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Ionic conductivity in the ternary system $(ZrO_2)_{1-0.08x-0.12y}$–$(Y_2O_3)_{0.08x}$–$(CaO)_{0.12y}$

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The total electrical conductivity of the samples in the ternary system $(ZrO_2)_{1-0.08x-0.12y}$–$(Y_2O_3)_{0.08x}$–$(CaO)_{0.12y}$ was measured by a direct current four-probe method in the temperature range 773 to 1673 K. It was found that partial replacement of Y_2O_3 by CaO in the system ZrO_2–Y_2O_3 may enhance the electrical conductivity at higher temperatures. At lower temperatures, however, doping CaO as the third component into the system ZrO_2–Y_2O_3 depresses the conductivity. The observed mixed dopant effect was then analyzed by considering the combined effect of both parameters appeared in the traditional Arrhenius equation, the activation energy, E, and the preexponential factor, σ_0, on the temperature-dependence of the measured conductivity.

1. Introduction

Yttria-stabilized zirconia (YSZ) has been recognized as a good solid electrolyte in many important applications at high temperatures, such as oxygen sensors for metal processing or combustion control, fuel cells for electricity generation, and oxygen pumps for partial pressure regulation. During the past thirty years, numerous work has been conducted to investigate the electrical behavior of YSZ [1–5]. It has been stated that the most conductive composition in the ZrO_2–Y_2O_3 system is ZrO_2 stabilized in the fluoride structure by the addition of about 8–9 mol% Y_2O_3 and the typical values of the oxygen-ion conductivity of this YSZ composition are about 0.1 S/cm at 1000°C and about 0.03 S/cm at 800°C.

Recently, a considerable interest has arisen in the mixed dopant effect on the ionic conductivity in several ternary systems containing ZrO_2 and Y_2O_3. For example, the system $(ZrO_2)_{0.9}$–$(Y_2O_3)_{0.1-x}$–$(Yb_2O_3)_x$ was examined by Corman and Stubican [6] and a slight but steady increase in conductivity was observed when Y_2O_3 is replaced gradually by Yb_2O_3. Similar phenomena were also been reported by Ciacchi *et al.* [7] and Kaneko *et al.* [8] when examining the ternary system ZrO_2–Y_2O_3–Sc_2O_3, where the total dopant contents were restricted to 8 mol%. The enhancement in conductivity of the ZrO_2 and Y_2O_3 containing ternary systems by doping Yb_2O_3 or Sc_2O_3 as the third component may be attributed partially to the fact that the ionic conductivities of both Yb_2O_3– and Sc_2O_3–stabilized zirconia are higher than that of YSZ at higher temperatures [7, 8].

It is well-known that the ionic conductivity of cubic zirconia stabilized with a divalent oxide, such as CaO, MgO, etc, is usually lower than that of YSZ [9, 10]. A recent study by Fernandes *et al.* [11] on the ternary system $(ZrO_2)_{0.88}$–$(Y_2O_3)_x$–$(CaO)_{0.12-x}$ showed that the grain conductivity in this system increases as x increases from 0 to 4 mol%, and then decreases slightly for x larger than 4 mol%. This seems to say that, at least at some certain situations, the ionic conductivity of YSZ may also be enhanced by doping CaO as the third component into the ZrO_2–Y_2O_3 system. If this were the case, the ternary system ZrO_2–Y_2O_3–CaO may be very attractive, mainly because of the relatively lower cost of CaO compared with that of Y_2O_3.

The purpose of the present study is, therefore, to investigate the electrical behavior of the ternary system $(ZrO_2)_{1-0.08x-0.12y}$–$(Y_2O_3)_{0.08x}$–$(CaO)_{0.12y}$. Note that, in the system we observed, the total dopant contents were not kept constant. The reason why we chose such a composition is that the compositions $(ZrO_2)_{0.92}$–$(Y_2O_3)_{0.08}$ and $(ZrO_2)_{0.88}$–$(CaO)_{0.12}$ correspond to the maximum conductivities of ZrO_2–Y_2O_3 and ZrO_2–CaO binary systems, respectively [9, 10]. Such a choice makes it much easier and more direct to compare the electrical behavior of the ternary system with that of the most conductive composition in the ZrO_2–Y_2O_3 system. In this study, only a direct current (d.c.) technique was employed to measure the conductivities of the materials we investigated, for it is the total conductivity, rather than the grain or the grain-boundary conductivity, that can be used as an index for evaluating the applicability of a given material in a certain situation. A detailed analysis on the grain-boundary effect in the ternary system $(ZrO_2)_{1-0.08x-0.12y}$–$(Y_2O_3)_{0.08x}$–$(CaO)_{0.12y}$ will be reported later.

