Electrical conductivity of metastable $\kappa$-CeZrO$_4$ phase possessing ordered arrangement of Ce and Zr ions

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Abstract

Electrical conductivity $\sigma_f$ of metastable $\kappa$-CeZrO$_4$ possessing ordered arrangement of Ce and Zr ions in a manner similar to a pyrochlore-type was measured as a function of temperature and time, and compared with tetragonal metastable $t'(Ce_0.5Zr_0.5)O_2$ and $t''_{\text{meta}}(Ce_0.5Zr_0.5)O_2$ phases possessing random arrangement of the cations. The $\kappa$ disk was prepared by reoxidizing a pyrochlore-type precursor in O$_2$ gas at 873 K. The $\sigma_f$ as measured for the $\kappa$-CeZrO$_4$ was reproducible as a function of temperatures between 957 and 1190 K. At increasing temperatures above 1233 K, the $\sigma_f$ decreased gradually with time due to the phase transition: $\kappa \rightarrow t'$, and became consistent with the $t'$. Although the $\kappa$-CeZrO$_4$ phase is thermodynamically less stable than the $t'(Ce_0.5Zr_0.5)O_2$, it was virtually stable up to around 1233 K. It was found from the change in the $\sigma_f$ due to the phase transition that the $\sigma_f$ for the metastable $\kappa$-CeZrO$_4$ was an order of magnitude higher than that for the $t'$ and was similar to that for the $t''_{\text{meta}}$. It was previously reported that a phase transition, $t''_{\text{meta}} \rightarrow t''$, occurred above 1143 K. The phase transition, $\kappa \rightarrow t'$, accompanied by redistribution of the cations appeared to occur at higher temperatures than that for $t''_{\text{meta}} \rightarrow t''$ leaving random cation arrangement. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ceria; Zirconia; Electrical conductivity; Metastable phase; Phase transition; Fluorite-related structure; Pyrochlore-type

1. Introduction

Ceria–zirconia based oxides may be available as the electrode for solid oxide fuel cell (SOFC) because they exhibit high mixed conduction of oxygen ion and electron [1,2]. The electrical conductivity of $x$CeO$_2$–$(1 - x)$ZrO$_2$ oxides has been investigated at intermediate temperatures as 1273 K over the wide composition range [3]. In the intermediate composition range of the CeO$_2$–ZrO$_2$ system, no compound exists in the equilibrium phase diagram, except for the CaF$_2$-type cubic phase over 1823 K [4,5]. When it is cooled in the furnace, in spite of its low cooling rate, a tetragonal $t'$ or $t''$ phase possessing random distribution of Ce and Zr ions can appear without the phase separation [6,7]. The $t'$ phase may be obtained when the powders coprecipitated from an acid solution are heated around 1273 K. It is believed that the tetragonal $t'$ and $t''$ phases are metastable [7]. Very recently, some authors have reported the other metastable phases, i.e., a series of $t''_{\text{meta}}(Ce_0.5Zr_0.5)O_2$ [8]. In view of the existence of these metastable phases, the electrical conductivity of $x$CeO$_2$–$(1 - x)$ZrO$_2$ oxides should be investigated in connection with their crystal structure as well as compositional dependence.

The metastable phases appearing in the $x$CeO$_2$–$(1 - x)$ZrO$_2$ system maintain the distribution of cations in the respective precursors [8]. When oxygen can be intercalated in a pyrochlore-type Ce$_2$Zr$_2$O$_7$ [5], a metastable $\kappa$-CeZrO$_4$ phase appears around $x = 0.5$ [8–11]. The $\kappa$ phase also possesses the ordered arrangement of Ce and Zr ions in a manner similar to the pyrochlore, unlike the tetragonal $t'(Ce_0.5Zr_0.5)O_2$ and $t''_{\text{meta}}(Ce_0.5Zr_0.5)O_2$ [8]. The $\kappa$ phase is thermodynamically less stable than the $t'(Ce_0.5Zr_0.5)O_2$ [12]. The crystallographic character of the $\kappa$-CeZrO$_4$ phase obtained has been recently studied in detail [13]. The objective of the present investigation is to measure the electrical conductivity of the metastable $\kappa$-CeZrO$_4$. The data obtained have been compared and discussed with those of the tetragonal metastable phases [14].

