

## Effects of Yttria and Calcia Co-Doping on the Electrical Conductivity of Zirconia Ceramics

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### ABSTRACT

Zirconia polycrystals co-doped with x mol% CaO and (10-x) mol% Y<sub>2</sub>O<sub>3</sub> were prepared by solid state reaction method. The compositions were chosen for nominally the same oxygen vacancy concentration of 5 mol%. X-ray diffraction patterns indicated the formation of cubic zirconia by heat treatment at 1600°C. Impedance spectroscopy was applied to deconvolute the bulk and grain boundary response. Electrical conductivity was measured using the complex impedance technique from 516 to 874 K in air. Maximum conductivity was exhibited by the composition with equal amounts of CaO and Y<sub>2</sub>O<sub>3</sub>, which may be ascribed to the smaller degree of defect-interactions in that composition due to the competition of different ordering schemes between the two systems. When compared to the composition containing Y<sub>2</sub>O<sub>3</sub> only, co-doping of CaO increases the grain boundary resistance considerably. The activation energy of grain and grain boundary conductivity was 1.1 eV and 1.2 eV, respectively, with no appreciable dependence on dopant compositions.

**Key word :** Zirconia, Codoping, Conductivity, Defect-interaction

### 1. Introduction

Calcium (CaO) and yttria (Y<sub>2</sub>O<sub>3</sub>) are the most representative dopants for stabilized zirconia as solid electrolytes, although CaO is falling out of use mainly due to inferior conductivity and severe aging effects. In stabilized zirconia, for example, Ca<sup>2+</sup> or Y<sup>3+</sup> substitutes Zr<sup>4+</sup> and oxygen vacancies (V<sub>O</sub><sup>••</sup>) are formed at oxygen sites (O<sub>O</sub>) by the charge neutrality condition, i.e.,



The primes and dots represent effectively negative and positive charge, respectively. Understanding of the effects of dopant types and concentrations on the conductivity in a zirconia system is important for the development of solid electrolytes with higher conductivity values at lower operating temperatures.

A dopant concentration of around 10 mol% in stabilized zirconia is certainly beyond the 'dilute limit' below which point defect thermodynamics is applicable. The electrical characteristics of zirconia have been discussed in terms of defect interactions. Because the lower-valent dopants generate oxygen vacancies by electroneutrality condition, as shown in Eqs. (1) and (2), the defect interactions in zirconia

systems have been mainly ascribed to electrostatic origin, i.e. Coulombic association between effectively negatively charged dopants (Ca<sub>Zr</sub>'' or Y<sub>Zr</sub>') and the effectively positively charged oxygen vacancies V<sub>O</sub><sup>••</sup>.

Interactions of the elastic origin also play a significant role in the electrical characteristics of zirconia system. For example, the well-known conductivity bend around 650°C in yttria-doped zirconia materials (Fig. 1(a), left) may be better ascribed to the ordering of oxygen vacancies by elastic attraction rather than the Coulombic association between dopant and oxygen vacancies. This is shown by recent theoretical calculations<sup>1)</sup> and supported by many experimental results, although the interpretation of some experimental results may be not unequivocal. Probably one clearly demonstrative example is the case of scandium-doped zirconia. Although scandium-doped zirconia is known to exhibit the highest conductivity among zirconia systems, at ca. 1000°C, with a very low activation energy of ~0.6 eV, it undergoes a severe conductivity drop around 600°C. The elastic character of the interaction is clear as the conductivity drop is concordant with the cubic-rhombohedral phase transition in the case of specimens with a higher Sc concentration, in which the rhombohedral phase is a phase of ordered oxygen vacancies. A representative vacancy-ordered structure is Zr<sub>3</sub>M<sub>4</sub>O<sub>12</sub>, where M can be Y, Yb and Sc. While the size-matching Sc dopant offers the highest conductivity at high temperatures,<sup>2)</sup> it is noteworthy that oversized dopants such as Y impede the vacancy ordering and thus can be beneficial in keeping the low-temperature conductivity high. The conductivity decrease after maximum

