufficiently small; the ratio of $P(H_2O)/P(H_2)$ in the circulating Ar +1% H_2 gas mixture approached a constant value of 4.2×10^{-4}. The heating–reduction run was then started by heating the sample at a rate of 2 K min^{-1} to 1123 K; the temperature was kept at 1123 K for 150 h, and then cooled to room temperature. The reduction rate of the t' phase, i.e., the amount of oxygen released from it, was evaluated by monitoring the change in the electrical current, I. The term $\{I - I_\infty(t)\}$ is attributable to oxygen ionic current. It and its integration with time are related to the mole number per second and total mole number of oxygen atoms released from the sample, respectively. Thus, the average oxygen content in the reduced phase, $CeZrO_{3.5+\delta}$, could be evaluated; the δ value of the precursor prepared in the present study was $\delta = 0.15$. The reduced $CeZrO_{3.5+\delta}$ phase was oxidized at 873 K for 10 h in O_2 gas to attain t'_{meta}-$(Ce_{0.5}Zr_{0.5})O_2$ phase.

The t' and one of the reoxidized disks obtained were identified by the X-ray powder diffraction method (Cu$K\alpha$ radiation, using curved graphite $K\beta$ filter, 40 kV, 200 mA) (MXP18, MAC Science, Yokohama, Japan). They were also subjected to Raman spectral analysis with a double monochrometer and photomultiplier detector (JASCO, NR1100, Nihon Bunko, Tokyo, Japan). The spectra were excited with an Ar ion laser operating at a 514.5-nm wavelength.

Measurements of Electrical Conductivity and Ionic Transference Number

The electric conductivity was measured by the DC four-probe method. The surfaces of the t'_{meta} and t' disks were first removed and then cut into 10-mm × 10-mm × 2-mm sheets, respectively. Four platinum wires were wound on the sheet; the distance between the inner wires for voltage measurement was approximately 2 mm. Platinum paste with surface-active solvent was painted on the areas of the sheet–wire contact and heated at 1073 K for 4 h in air. The measurements were carried out in an atmosphere of pure O_2, Ar +10% O_2, and Ar +1% O_2 commercially supplied, respectively. The precise values of the oxygen partial pressure in the latter two gas mixtures were $0.094P^*$ and $0.0099P^*$, respectively, where P^* is atmospheric pressure. These values were determined by using an oxygen sensor employing a yttria-stabilized zirconia tube.

The oxygen concentration cell, Pt, gas(1)/$(Ce_{0.5}Zr_{0.5})O_2$ (t'_{meta} or t')/gas(2), Pt, was constructed to determine the average ionic transference number of the sample. Platinum paste with surface-active solvent was painted on both surfaces of the disk (14 mm diameter and 1.5 mm thickness) and heated at 1073 K for 4 h in air. Platinum leads were pressed onto the surfaces using alumina tubes which were used to pass the gases. To separate the compartments for two electrodes, alumina tubes were pressed on both sides of the sample disk via Au rings. The gas tightness of the compartments was confirmed by passing gas into one of the compartments and checking the gas flow in another.

At a preselected temperature, O_2 gases were first passed at both electrodes so that the base emf, E_0, attributable to thermoelectric emf could be measured. After that, the gas at an electrode, for instance, gas(1), was replaced with Ar +1% O_2 gas and the emf, E_1, was measured. Further, on passing O_2 gases at both electrodes, the base emf, E_0, was measured again. Then, on replacing gas(2) with Ar +1% O_2 gas, the emf, E_2, was measured.