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TABLE I Composition of samples in the system $(ZrO_2)_{1-0.08x-0.12y}$–$(Y_2O_3)_{0.08x}$–$(CaO)_{0.12y}$

Sample denotation		CYZ01	CYZ02	CYZ03	CYZ04	CYZ05
Composition (mol%)	Content of YSZ powder, x	1.00	0.75	0.50	0.25	0.00
	Content of CSZ powder, y	0.00	0.25	0.50	0.75	1.00

2. Experimental

Two types of ultra-fine powders, yttria-stabilized zirconia with 8.0 mol% Y_2O_3 (YSZ) and calcia-stabilized zirconia with 12.0 mol% CaO (CSZ), were prepared firstly by a co-precipitation method, respectively. After washing by distilled water, the co-precipitated products were calcined in air at 800°C for 2 h. The two types of powders, YSZ and CSZ, were then mixed in proper proportions (Table I) by the conventional ball milling with ethyl alcohol and zirconia balls in a plastic pot for 24 h. After drying at 80°C for 5 h in air, all mixed powders were uniaxially pressed at about 100 MPa and then isostatically pressed at about 220 MPa to form discs of about 25 mm diameter. Finally, all discs were divided into three groups and sintered in air at 1500°, 1550° and 1600°C for 3 h, respectively.

The crystal structure of the sintered samples was characterized with a X-ray diffractometer using Cu-k_α radiation at room temperature and the results indicated that all samples prepared in the present study consist of a single phased fluorite-type solid-solution with cubic symmetry. No other phases were observed in the XRD experiments.

The density of the sintered samples was determined by the Archimedes method and achieved about 90% of the theoretical value.

The total conductivity, σ, of each sample was measured as a function of temperature by a d.c. four-probe method. The sintered sample was cut into the shape of a rectangle and four platinum-paste electrodes were fixed on it as current and voltage probes. The sample was then set on an alumina holder and heated in an electric furnace. The conductivity measurements were made over the temperature range 773 to 1673 K at about 50 K temperature intervals during the cooling cycle. About 30 min was given after each temperature change before recording data. At each temperature, at least five conductivity-data were recorded and then an average value of these measured conductivity-dada was used for the following analysis.

3. Results

The compositional dependence of the electrical conductivity for all samples sintered at 1550°C is depicted in Fig. 1, where the isothermal variation of the measured d.c. electrical conductivity, σ, is shown as a function of x, the mole fraction of YSZ powder used in preparing the sample. It can be seen that, in the lower temperature range, $T < 1273$ K, the highest conductivity is always observed at $x = 1$, i.e., the sample CYZ01 with a composition of $(ZrO_2)_{0.92}$–$(Y_2O_3)_{0.08}$. When temperature is elevated further, however, the $\sigma - x$ curves tend to flatten, i.e., the differences between the conductivities of all the five samples become smaller. Note that the highest conductivity no longer appears at $x = 1$ at higher temperature. Especially, the conductivity of sample CYZ02, $(ZrO_2)_{0.91}$–$(Y_2O_3)_{0.06}$–$(CaO)_{0.03}$, at 1673 K is about 20% higher than that of sample CYZ01. These findings seem to suggest that partial replacement of Y_2O_3 by CaO in the binary system ZrO_2–Y_2O_3 may result in an increase in the total electrical conductivity at higher temperature.