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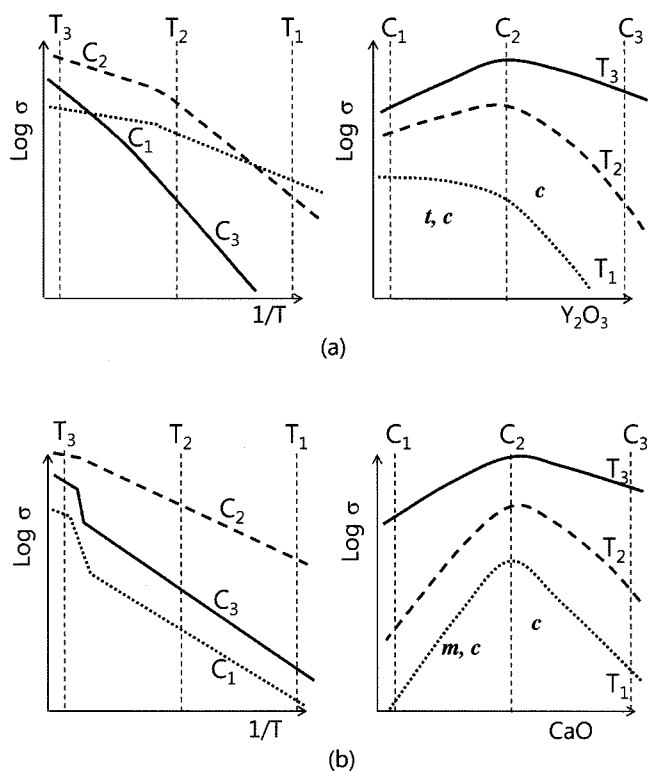


Fig. 1. Schematic diagram of conductivity behavior of zirconia doped with  $Y_2O_3$  (a) and CaO (b). Left column: schematic temperature dependence of three different dopant compositions in which  $C_2$  is the maximum conductivity composition at high temperatures in the cubic phase region near the tetragonal/cubic phase boundary and  $C_1$  and  $C_3$  are a lower and a higher concentration, respectively. Right column: the isothermal conductivity curves versus dopant concentrations in three different temperatures of  $T_1$ ,  $T_2$ , and  $T_3$ .

conductivity composition is also ascribed to the formation of microdomains of ordered phases. (Fig. 1(a), right)

The inferior conductivity of calcia-stabilized zirconia to that of yttria-stabilized zirconia is often ascribed to the stronger Coulombic interaction due to the higher charge of dopants, i.e.  $Ca_{Zr}''$  versus  $Y_{Zr}'$ . However, Fig. 1 shows that the conductivity characteristics of the two systems are quite different from each other. Calcia-doped zirconia does not exhibit the conductivity bend but a stepwise transition at ca.  $1200^\circ C$ , which may be an order-disorder transition. The composition dependence exhibits a maximum which is more pronounced at lower temperature, unlike the behavior of yttria-stabilized zirconia. Low conductivity at lower dopant amounts is related to the presence of monoclinic phase. Yttria can stabilize zirconia in tetragonal and cubic phase more effectively. The lower conductivity and severe aging effect at higher dopant concentrations was ascribed to the formation of microdomains of  $CaZr_4O_9$ , a vacancy-ordered phase, which can be distinguished from  $Zr_3M_4O_{12}$  in yttria-doped zirconia. The two crystals are representative vacancy-ordered structures based on the fluorite structure.<sup>7,8</sup> It should be noted that the ordered structures are not

directly related to the charge of the dopants.  $Mg^{2+}$  and  $N^{3-}$  doping leads to the ordering scheme, similar to  $Zr_3M_4O_{12}$  with  $M=Y^{3+}$ ,  $Yb^{3+}$  and  $Sc^{3+}$ .<sup>9</sup>

The motivation of the current work is thus to examine the effect of dopant concentration in zirconia co-doped with calcia and yttria. This codoping system was studied in 1964 by Strickler *et al.*<sup>4</sup> and recently revisited in-depth by Gong *et al.*<sup>5</sup> In Ref. 5 the compositions were prepared as mixtures of 8 mol%  $Y_2O_3$ - $ZrO_2$  and 12 mol% of  $CaO$ - $ZrO_2$  and thus the total vacancy concentrations vary with the compositions. Bucko studied co-doped compositions with fixed total vacancy concentrations but the conductivity behavior reported is limited to the temperature  $350^\circ C$ .<sup>6</sup>

The compositions in the present work,  $ZrO_2 + (10-x)$  mol%  $Y_2O_3 + x$  mol%  $CaO$  ( $x=0, 2.5, 5.0, 7.5$ ), were chosen to nominally contain 5 mol% oxygen vacancies according to Eq. (1) and (2). The samples are abbreviated as 10Y, 7.5Y2.5Ca, 5Y5Ca, and 2.5Y7.5Ca when applicable.