The emf can be related to the oxygen partial pressure $P(O_2)$ in the Ar + O_2 gas mixture and the average ionic transference number, $\bar{t}_{ion}$, of the oxide by

$$|E| = (|E_1 - E_0| + |E_2 - E_0|)/2$$
$$= \bar{t}_{ion}|(RT/4F) \ln\{P(O_2)/P^*\}|, \qquad [1]$$

where R is the gas constant, T is the experimental temperature, and F is the Faraday constant. When calculating the theoretical value, $|E_{th}|$, for $\bar{t}_{ion} = 1$, $\bar{t}_{ion}$ can be evaluated by using the following equation:

$$\bar{t}_{ion} = |E|/|E_{th}|. \qquad [2]$$

3. EXPERIMENTAL RESULTS

Electrical Conductivity in O$_2$ Gas

The σ_t values, obtained when a t'$_{meta}$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ disk was used as a starting sample, are plotted against reciprocal temperature in Fig. 1. The sample was heated from room temperature, and the σ_t measurement was started by keeping the temperature at 973 K. Because the σ_t value increased slightly with time, after the value indicated by a small symbol of ■ was recorded, the sample was heated to 1073 K. In a few minutes, the σ_t value became very stable with less than 1% drift. It was confirmed that there was ohmic contact between the disk and leads from the linear relationship between the passed current and measured voltage. After that, the sample was cooled, and kept at a preselected temperature, and then the σ_t was measured. The measured σ_t values obtained in this cooling process are indicated by the large symbol □. The σ_t values obtained in the successive heating process are indicated by the large symbol ▲. At temperatures below 1073 K, it was confirmed that the measured σ_t values are very reproducible in the cooling and heating processes; the $\ln(\sigma_t T)$ changed linearly with reciprocal temperature. The least-squares treatment of the stable σ_t values indicated by the large symbols ■, □, and ▲ between 973 and 1073 K gave the equation

$$\log(\sigma_t T / \text{S m}^{-1}\,\text{K}) = 8.96 - 7380/(T/\text{K}), \qquad [3]$$

which gave $\sigma_t = 0.11\ \text{S m}^{-1}$ at 1073 K. Based on the equation $\sigma_t T = \sigma_\circ \exp(-E_a/kT)$, $E_a = 1.46$ eV was evaluated, where k is the Boltzmann constant.
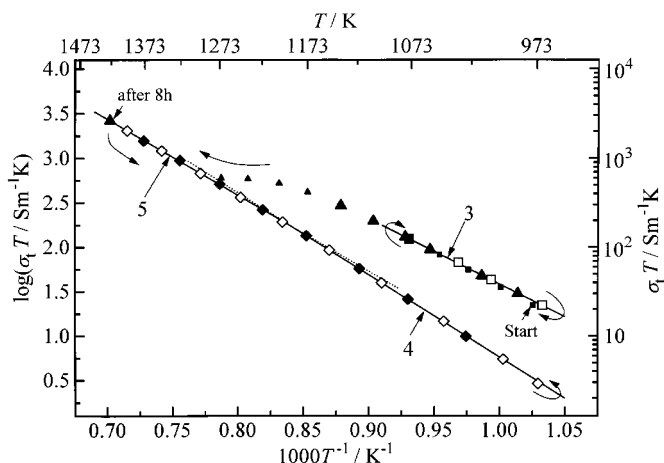
FIG. 1. Temperature dependence of electrical conductivity, σ_t, for t'$_{meta}$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ as a starting phase under O$_2$ gas at atmospheric pressure. Solid and open points indicate the values measured in the heating and cooling runs, respectively. Large and small points indicate the values obtained by maintaining the temperature for several minutes and instantly on changing the temperature, respectively.

σ_t was expressed as a function of temperature up to 1143 K. However, as the temperature was further increased, σ_t at above 1173 K began to decrease with time rather than temperature. When the sample was annealed at 1423 K for 8 h, the σ_t value became stable again independent of time. As the temperature was decreased, the σ_t values showed another relationship with temperature; the $\ln(\sigma_t T)$ vs $1/T$ line appeared to bend at around 1189 K. In the cooling process, the σ_t values obtained during retention at a preselected temperature are indicated by ◇. The σ_t values obtained in the successive heating process from 973 K, indicated by ◆, agreed well with those in the cooling process. The relationship between σ_t and temperature was expressed by Eq. [4] below 1189 K and Eq. [5] above 1189 K,

$$\log(\sigma_t T / \text{S m}^{-1}\,\text{K}) = 10.01 - 9250/(T/\text{K}), \qquad [4]$$

which gave $\sigma_t = 0.023\ \text{S m}^{-1}$ at 1073 K, and $E_a = 1.84$ eV, and

$$\log(\sigma_t T / \text{S m}^{-1}\,\text{K}) = 9.42 - 8550/(T/\text{K}), \qquad [5]$$

which gave $\sigma_t = 1.1\ \text{S m}^{-1}$ at 1373 K, and $E_a = 1.70$ eV.