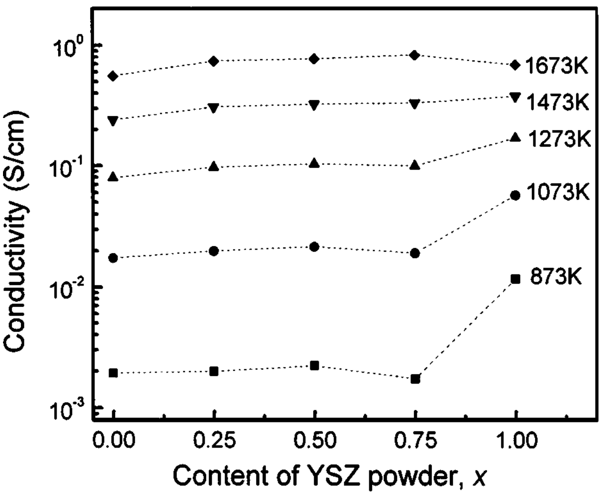
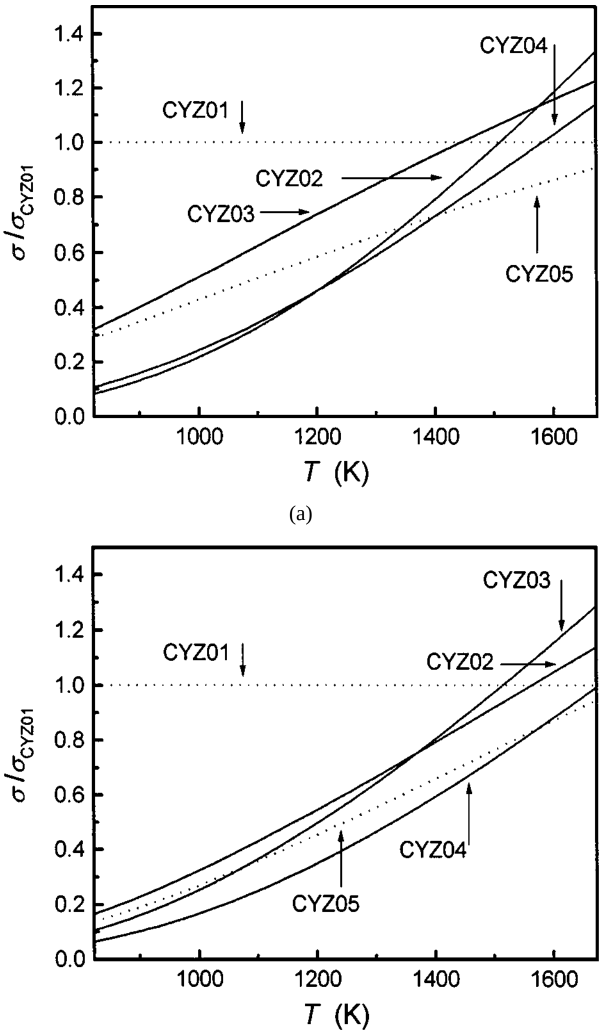


Figure 1 Electrical conductivity as a function of composition for samples sintered at 1550°C.

Similar conclusion can also be deduced by analyzing the experimental data for samples sintered at 1500°C and 1600°C. Comparisons between the electrical conductivities of all of the five samples sintered at 1500°C and 1600°C are shown in Fig. 2a and b, respectively, where the ratio of the measured electrical conductivity of each sample to that of CYZ01, i.e., the binary sample with a composition of $(ZrO_2)_{0.92}$–$(Y_2O_3)_{0.08}$, is plotted as a function of temperature. The temperature dependence of the mixed dopant effect is clear in each case: at the lower temperature range, all the ternary samples, CYZ02, CYZ03 and CYZ04, show a lower conductivity when compared with the binary sample CYZ01; however, a pronounced mixed dopant effect on the conductivity appears as the temperature is elevated.

The experimental phenomena shown in Figs 1 and 2 are rather different with those observed in the ternary systems ZrO_2–Y_2O_3–Yb_2O_3 [6] and ZrO_2–Y_2O_3–Sc_2O_3 [7, 8], where a continuously increasing tendency in conductivity was observed as the amount of Y_2O_3 replaced by Yb_2O_3 or Sc_2O_3 increases and no minimum or maximum appears in the measured conductivity–composition curves. A maximum in the conductivity–composition curves was observed by Chiba *et al.* in the system $(ZrO_2)_{0.7}$–$(Sc_2O_3)_{0.3-x}$–$(Yb_2O_3)_x$ [12]. But this maximum appears in the whole temperature range investigated, 600–1300 K, not only in the lower or higher temperature ranges.