2. Experimental

To obtain the $\kappa$-CeZrO$_4$ sample having a uniform distribution of Ce and Zr ions in it, the single phase of $t'(Ce_0.5Zr_0.5)O_2$ was first prepared. Powdered raw materials...
of CeO₂ (Na: <100 ppm, Fe: <10 ppm) and ZrO₂ (HfO₂: 3.8 mass%, Na: <100 ppm, Fe: <100 ppm), which were supplied by Santoku Kinzoku Kogyo Co., Ltd, were thoroughly mixed at a molar ratio of 1:1 using a ball mill, and pressed into 17 mm diameter pellets under 100 MPa. These were sintered in air at 1923 K for 50 h to attain a single phase with a cubic CaF₂-type structure. When these were cooled by cutting the electric power off in the furnace, the phase became single t’-(Ce₀.₅Zr₀.₅)O₂.

The preparation of the κ-CeZrO₄ phase from the t’-(Ce₀.₅Zr₀.₅)O₂ was carried out in a manner similar to that described in a previous report [8]. After the t’ pellets were crushed into grains, these were loaded in an alumina tube equipped in a conventional electric furnace. On passing pure H₂ gas at a flow rate of 100 cm³ min⁻¹, the sample was heated at a rate of 2 K min⁻¹, and kept at 1573 K for 10 h to obtain a pyrochlore-type Ce₂Zr₂O₇₋₋₂₈ precursor. After the precursor was cooled at a rate of 2 K min⁻¹, it was ground into powder using an agate mortar with pestle and then ball mill. The powder was mixed in a molar ratio of 9:1 with raw material powders of CeO₂ and ZrO₂ as binding agents with Ce/Zr composition ratio = 1, and pressed into 17 mm diameter disk under 100 MPa. The disk was loaded in an alumina tube and then reduced and sintered at 1823 K for 10 h by passing pure H₂ gas. After it was cooled to room temperature, pure O₂ gas was introduced. The sample disk was reoxidized by annealing in the O₂ gas at 873 K for 10 h to attain the κ-CeZrO₄ phase.

According to the powder X-ray diffraction analysis, the formation of a perovskite-type phase, i.e. CeAlO₃, was recognized on the surface of the κ disk; the aluminum vapor may come from the alumina tube, when the sample was annealed at a high temperature as 1823 K in the strong reducing H₂ gas. After the surface of disk was removed by emery paper, the disk obtained was subjected to the powder X-ray diffraction analysis (Cu Kα radiation, using curved graphite Kα-fiber, 40 kV–200 mA) (MXP18, MAC Science, Yokohama, Japan), and Raman spectroscopy. The Raman spectra were recorded by a spectrometer with a double monochromator and photomultiplier detector (JASCO, NR1100, Nihon Bunko, Tokyo, Japan) under the excitation of Ar ion laser of 514.5 nm (Innova 90C, Coherent, Santa
Clara, CA). It was confirmed according to the analyses that the disk obtained consisted of a single κ-CeZrO$_4$ phase. The relative density of the disk was 90%.

The electrical conductivity was measured by the DC-four probe method. The κ-CeZrO$_4$ disk was cut into 10 mm × 10 mm × 2 mm sheet. Platinum paste with surface active solvent was painted on the four parts of the sheet to attain the sheet–wire contact and heated at 1073 K for 4 h in air. Four platinum wires were wound on the platinum-coated areas; the distance between the inner platinum-coated areas for voltage measurement was approximately 2 mm. 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 value of the oxygen partial pressure in the latter two gas mixtures was 0.094P$_{O_2}$ and 0.0099P$_{O_2}$, respectively; where P$_{O_2}$ is atmospheric pressure. These values were determined by using an oxygen sensor employing a yttria stabilized zirconia tube.