The σ_t values measured for t'-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ as a starting phase are shown in Fig. 2 as a function of temperature; the data obtained in the heating and successive cooling processes are indicated by ■ and □, respectively. The σ_t values were very stable with time as a function of temperature; the ohmic contact was confirmed at 973 and 1423 K in this heating process. The σ_t value in the cooling and heating processes lay on a line possessing a bend at around 1191 K; the relationship was expressed by Eq. [6] below 1191 K and Eq. [7] above 1191 K,

$$\log(\sigma_t T / \text{S m}^{-1}\,\text{K}) = 10.13 - 9170/(T/\text{K}), \qquad [6]$$

which gave $\sigma_t = 0.036\ \text{S m}^{-1}$ at 1073 K, and $E_a = 1.82$ eV, and

$$\log(\sigma_t T / \text{S m}^{-1}\,\text{K}) = 9.70 - 8650/(T/\text{K}), \qquad [7]$$

which gave $\sigma_t = 1.8\ \text{S m}^{-1}$ at 1373 K, and $E_a = 1.72$ eV. In Fig. 2, the σ_t values measured in the second heating and cooling processes are indicated by ▲ and △, respectively; all the data for t'-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ were reproducible.

The σ_t values for t'$_{meta}$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ as the starting phase, obtained after annealing at 1423 K, were close to those for t'-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$, and their temperature dependences of the phases agreed well with each other. The results may be due to the fact that the t'$_{meta}$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ phase became t'-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ during the annealing at 1423 K, as demonstrated by the Raman spectra analyses. On close observation, however, Eq. [4] for the t' change from t'$_{meta}$ is
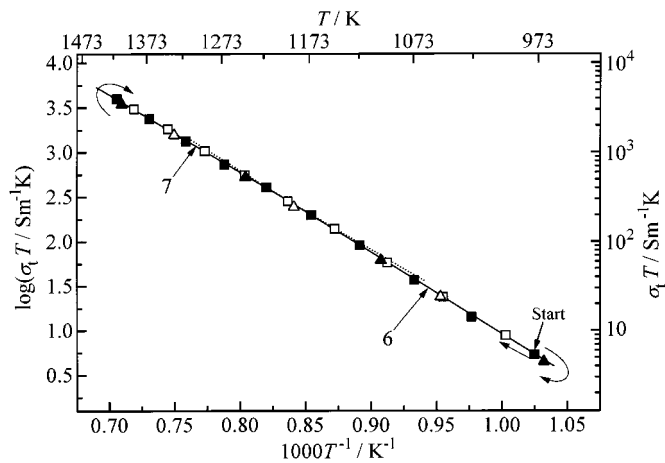
FIG. 2. Temperature dependence of the electrical conductivity, σ_t, of t′-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ under O$_2$ gas at atmospheric pressure. ■, first heating run; □, first cooling run; ▲, second heating run; △, second cooling run.

FIG. 3. Typical dependence of the electrical conductivity, σ_t, on the oxygen partial pressure, $P(O_2)$. □, at 973 K for t′$_{meta}$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$; ■, at 973 K for t′-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$; ▲, at 1373 K for t′-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$. P^* is atmospheric pressure.