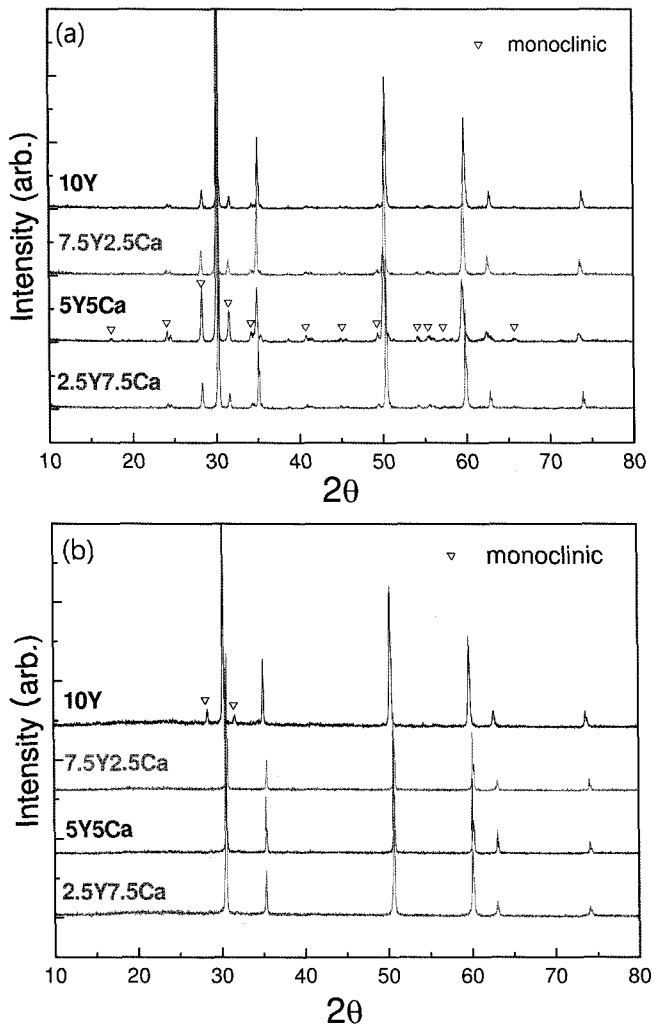
## 2. Experimental

Powders of  $ZrO_2$  (Fluka, 99%),  $Y_2O_3$  (reagent grade), and  $CaCO_3$  (Samchun LTD, 98%) were weighed for the compositions  $ZrO_2 + (10-x)$  mol%  $Y_2O_3 + x$  mol%  $CaO$  ( $x=0, 2.5, 5.0, 7.5$ ), and then mixed for 24 h by ball-milling using zirconia ball in ethanol solvent. The mixtures were ground and heat treated at  $1630^\circ C$ . As the powders with CaO-rich compositions agglomerated severely during heat-treatment, the powders with 7.5 mol% CaO were heat-treated for 4.5 h. The other compositions were heat-treated for 11 h. After calcination the powders were ground again and uniaxially pressed into disk pellets. Pellets were sintered at  $1600^\circ C$  for 5 h. X-ray diffractions (XRD) were taken using a Shimadzu XRD-7000. The diffraction studies were performed using  $Cu K_{\alpha 1}$  radiation with  $\theta$ - $2\theta$  goniometer, divergence slit  $1^\circ$ , receiving slit 0.15 mm and a proportional detector. The working conditions were 40 kV and 30 mA for the X-ray tube, scan speed  $2^\circ/min$ , sampling pitch  $0.02^\circ$ , and  $2\theta$  range from  $10^\circ$  to  $80^\circ$ .

After the large surface of the sintered disk samples was polished with SiC abrasive papers, silver paste was applied as electrodes. Impedance was measured from 516 K to 874 K in the frequency range 100 Hz to 10 MHz with an AC voltage of 100 mV using an impedance analyzer (Solartron 1260) combined with a dielectric interface (Solartron 1296). The data analysis was performed using commercial software (Zview, Scribner Associates Inc.).