3. Experimental results

Fig. 1a and c shows the powder XRD patterns for the prepared κ-CeZrO$_4$ disk and the starting t$^i$-(Ce$_{0.8}$Zr$_{0.2}$)O$_2$ phase, respectively. For the t$^i$ phase, the diffraction peaks were indexed on the basis of the pseudofluorite cell; the 112 diffraction peak characteristic of the tetragonal t$^i$ was observed. For the κ phase, fundamental diffractions for CaF$_2$-type structure and sharp diffractions characteristic of the ordered arrangement of constituent cations with indices of all odd numbers of hkl and 422 were clearly observed. Further, many small superlattice diffractions were observed. It has been reported that these small superlattice diffractions were broadened due to antiphase domain boundaries, when the pyrochlore-type precursor was prepared at temperatures lower than 1373 K [8,15,16]. The κ-CeZrO$_4$ prepared in this study involved negligible antiphase domain boundaries. Lattice parameter a and lattice volume V of the κ phase were 1.05248 (2) nm and 1.1659 (1) nm$^3$, respectively, and agreed excellently with those reported previously [8]; the number in the parentheses shows the standard deviation estimated in the last digit. Fig. 2a and c shows the Raman spectra for the prepared κ-CeZrO$_4$ disk and the starting t$^i$ phase, respectively. The spectrum for the κ-CeZrO$_4$ prepared also agreed well with the typical one reported previously [8].

Fig. 3 shows the temperature dependence of the σ$_r$ values measured when the κ-CeZrO$_4$ sample was heated and cooled in O$_2$ gas repeatedly; the data indicated by small symbols correspond to their time dependence. The sample was heated from room temperature, and the σ$_r$ measurement was started by keeping the temperature at 957 K. In a few minutes, after the constant temperature was attained, the σ$_r$ 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 heated, and kept at a preselected temperature, and then the σ$_r$ was measured. The measured σ$_r$ values obtained in this heating process are indicated by the large symbol ■. The σ$_r$ values obtained in the successive cooling process from
1070 K are indicated by the symbol □. The \( \sigma_t \) values obtained in the successive heating process from 970 K are indicated by the symbol ▲. At temperatures below 1190 K, it was confirmed that the measured \( \sigma_t \) 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 \( \sigma_t \) values indicated by the large symbols ■, □ and ▲ between 957 and 1190 K gave Eq. (1):

\[
\log(\sigma_t/T \text{ S m}^{-1} \text{ K}) = 9.97 - 8440/(T/\text{K})
\]  

(1)

which gave \( \sigma_t = 0.12 \text{ S m}^{-1} \) at 1073 K. Based on the equation: \( \sigma_t T = \sigma_0 \exp(-E_a/kT) \), \( E_a = 1.67 \text{ eV} \) was evaluated, where \( k \) is the Boltzmann constant.

As the temperature was increased above 1070 K, the \( \sigma_t \) measured followed first the relationship (1), and then gradually deviated negatively from it above 1233 K. The \( \sigma_t \) measured might be expressed as a function of temperature up to 1233 K. However, as the temperature was further increased, the \( \sigma_t \) began to decrease clearly with time rather than temperature. When the sample was heated at 1313 K and cooled to 1223 K without keeping at a preselected temperature, change in the \( \sigma_t \) in the heating and cooling processes are indicated by the small symbols ▲ and △, respectively. Below 1158 K, the \( \sigma_t \) was measured again during retention at a preselected temperature, where the \( \sigma_t \) changed as a function of temperature. The \( \sigma_t \) values measured on the cooling process and the successive heating from 970 K are indicated by the large symbol of △ and ▼, respectively. The least squares treatment of these stable \( \sigma_t \) values gave Eq. (2):

\[
\log(\sigma_t/T \text{ S m}^{-1} \text{ K}) = 9.74 - 8560/(T/\text{K})
\]  

(2)

which gave \( \sigma_t = 0.054 \text{ S m}^{-1} \) at 1073 K and \( E_a = 1.70 \text{ eV} \).