found to give 1/1.6 times smaller σ_t values than Eq. [6] for t′; the σ_t data obtained by the DC four-probe method may depend on the density of the sample. The relative density of t′$_{meta}$ and t′ as prepared was 92% and 97%, respectively, while that of the t′ change from t′$_{meta}$ was 94%. Thus, the σ_t values for t′$_{meta}$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ with a higher relative density were evaluated by multiplying Eq. [3] by 1.6 and normalizing with respect to the σ_t values for t′. The σ_t–T relationship for t′$_{meta}$ recommended in the present study is
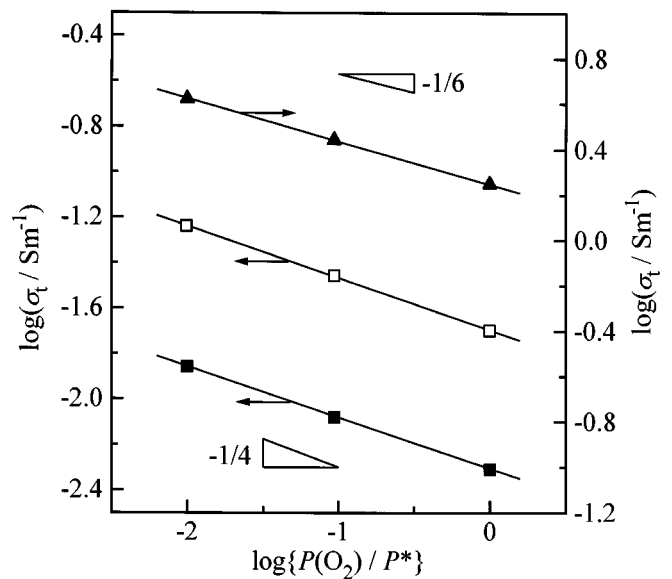
$$\log(\sigma_t T / \text{S m}^{-1} \text{ K}) = 9.16 - 7380/(T/\text{K}), \qquad [8]$$

which gave $\sigma_t = 0.18$ S m^{-1} at 1073 K, and $E_a = 1.46$ eV.

The σ_t for t′$_{meta}$ was increased with decreasing oxygen partial pressure, $P(O_2)$, much like that for t′. Figure 3 shows the dependence of σ_t as measured at 973 K for t′$_{meta}$, together with those at 973 and 1373 K for t′. The dependence was expressed by the relation $\sigma_t \propto P(O_2)^{-1/n}$. The values of n for t′$_{meta}$ and t′ are summarized in Table 1.

Thermal Stability of t′$_{meta}$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$

The t′$_{meta}$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ disk loaded in a quartz glass tube was annealed in O$_2$ gas at 1073 or 1423 K for 2 h. The sample quenched in ice and water was subjected to powder XRD and Raman spectra analyses. Figures 4b and 4c show the powder XRD patterns for the quenched samples, compared to those for t′$_{meta}$ and t′ as prepared; the diffraction peaks were indexed on the basis of a CaF$_2$ lattice. All the samples were tetragonal phases; the (112) diffraction peak attributable to the displacement of oxygen atoms along the c-axis was observed. The lattice parameters a_F and c_F and unit volume V for the phases as prepared in the present study were respectively 0.52590(6) nm, 0.52957(5) nm, and

0.14646(4) nm^3 for t′$_{meta}$, and 0.52605(7) nm, 0.53077(7) nm, and 0.14688(4) nm^3 for t′; the number in the parentheses shows the standard deviation estimated in the last digit. The lattice constant of t′$_{meta}$ was slightly smaller than that of t′, as reported previously (7); however, the difference was too small for the quenched samples to be distinguished by XRD analysis. Figures 5b and 5c show the Raman spectra for the quenched samples, compared to those for t′$_{meta}$ and t′ as prepared. Raman spectral analysis makes it possible to distinguish t′$_{meta}$ and t′ phases; the sharp Raman band at around 566 cm^{-1} indicates that the phase annealed at 1073 K was still t′$_{meta}$. However, the phase annealed at 1423 K could be identified as t′, because the Raman band

TABLE 1
Dependence of the Total Electrical Conductivity, σ_t, of t′$_{meta}$- and t′(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ Phases on Oxygen Partial Pressure, $P(O_2)$

Phase	T/K	n^a
t′$_{meta}$	973	4.4 ± 0.1
	1073	4.5 ± 0.1
t′	973	4.5 ± 0.1
	1073	4.6 ± 0.1
	1173	5.0 ± 0.1
	1273	5.2 ± 0.1
	1373	5.3 ± 0.1