## 3. Results and Discussion

The XRD patterns of the four compositions in Fig. 2(a) show that the cubic zirconia phase formed as a main phase by calcination at  $1630^\circ C$ , but considerable monoclinic phase was still observable. The composition with equal amounts of Ca and Y (5Y5Ca) exhibited the highest intensity of the monoclinic phase, as indicated in the figure. A close look at

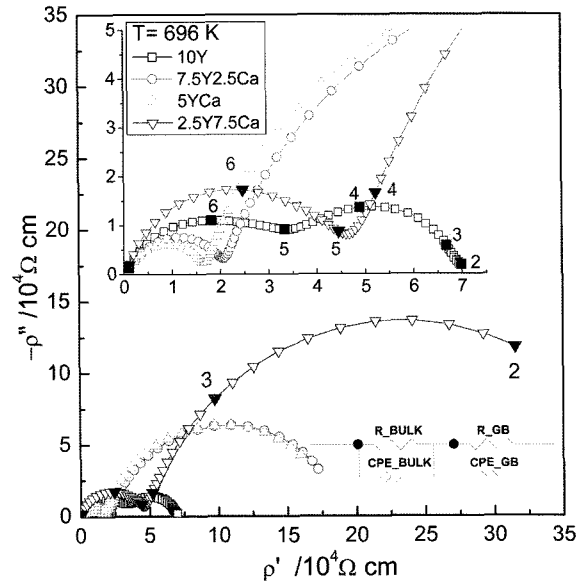


**Fig. 2.** XRD pattern of  $\text{ZrO}_2 + (10-x) \text{ mol}\% \text{ Y}_2\text{O}_3 + x \text{ mol}\% \text{ CaO}$  ( $x=0, 2.5, 5.0, 7.5$ ) for the powders after calcination at  $1630^\circ\text{C}$  (a) and of the pellets after sintering at  $1600^\circ\text{C}$  for 6 h (b).

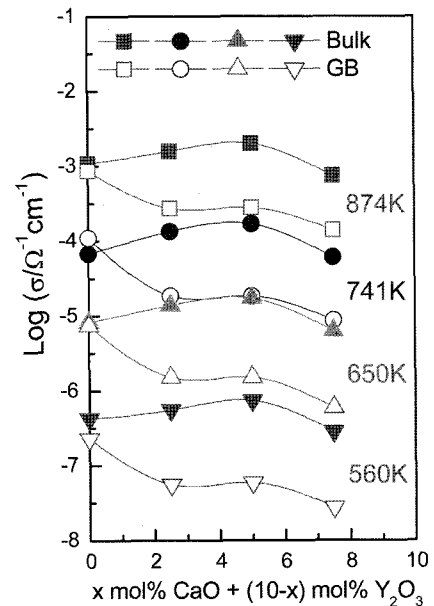
the pattern in the  $2\theta$  range of  $72^\circ$  and  $76^\circ$  indicated a negligible amount of a tetragonal phase.

Fig. 2(b) shows the XRD pattern of the pellets sintered at  $1600^\circ\text{C}$  for 6 h after calcinations. Monoclinic phase becomes negligible for the compositions containing CaO but remains appreciable for the composition containing  $\text{Y}_2\text{O}_3$  only (10Y).

Fig. 3 shows the impedance spectra of the four compositions at 696 K. All the impedance responses can be separated into two responses for the measurement temperature and frequency range. An equivalent circuit was constructed as two R-CPE (Constant Phase Element) parallel circuits connected in series. The numbers indicated in the spectra represent the frequency values such as 2 for  $10^2$  Hz, 3 for  $10^3$  Hz, etc. High-frequency response was interpreted as bulk impedance and low-frequency response as grain boundary impedance. As Fig. 4 shows, bulk conductivity first increases and then decreases, with the CaO addition exhibiting a maximum. When adding only  $\text{Y}_2\text{O}_3$ , (apparent)



**Fig. 3.** Impedance spectra of zirconia co-doped with CaO and  $\text{Y}_2\text{O}_3$ . The spectra were fitted by an equivalent circuit constituted of the two R-CPE parallel circuits in series connection.



**Fig. 4.** Compositional dependence of isothermal bulk and grain boundary conductivity.

grain boundary conductivity normalized with the sample shape factor is similar to the bulk conductivity. With CaO co-doping, grain boundary conductivity became smaller by ca. one order of magnitude, independent of CaO contents.