As the temperature was further increased above 1233 K, the \( \sigma_t \) values decreased again with time. To attain the stable \( \sigma_t \) value, the sample was annealed at 1423 K; in 18 h, the \( \sigma_t \) became stable independent of time. As the temperature was decreased, the \( \sigma_t \) changed as a function of temperature; the \( \sigma_t \) values measured during retention at a preselected temperature were indicated by ◊. The \( \sigma_t \) values obtained in the successive heating process from 979 K, indicated by the ◦, agreed well with those in the cooling process. The \( \ln(\sigma_t/T) \) vs 1/T line appeared to bend at around 1182 K. The relationship between \( \sigma_t \) and temperature was expressed by Eq. (3) below 1182 K and Eq. (4) above 1182 K.

\[
\log(\sigma_t/T \text{ S m}^{-1} \text{ K}) = 9.99 - 9360/(T/\text{K})
\]  

(3)

which gave \( \sigma_t = 0.017 \text{ S m}^{-1} \) at 1073 K and \( E_a = 1.86 \text{ eV} \), and

\[
\log(\sigma_t/T \text{ S m}^{-1} \text{ K}) = 9.63 - 8930/(T/\text{K})
\]  

(4)

which gave \( \sigma_t = 0.97 \text{ S m}^{-1} \) at 1373 K and \( E_a = 1.77 \text{ eV} \).

Figs. 1b and 2b show the powder XRD pattern and Raman spectrum, respectively, for the sample after the electrical conductivity measurements. The analytical data agreed well with those of the \( \tau' \) phase. It was concluded that decrease in the \( \sigma_t \) with time above 1233 K came from the transition of \( \kappa\text{-CeZrO}_4 \) to \( 
\tau'(\text{Ce}_0.5\text{Zr}_0.5\text{O}_2)\text{O}_2 \). The temperature dependence of \( \sigma_t \) values for the \( 
\tau'(\text{Ce}_0.5\text{Zr}_0.5\text{O}_2)\text{O}_2 \) has been recently measured using the disk with the relative density of 97%; \( \sigma_t = 0.036 \text{ S m}^{-1} \) at 1073 K was reported [14]. Eq. (3) for the \( \tau' \) phase gave approximately 1/2 times smaller \( \sigma_t \) values than the reliable data reported previously; the discrepancy between the present and previous data came from the low relative density of the \( \kappa \) sample prepared in this study. Thus, the \( \sigma_t \) values for \( \kappa\text{-CeZrO}_4 \) with a higher relative density were evaluated by multiplying Eq. (1) by 2.1 and normalizing with the respect to the \( \sigma_t \) values for the \( \tau' \) with relative density of 97%. The \( \sigma_t-T \) relationship for \( \kappa\text{-CeZrO}_4 \) recommended in the present study is

\[
\log(\sigma_t/T \text{ S m}^{-1} \text{ K}) = 10.29 - 8440/(T/\text{K})
\]  

(5)

which gave \( \sigma_t = 0.25 \text{ S m}^{-1} \) at 1073 K and \( E_a = 1.67 \text{ eV} \).

The \( \sigma_t \) for the \( \kappa \) was increased with decreasing oxygen partial pressure, \( P(O_2) \). Fig. 4 shows the \( P(O_2) \) dependence of \( \sigma_t \) as measured at 973 and 1073 K. The dependence was expressed by the relation of \( \sigma_t \propto P(O_2)^{-1/n} \); the values of \( n \) were 4.3 at 973 K and 4.5 at 1073 K, respectively.

4. Discussion

The relative density of the \( \kappa \) disk prepared in this study was low as 90%. When the pyrochlore powders ground was pressed without the addition of CeO2 and ZrO2 powders and then annealed in H2 gas, the relative density of the \( \kappa \)-phase disk obtained became higher than 93%; however, serious cracks were recognized in it. When the pyrochlore pellet was ground using an agate mortar with pestle and ball mill before pressing, its surface might be oxidized. During the successive annealing of the pyrochlore disk in H2 gas,
the formation of H₂O gas might occur in it. Further, the intercalation of oxygen into the pyrochlore leads to decrease in the unit cell volume of the crystal [8]. These factors may cause the cracks. Some improvements on the procedure have been needed to prepare a crack-free κ-phase disk with higher relative density.