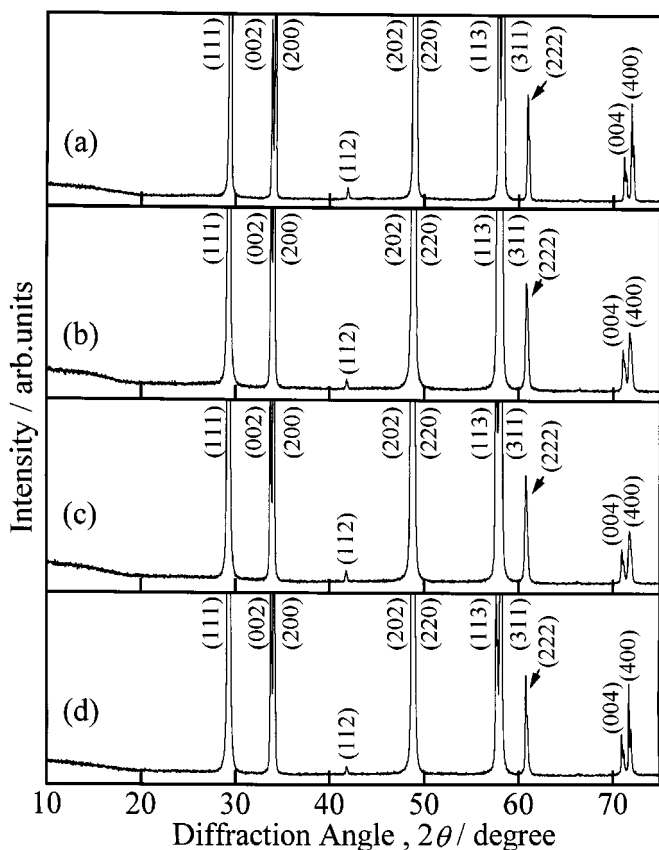^{a}The dependence parameter, n, was evaluated on the basis of the equation $\sigma_t \propto P(O_2)^{-1/n}$.

emf to a change in $P(O_2)$ was very fast and the emf stabilized in 1 min. In the case of the t'-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ phase, the emf stabilized in 10 min. For both cases, a small but clear emf due to the $P(O_2)$ difference could be observed; the measured emf and evaluated $\bar{t}_{ion}$ values are summarized in Table 2. As can be seen from this table, both the t'$_{meta}$ and t' prepared in the present study exhibited predominant electronic conductions.

4. DISCUSSION

It was pointed out in a previous study (7) that the temperature for precursor preparation and the oxygen content δ in CeZrO$_{3.5+\delta}$ are important factors for the structure of the reoxidized CeZrO$_4$ compound. The reduction of approximately 100 mg of t' powder was completed and the annealing at 1123 K terminated in 10 h; the reoxidized phase was t'$_{meta}$. In the present study, when a small piece of t' disk of approximately 0.24 g was reduced for 150 h, the reoxidized phase
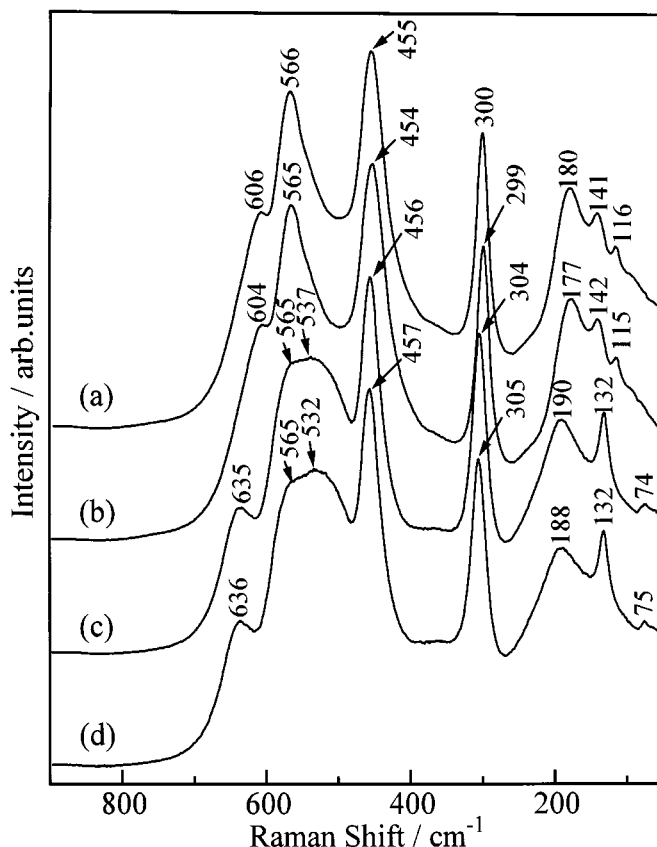