Fig. 5 shows the temperature dependence of bulk and grain boundary conductivity for the four compositions of zirconia. The activation energy of bulk and grain boundary conductivity was estimated as shown in Fig. 6. The activation energy of conductivity is 1.1 eV for the bulk and 1.2 eV for the grain boundary. They are independent of the compositions.

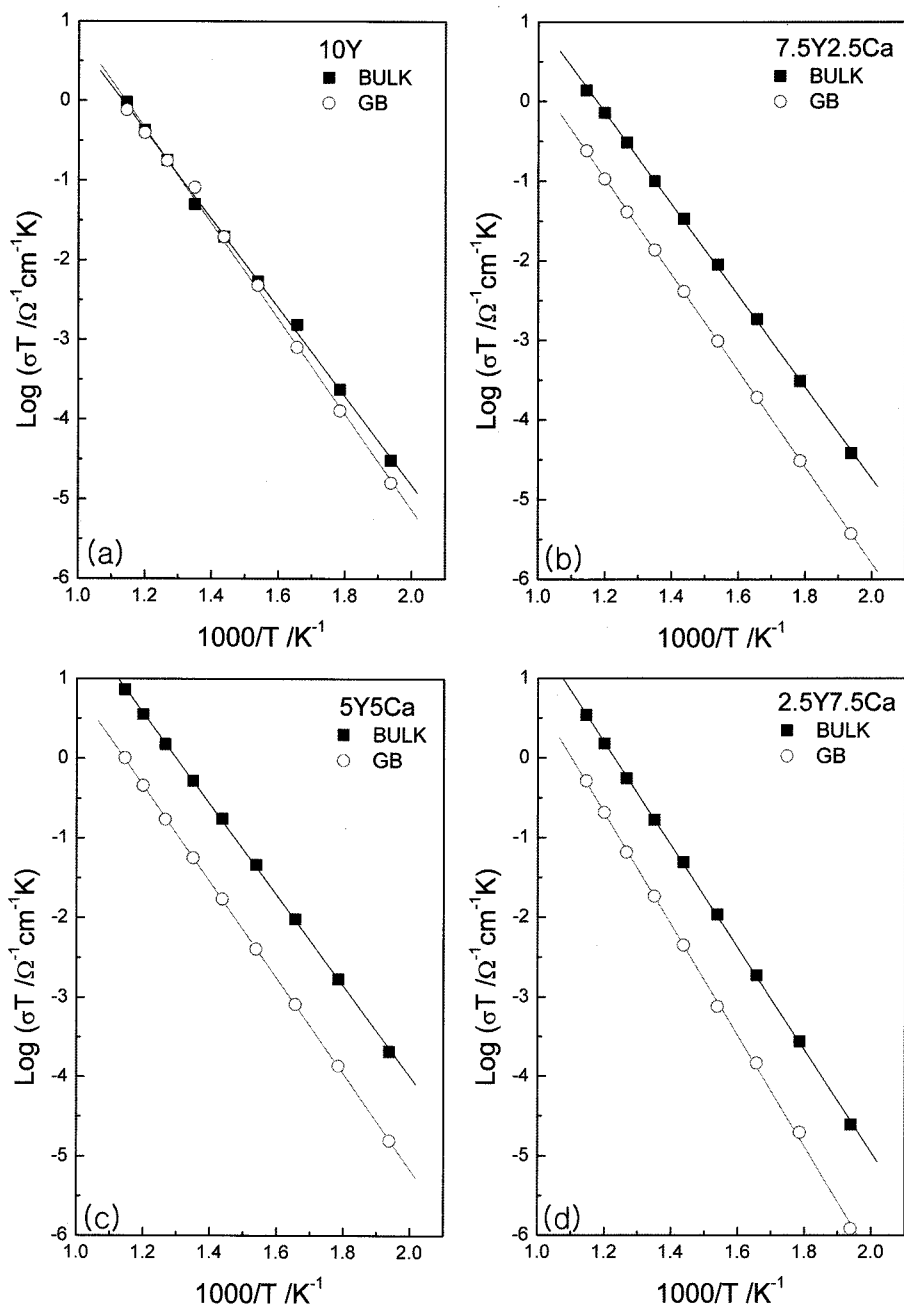


Fig. 5. Temperature dependence of bulk and grain boundary conductivity of zirconia co-doped with CaO and  $Y_2O_3$ ,  $ZrO_2 + (10-x)$  mol%  $Y_2O_3 + x$  mol% CaO where  $x=0$  (10Y) (a), 2.5 (7.5Y2.5Ca) (b), 5.0 (5Y5Ca) (c), 7.5 (2.5Y7.5Ca) (d).