After the κ phase prepared in this work became the t'-\((\text{Ce}_0.5\text{Zr}_{0.5})_2\text{O}_2\) in the electrical conductivity measurement, the temperature dependence of the \(\sigma_i\) observed agreed well with the feature reported previously for the t'-\((\text{Ce}_0.5\text{Zr}_{0.5})_2\text{O}_2\) disk with high relative density; it was reported that the \(\log(\sigma_i T)\) plotted against \((1/T)\) lay on a line possessing a bend around 1191 K [14]. It could be concluded that the electrical conductivity data obtained in this work reflected only the conductivity of the sample bulk. In Table 1, the dependence of the total electrical conductivity, \(\sigma_i\), of κ-CeZrO₄ phase on oxygen partial pressure, \(P(\text{O}_2)\), are compared to the previous results for t'-\((\text{Ce}_0.5\text{Zr}_{0.5})_2\text{O}_2\) and t'\(_{\text{met}}\)-\((\text{Ce}_0.5\text{Zr}_{0.5})_2\text{O}_2\) phases [14]. The \(P(\text{O}_2)\) dependences of \(\sigma_i\) for the κ phase were quite similar to those for the t' and t'\(_{\text{met}}\) phases; the dependence parameter \(n\) was smaller than 6 and appeared to increase with temperature. This result may come from the association of doubly ionized oxygen vacancies with trivalent cerium ions, \((\text{V}^\text{\text{\`}}}\text{Ce}^\text{\text{\`}})\). The formation of oxygen vacancies may proceed by the reactions:

\[
\text{O}_3^2+ 2\text{Ce}^\text{\text{\`}} \rightarrow \text{O} + 2\text{Ce}^\text{\text{\`}} + 1/2\text{O}_2
\]

\[
\rightarrow \text{(V}^\text{\text{\`}}\text{Ce}^\text{\text{\`}}) + \text{Ce}^\text{\text{\`}} + 1/2\text{O}_2
\]

The concentration of the free trivalent cerium ions, \([\text{Ce}^\text{\text{\`}}]_i\), is propositional to \(P(\text{O}_2)^{-1/4}\), i.e. \(n = 4\), because of \([\text{(V}^\text{\text{\`}}\text{Ce}^\text{\text{\`}})]_i = [\text{Ce}^\text{\text{\`}}]_i\). As the association is decreased, the \(n\) value is increased. It was inferred in the previous report that the t' and t'\(_{\text{met}}\) possessing disordered arrangement of Ce and Zr ions may be predominant electronic conductor according to the hopping mechanism between Ce\(^{3+}\) and Ce\(^{4+}\). In a similar manner to the previous experiments [14], the average ionic transference number \(I_{\text{ion}}\) of the κ phase was evaluated from the emf data constructing an oxygen concentration cell: Pt, \(\text{O}_2\) gas/κ-CeZrO₄/Ar gas, Pt. Although the data was less reliable because of the low relative density of the κ disk used, the value of \(I_{\text{ion}}\) for κ-phase was smaller than 0.01; the κ may be also possibly a predominant electronic conductor. The κ-CeZrO₄ possesses arrays of Ce and Zr ions, respectively, in the (110) direction, unlike the t' and t'\(_{\text{met}}\). A relation between the \(P(\text{O}_2)\) dependence of \(\sigma_i\), and the crystal structure could not be recognized in this study.

In Fig. 5, the electrical conductivity, \(\sigma_i\), for κ-CeZrO₄ phase in \(\text{O}_2\) gas are compared to those for t'- and t'\(_{\text{met}}\)-\((\text{Ce}_0.5\text{Zr}_{0.5})_2\text{O}_2\) phases. The unit cell volume of the phases decreases in order of t', t'\(_{\text{met}}\) and κ-CeZrO₄ [8]. The difference in \(\sigma_i\) may be interpreted as decrease in the distance between Ce\(^{3+}\) and Ce\(^{4+}\) ions. The metastable tetragonal t'\(_{\text{met}}\)-\((\text{Ce}_0.5\text{Zr}_{0.5})_2\text{O}_2\) phase appeared when its precursor Ce\(_2\)Zr\(_2\)O\(_{7+2δ}\) with \(δ > 0.29\) was oxidized at 873 K. It should be emphasized that the t'\(_{\text{met}}\) displays various metastable states depending on the \(δ\) value [17] and therefore, the \(\sigma_i\) value for the t'\(_{\text{met}}\) may change with its precursor composition, \(δ\).