FIG. 4. Powder XRD patterns for t'$_{meta}$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ samples after annealing in O$_2$ gas compared to those for t'$_{meta}$ and t' phases. (a) t'$_{meta}$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ phase as prepared, (b) quenched after annealing at 1073 K corresponding to line 3 in Fig. 1, (c) quenched after annealing at 1423 K corresponding to line 5 in Fig. 1, and (d) t'-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ phase as prepared. Diffraction peaks are indexed on the basis of pseudo-fluorite unit cell.

appeared at around 532 cm^{-1}. Thus, the decrease in σ_t for t'$_{meta}$ with time could be attributed to a phase transition from t'$_{meta}$ to t'. After annealing of the phase at 1423 K, the measured σ_t values were very reproducible as a function of temperature. This indicates that the reverse transition from t' to t'$_{meta}$ did not take place. It has not been confirmed whether the t' phase is metastable; one may emphasize that t'$_{meta}$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ is a metastable phase and its thermodynamic stability is lower than that of t'-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$. As is clear in Fig. 1, despite its low thermodynamic stability, the t'$_{meta}$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ phase was virtually thermally stable up to around 1143 K.

Ionic Transference Number

The typical change in emf with time is shown in Fig. 6. In the case of the t'$_{meta}$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ phase, the response of

FIG. 5. Raman spectra for t'$_{meta}$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ samples after annealing in O$_2$ gas compared to those for t'$_{meta}$ and t' phases. (a) t'$_{meta}$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ phase as prepared, (b) quenched after annealing at 1073 K corresponding to line 3 in Fig. 1, (c) quenched after annealing at 1423 K corresponding to line 5 in Fig. 1. and (d) t'-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ phase as prepared.

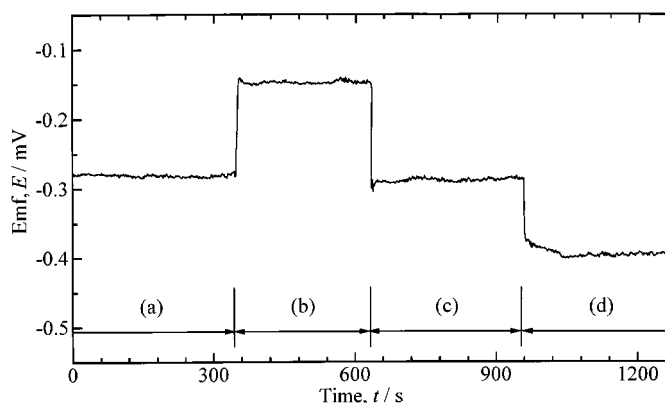**FIG. 6.** Change in emf of the cell: Pt, gas(1)/t′$_{meta}$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$/gas(2), Pt at 1073 K with time. (a, c) gas(1): 100% O$_2$, gas(2): 100% O$_2$; (b) gas(1): 0.99% O$_2$, gas(2): 100% O$_2$; (d) gas(1): 100% O$_2$, gas(2): 0.99% O$_2$.

was κ phase. Another factor may be the time spent annealing the precursor after a small δ value was attained; the Ce and Zr ions may take on an ordered arrangement with time. The reduction of three t′ disks of 4.8 g proceeded very slowly, taking more than 150 h; the rate per second of oxygen release from the samples was maximum at 10 h, and it decreased to two-thirds after 150 h. The rate-limiting step might be the transfer of oxygen with a circulating Ar +1% H$_2$ mixture of $P(H_2O)/P(H_2) = 4.2 \times 10^{-4}$ from the sample surface to the electrochemical pump; the time spent annealing after a small δ value was attained might be fairly short. As a result, the reoxidized phase was t′$_{meta}$. In order to prevent a possible thin κ film from forming on the surface of the samples, care was taken to remove the surface before the electrical conductivity measurement.