(a)

(b)

Figure 2 Comparisons of the conductivities for samples sintered at (a) 1500°C and (b) 1600°C.

4. Discussion

Our experimental results showed that a conductivity maximum can be obtained in the ternary system $(ZrO_2)_{1-0.08x-0.12y}$–$(Y_2O_3)_{0.08x}$–$(CaO)_{0.12y}$ only at relatively higher temperatures. At the lower temperatures, partial replacement of Y_2O_3 by CaO in the system ZrO_2–Y_2O_3 may depress the conductivity. Such a mixed dopant effect has rarely been reported in literature concerning the ZrO_2-based electrolytes and warrants a further discussion.

Although no experiment was carried out to ascertain the type of charge carrier in the present study, the dominant charge carrier in the samples considered here was assumed in the following discussion to be oxygen ion. This assumption seems to be reasonable because many papers have already reported that the electrical conductivity in both ZrO_2–Y_2O_3 and ZrO_2–CaO binary systems is due to the migration of oxygen ion through the oxygen vacancy [9, 10].

Much attention has been paid to the variation of the activation energy for conduction, E, with the composition when the dopant effect on the ionic conductivity was investigated in a given ZrO_2-based ternary system. The activation energy of conduction for a given sample can be deduced by analyzing the measured temperature dependence of the conductivity according to the traditional Arrhenius equation [9, 10]:

$$\sigma = \sigma_0 \exp\left(-\frac{E}{\kappa T}\right) \qquad (1)$$

where T is the absolute temperature, κ is the Boltzmann constant, and preexponential factor σ_0 is a material constant.

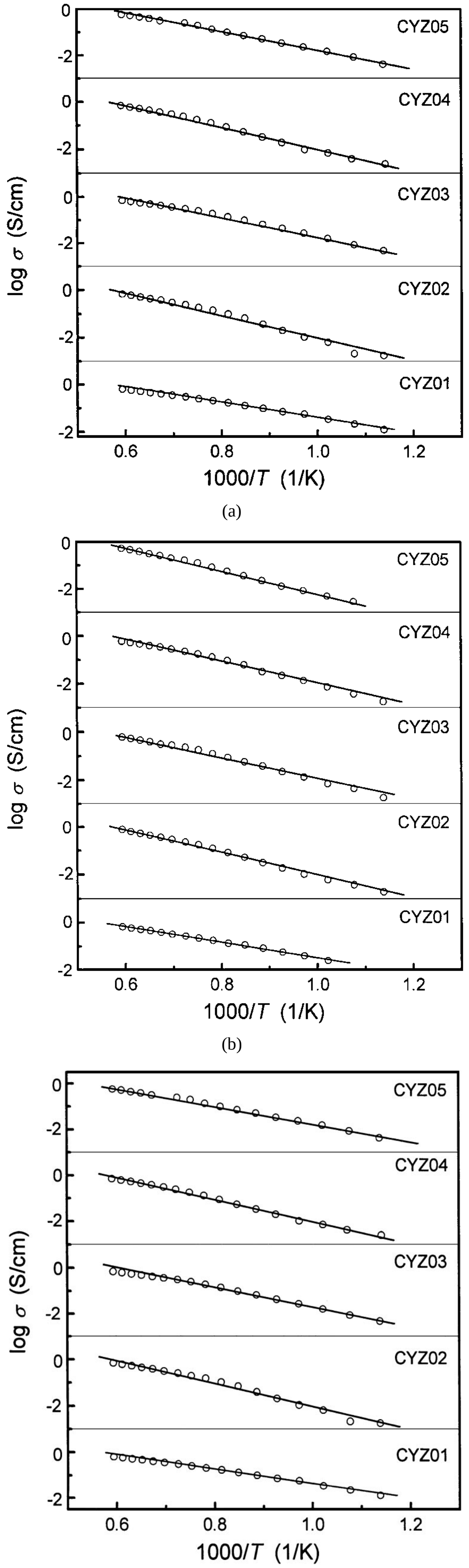
Ananthepadmanabhan *et al.* [13] found that the activation energy, E, in the system $[(ZrO_2)_{1-x}$–$(CeO_2)_x]_{0.9}$–$(Y_2O_3)_{0.1}$ increases as the ratio of the fraction of ZrO_2 replaced by CeO_2, x, increases from 0 to 0.5 and then decreases when x increases further. This result was used to explain why a minimum was observed when $x = 0.5$ in conductivity–composition curves measured in the temperature range 1073 to 1471 K. When studying the electrical behavior in the system $(Y_{1-x}Sc_x)_{0.3}Zr_{0.7}O_{1.85}$, Yamamura *et al.* [14] also pointed out that, corresponding to the increase in the conductivity measured at 1273 K, the activation energy decreases with the increasing x. In fact, the activation energy has also been used as an index by many authors to compare the conductivities between different ZrO_2-based binary system. A well-known fact is that, among all the ZrO_2-based binary systems, the system ZrO_2–Sc_2O_3 exhibits the highest ionic conductivity at higher temperatures while also the lowest activation energy [9, 10].