As seen in Fig. 3, the phase transition of κ-CeZrO₄ \(\rightarrow\) t' was accompanied by the redistribution of Ce and Zr occurred above 1273 K; it was completed at a high temperature as 1423 K [14]. It was reported that the phase transition of t'\(_{\text{met}}\) \(\rightarrow\) t' leaving random arrangement of Ce and Zr ions occurred above 1143 K; it was completed around 1273 K. The higher temperature and slower rate of the phase transition, κ-CeZrO₄ \(\rightarrow\) t' were attributable to the activation energy for the redistribution of Ce and Zr ions. Thus, the

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**Table 1**

Dependence of the total electrical conductivity, \(\sigma_i\), of κ-CeZrO₄ phase on oxygen partial pressure, \(P(\text{O}_2)\), compared to the previous results for t'-\((\text{Ce}_0.5\text{Zr}_{0.5})_2\text{O}_2\) and t'\(_{\text{met}}\)-\((\text{Ce}_0.5\text{Zr}_{0.5})_2\text{O}_2\) phases [14].

| Phase    | \(T\) (K) | \(n^a\) | \(\sigma_i\) (\(P(\text{O}_2)\)^{-1/4}) |
|----------|-----------|---------|-----------------------------|
| κ        | 973       | 4.3±0.1 | 0.01±0.001                  |
|          | 1073      | 4.5±0.1 | 0.01±0.001                  |
| t'\(_{\text{met}}\) | 973       | 4.4±0.1 | 0.01±0.001                  |
|          | 1073      | 4.5±0.1 | 0.01±0.001                  |
| t'        | 973       | 4.5±0.1 | 0.01±0.001                  |
|          | 1073      | 4.6±0.1 | 0.01±0.001                  |
|          | 1173      | 5.0±0.1 | 0.01±0.001                  |
|          | 1273      | 5.2±0.1 | 0.01±0.001                  |
|          | 1373      | 5.3±0.1 | 0.01±0.001                  |

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\(a\) The dependence parameter, \(n\), was evaluated on the basis of the equation \(\sigma_i \propto P(\text{O}_2)^{-1/4}\).
5. Conclusions

Electrical conductivity $\sigma_t$ of metastable $\kappa$-CeZrO$_4$ possessing ordered arrangement of Ce and Zr ions in a manner similar to a pyrochlore-type was measured by the DC-four probe method. The $\kappa$ disk was prepared by reoxidizing the pyrochlore-type precursor in O$_2$ gas at 873 K. The data obtained was evaluated as a function of temperature and time and compared with those for the tetragonal metastable $t'$-($\text{CeO}_{0.2}\text{Zr}_{0.8}$)O$_2$ and $t'_\text{meta}$($\text{CeO}_{0.2}\text{Zr}_{0.8}$)O$_2$ phases.

(i) The $\sigma_t$ for $\kappa$-CeZrO$_4$ was approximately an order of magnitude higher than that for the $t'$. Its temperature dependence of between 957 and 1190 K, estimated from comparison with the data for the $t'$ having a higher relative density, was expressed by a linear relationship:

$$\log(\sigma_t T/S \text{ m}^{-1} \text{ K}) = 10.29 - 8440/(T/K)$$

(ii) At temperatures above 1233 K, the $\sigma_t$ decreased gradually with time and agreed finally with that for $t'$. The change in $\sigma_t$ came from the fact that a phase transition, $\kappa \rightarrow t'$ occurred. The present result was consistent with the previous thermodynamic data that the $\kappa$-CeZrO$_4$ was thermodynamically less stable than the $t'$-($\text{CeO}_{0.2}\text{Zr}_{0.8}$)O$_2$.

(iii) The transition temperature for $\kappa \rightarrow t'$ accompanied by change in the cation arrangement, i.e. ordered $\rightarrow$ disordered, appeared to be higher than that for $t'_\text{meta} \rightarrow t'$ leaving random cation arrangement. The $\kappa$-CeZrO$_4$ was virtually thermally stable even in high temperatures as 1233 K.

(iv) The $P(O_2)$ dependence of $\sigma_t$ as measured for $\kappa$ was quite similar to those for $t'$ and $t'_\text{meta}$. The $\kappa$-CeZrO$_4$ may be a predominant electronic conductor according to the hopping mechanism.

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