The electrical conductivity of xCeO$_2$–$(1 - x)$ZrO$_2$ solid solutions in the intermediate composition range has been measured by several investigators using a frequency dispersion technique (8–11). They prepared the samples by heating mixed powders of CeO$_2$ and ZrO$_2$ at 1823, 1873 or 1923 K and then cooling them to room temperature; therefore, the sample phases might be t′, although the Raman spectral analyses of these samples were not reported. The previous results of σ_t for $x = 0.5$ under atmospheric O$_2$ gas are shown in Fig. 7, together with the present data for t′$_{meta}$ and t′. All the data except for those of Asquiedge *et al.* (8) were obtained in air; therefore, the values under O$_2$ gas were estimated using the relation $\sigma_t \propto P(O_2)^{-1/5}$. The previous data for t′ agree well, except for those of Chiodelli *et al.* (9). The CeO$_2$ powders used by the latter group contained Ca impurities in the order of 400 ppm; further, the cooling rate of the cubic phase from 1873 K was relatively fast. It has been inferred in a previous study (12) that t′ may be of a generic form. A doping of Ca and also a very fast cooling rate might lead to a difference of oxygen displacement in the t′ phase. The data for t′ obtained in the present study are consistent with previous data.

As can be seen from Table 1, $P(O_2)$ dependences of σ_t for t′$_{meta}$ and t′ were quite similar; the dependence parameter n was smaller than 6 and increased gradually with temperature; this result may come from the association of doubly ionized oxygen vacancies with trivalent cerium ions. Recently, two linear relationships between σ_t and temperature, i.e., an upwardly convex $\ln(\sigma_t T) - 1/T$ curve, have been suggested in a study using the association model (13). The present data for temperature dependence of σ_t for t′, i.e., a bend at around 1173 K, may be interpreted by a similar model; however, there is one other possibility. The authors measured the temperature dependence of $P(O_2)$ over t′ and pyrochlore phase mixture, where the total composition was expressed as Ce$_2$Zr$_2$O$_{8-z}$. The $P(O_2)$ vs temperature line

TABLE 2
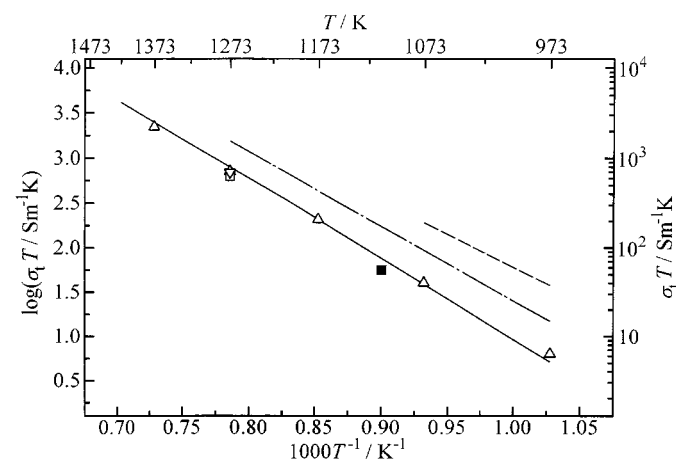**Measured Emf of the Oxygen Concentration Cell: Pt, Gas(1)/(Ce$_{0.5}$Zr$_{0.5}$)O$_2$/Gas(2), Pt, and the Mean Ionic Transference Number, $\bar{t}_{ion}$, Evaluated**

| Phase | T/K | 100% O$_2$, 9.4% O$_2$ | | 100% O$_2$, 0.99% O$_2$ | |
		Measured emf, $|E|$/mV	$\bar{t}_{ion}$	Measured emf, $|E|$/mV	$\bar{t}_{ion}$
t′$_{meta}$	973	0.04	<0.001	0.07	<0.001
	1073	0.08	~0.001	0.12	~0.001
t′	973	2.81	0.057	3.97	0.041
	1073	1.70	0.031	2.57	0.024
	1173	1.68	0.028	2.85	0.024