The variation of electrical conductivity with temperature for all of the fifteen samples is shown in Fig. 3, where $\log \sigma$ is plotted against reciprocal temperature. The linear nature of the graphs in all cases suggests that the temperature dependence of the conductivity can be described approximately with Equation 1. The parameters included in Equation 1, E and σ_0, for each sample are calculated using a simple least-square regression analysis and summarized in Table II.

In Fig. 4, the conductivity data measured at 1073 K and 1673 K are replotted against the activation energy, E. Clearly, at the lower temperature (1073 K), the measured conductivity, σ, decreases with the increasing

TABLE II Parameters included in Equation 1 for test samples

Sample	E (eV)	σ_0 (S/cm)
Sintered at 1500°C		
CYZ01	0.609	48.60
CYZ02	0.998	969.82
CYZ03	0.796	218.63
CYZ04	0.940	552.71
CYZ05	0.769	133.96
Sintered at 1550°C		
CYZ01	0.643	58.99
CYZ02	0.969	703.35
CYZ03	0.922	462.00
CYZ04	0.927	473.53
CYZ05	0.890	269.12
Sintered at 1600°C		
CYZ01	0.655	75.27
CYZ02	0.924	556.07
CYZ03	1.003	1087.32
CYZ04	1.036	1055.87
CYZ05	0.924	462.54



(a)

(b)

(c)

Figure 3 Temperature-dependence of the conductivity for samples sintered at (a) 1500°C, (b) 1550°C and (c) 1600°C.

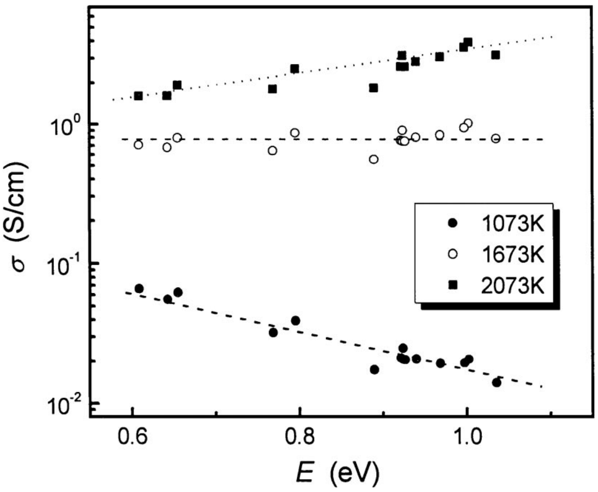


Figure 4 Variation of the conductivity at different temperatures with the activation energy.

activation energy, E, similar to the phenomena observed in other ternary systems mentioned above. At the higher temperature (1673 K), however, σ is observed to be nearly independent of E. The dotted line in Fig. 4 represents the activation-energy-dependence of the conductivity at 2073 K, where the conductivity data were calculated, rather than measured, from Equation 1 with the parameters listed in Table II. It can be seen that a reverse trend, i.e., the conductivity increases with E, may be expected when temperature is high enough. Thus it seems to be impossible or insufficient to explain the experimental results shown in Figs 1 and 2 only by comparing the activation energy data.