It is suggested that the activation energy of bulk conductivity of the value 1.1 V is characteristic of the present zirconia specimens with the nominal vacancy concentration of 5 mol%, irrespective of the dopant compositions. Single Arrhenius dependence was observed for the measurement temperature range, which corresponds to the 'association' regime below ca. 650°C for the yttria-doped zirconia system, or below ca. 1200°C for the calcia-stabilized zirconia as shown schematically in Fig. 1. This association has been considered to occur between dopants and vacancies by Coulombic interaction. The fact that the activation energy values are independent of the composition with differently

charged dopants may be considered to suggest the vacancy-vacancy association or ordering as the main origin of the defect-interaction in the present system.

The variation of the absolute value of the conductivity according to composition can be explained by variation in the degree of ordering or in the amount of the microdomains of the ordered structure. As introduced above, the calcia and yttria dopants lead to differently ordered superstructures, viz.  $CaZr_4O_9$  and  $Zr_3Y_4O_{12}$ , respectively, albeit the ordering of the nearest neighbor oxygen vacancies is similar in both structures.<sup>7,8)</sup> It is suggested that for the composition with similar amounts of Ca and Y, the competition of the two dif-

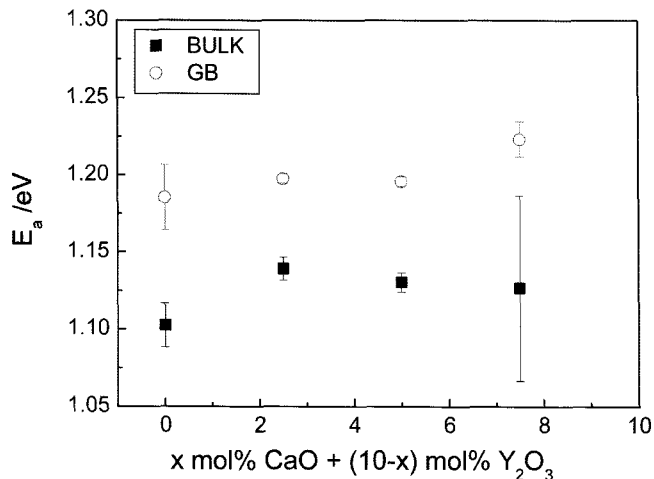


Fig. 6. Activation energy of bulk and grain boundary conductivity as a function of composition.

ferent ordering superstructures between two dopants leads to the lesser degree of ordering or to the lesser extent of ordered microdomain formation. This may explain the highest conductivity for the composition with equal amounts of Ca and Y in the present work.

The significant decrease in grain boundary conductivity with the addition of CaO may be ascribed to the Ca segregation along the grain boundaries. This is indirectly supported by the phase distribution of the specimens after prolonged heat treatment. While Fig. 2(b) shows almost complete cubic transformation for the CaO-containing compositions, a longer sintering time resulted in the reappearance of the monoclinic phase which is suggested to be related to the Ca segregation of the grain boundaries. In the case of the composition containing yttria only, longer heat treatment further reduced the monoclinic phase.

#### 4. Conclusion

We examined the electrical characteristics of yttria and calcia co-doped zirconia  $ZrO_2 + (10-x) \text{ mol\% } Y_2O_3 + x \text{ mol\% } CaO$  ( $x=0, 2.5, 5.0, 7.5$ ) with an equal amount of vacancy composition of 5 mol%. The bulk and grain boundary activa-

tion energy values were 1.1 eV and 1.2 eV, respectively, independent of the composition, which may suggest elastically-induced vacancy ordering as the origin of the defect interactions. The high absolute conductivity for the compositions with similar amounts of calcia and yttria may indicate a lesser extent of ordering as a result of competition between the two different ordered structures of the respective dopants. Large grain boundary resistance for the compositions containing CaO is ascribed to the segregation of Ca at the grain boundary.

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