FIG. 7. Electrical conductivity, σ_t, for t′$_{meta}$- and t′-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ phases in O$_2$ gas compared to the previous data for t′. — — —, present work for t′$_{meta}$ (Eq. [8]); ———, present work for t′ (Eqs. [6] and [7]); — · — · —, Chiodelli *et al.*; △, Roitti and Longo; ○, Pal'guev and Volchenkova; ■, □, Asquiedge *et al.* The values shown by the dot-dashed line and open points were estimated using $\sigma_t \propto P(O_2)^{-1/n}$ because the original data were for experimental data in air.

reflecting the thermodynamic stability of t′ bent at around 1275 K for $z = 0.47$; the temperature for bending decreased with decreasing z. The possibility that there are two kinds of t′, i.e., a phase transition among t′ phases, still remains.

$P(O_2)$ dependences of σ_t have been reported by Chiodelli *et al.* (9). The values of the n parameter for t′$_{meta}$ and t′ determined in the present study agreed well with previously obtained data; the dependence parameter n may not be sensitive to the oxygen displacement in the phases. In view of the fact that the $P(O_2)$ dependence of σ_t for t′$_{meta}$ quite resembles that for t′, the conduction mechanisms for these two phases may be similar; that is, t′$_{meta}$ and t′ may be the predominant electronic conductors according to the hopping mechanism. Their crystal structures are similar: the Ce and Zr ions take a disordered arrangement, and the local displacement of oxygen ions exists. A small but distinct difference is that the unit cell for t′$_{meta}$ is slightly smaller than that for t′; the size of a unit cell is closely related to the distance between the Ce ions, i.e., the hopping distance for conduction. Furthermore, the c_F/a_F ratios for these phases assuming a pseudo-fluorite unit cell differed slightly. In a recent study (7), the authors have reported that the c_F/a_F value for tetragonal phases with various ZrO$_2$-based compositions is closely related to the oxygen parameter, z; the derivation of the oxygen parameter, z, from 0.25 increases continuously with increasing c_F/a_F ratio. On the basis of this relationship, the oxygen parameters were estimated to be 0.220 for t′$_{meta}$ and 0.218 for t′ prepared in the previous study, respectively. One may expect a larger σ_t for cubic-type phase with $z = 0.25$. Thus, the larger σ_t for t′$_{meta}$ may be attributed to smaller unit cell and a smaller deviation of z from 0.25.

5. CONCLUSIONS

A novel tetragonal phase, t′$_{meta}$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$, was prepared by deoxidizing t′ at 1123 K and successively oxidizing the precursor at 873 K. The electrical conductivity σ_t of t′$_{meta}$ was measured as a function of temperature and time and compared with that for t′.

(1) The σ_t for t′$_{meta}$ was approximately an order of magnitude higher than that for t′ and its temperature dependence between 973 and 1073 K was expressed by a linear relationship:

$$\log(\sigma_t T/S\,m^{-1}\,K) = 9.16 - 7380/(T/K).$$

(2) At temperatures above 1173 K, the σ_t decreased gradually with time and agreed with that for t′. The change in σ_t came from the fact that a phase transition, t′$_{meta}$ → t′, occurred above 1173 K. The reverse transition, i.e., t′ → t′$_{meta}$ was not observed. It was concluded that t′$_{meta}$ is a metastable phase with lower thermodynamic stability than that of t′.

(3) The $P(O_2)$ dependence of σ_t for t′$_{meta}$ was quite similar to that for t′. t′$_{meta}$ and t′ may be predominant electronic conductors according to the hopping mechanism.

(4) The oxygen parameter, z, for the t′$_{meta}$ phase is closer to 0.25 than that for t′ phase; further, the unit cell of t′$_{meta}$ is smaller than that of t′. The larger σ_t for t′$_{meta}$ may be attributed to the structural difference.

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