In fact, as can be seen from Equation 1, the activation energy is not the only parameter used to characterize the temperature-dependence of the measured conductivity for a given sample. During the past years, however, little effort has been devoted to the preexponential factor, σ_0. A direct comparison between the two binary samples considered here, zirconia stabilized only with 8 mol% Y_2O_3 (YSZ01) and zirconia stabilized only with 12 mol% CaO (CYZ05), shows that CYZ05 exhibits a higher activation energy and a larger σ_0-value. The higher activation energy in the ZrO_2–CaO system has been considered for a long time to be the main reason why the observed conductivity in this system is lower than that in the ZrO_2–Y_2O_3 system [9, 10]. However, such an explanation seems to be somewhat lopsided, for a higher activation energy may result in a lower conductivity, but on the other hand, a larger σ_0-value may result in a higher conductivity. It seems to be more reasonable to analyzing the conductivity–composition relations by considering the combined effect of both the parameters appeared in Equation 1, i.e., the activation energy, E, and the preexponential factor, σ_0.

In continuation of this idea, let us examine the relationship between E and σ_0. Hohnke [15] has proposed that there exists a linear relationship between the logarithm of the preexponential factor, ln σ_0, and the activation energy, E, for all the binary systems involving ZrO_2. A similar linear relationship has been found by Rothman *et al.* [16] to be held in the ternary system ZrO_2–ThO_2–Y_2O_3. Our experimental data are shown

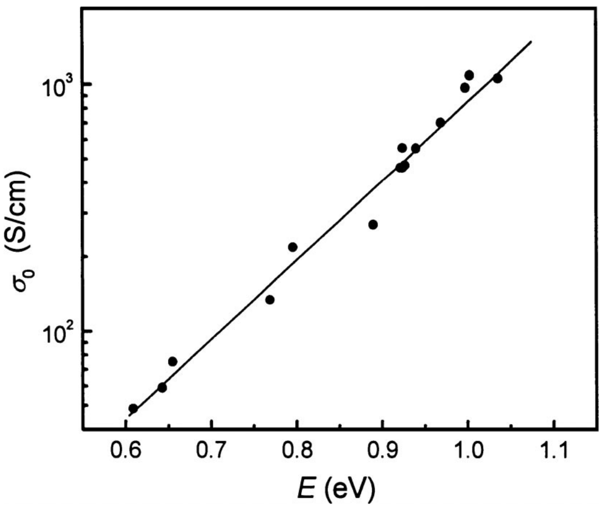


Figure 5 Variation of the pre-exponential factor, σ_0, with the activation energy, E.

in Fig. 5 and a $\ln \sigma_0 - E$ straight line is also observed, implying that Hohnke's empirical equation

$$\ln \sigma_0 = \alpha E + \beta \tag{2}$$

may also be suitable for the ternary system we investigated. A linear regression analysis gives: $\alpha = 7.4482$, $\beta = -0.6829$.

According to Hohnke's analysis [15], the slope of the $\ln \sigma_0 - E$ straight line, α, corresponds to $1/\kappa T_0$, where T_0 is a characteristic temperature at which all the Arrhenius plots, i.e., $\ln \sigma$ versus E curves, for samples in a given system will converge. The value of T_0 for the present ternary system, $(ZrO_2)_{1-0.08x-0.12y}$–$(Y_2O_3)_{0.08x}$–$(CaO)_{0.12y}$, is calculated to be about 1560 K, which is rather lower than those for the binary system ZrO_2–Y_2O_3 (about 2600 K) and ZrO_2–CaO (about 2200 K) [15].

Although the physical meaning of Equation 2 is still unclear, a useful relationship can be obtained by inserting Equation 2 and $\alpha = 1/\kappa T_0$ into Equation 1,

$$\sigma = \exp(\beta) \exp\left[\left(\frac{T - T_0}{\kappa T T_0}\right) E\right] \tag{3}$$

It is clear from Equation 3 that, at a given temperature, the conductivity, σ, is now dependent only on the activation energy, E. When $T < T_0$, increases with decreasing E; when $T > T_0$, σ increases with increasing E. Especially, σ would be independent of E when $T = T_0$.

The above discussion is in good agreement with our experimental results shown in Fig. 4 and seems to be a satisfactory explanation for the observed mixed dopant effect shown in Figs 1 and 2.

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