Lattice parameters of yttria-doped ceria solid electrolytes

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Abstract

Ceria-rare earth solid solutions are known as solid electrolytes with potential applications in oxygen sensors and solid oxide fuel cells. Trivalent rare earth ions enter into solid solution introducing anion vacancies for charge compensation. These oxygen vacancies are quite mobile at moderate temperatures giving rise to a comparatively high ionic conduction. In this study ceria-u mol% yttria solid solutions were prepared by solid state reactions with u ranging from 0 to 12. These solid solutions exhibit a fluorite-type structure with composition-dependent lattice parameters. The variation of the lattice parameter was studied and correlated with existing empirical equations and with an equation based on the ion-packing model. The effect of an effective ionic radius of Y^{3+} in eightfold coordination is also discussed.
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1. Introduction

Solid ionic conductors with the fluorite structure have been extensively studied due to its applications as oxygen sensors, oxygen pumps, and as solid electrolytes in solid oxide fuel cell (SOFC) systems.[1–3]

Rare earth-doped ceria solid electrolytes are of great interest especially for intermediate temperature SOFC application.[4,5]

Several properties of these solid solutions, like the ionic conductivity and phase stability, are dependent on physical and chemical characteristics of the precursor materials and sintered ceramics. Among these characteristics, the density and lattice parameters are of main concern.

In a fluorite-type structure the number of coordination for cations and anions are 8 and 4, respectively. The lattice parameter, a, for an ideal fluorite structure is given by:

$$a = \frac{4}{\sqrt{3}}(r_{\text{cation}} + r_{\text{anion}}) \quad (1)$$

where the constant $4/\sqrt{3}$ is derived from the unit cell geometry; r_{cation} and r_{anion} are the cation and anion radius, respectively.

In oxygen-ion conductors the doping with lower valent cations creates a number of anion vacancies for charge compensation. In addition, the unit cell frequently undergoes a contraction or an expansion depending upon the size of the dopant cation. This variation in the size of the unit cell with the dopant size, in many cases, obeys a linear relation known as Vegard's law.

In oxygen-ion conductors the variation in the lattice parameter of the fluorite structure has been studied theoretically as well as experimentally. There are basically two types of theoretical approach for the calculation of the lattice parameters of a solid solution with the fluorite structure of the type MO_2-$M'O_{1.5}$, where MO_2 corresponds to the matrix and $M'O_{1.5}$ to the dopant. Some studies have proposed equations which are based on the ion-packing model.[6–8] Others consist on equations resulting from the fitting of a number of experimental data.[9,10]

A recent proposed equation[8] based on the ion-packing model is:

$$a = \left\{ \frac{4}{\sqrt{3}}\Big[r_{M'} - r_{Ce} - 0.25r_O + 0.25r_{V_o^{\bullet\bullet}}\Big]u + \frac{4}{\sqrt{3}}[r_{Ce} + r_O]\right\}0.9971 \quad (2)$$

where $r_{M'}$, r_{Ce}, r_O, and $r_{V_o^{\bullet\bullet}}$ are the ionic radii of the dopant cation, cerium ion, oxygen ion and oxygen vacancy, respectively; u is the dopant molar fraction,

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and the constant (0.9971) accounts for the observed difference in the experimental value and that on the ICDD 34-394 for the lattice parameter of pure ceria. Values of the ionic radii for host and dopant cations and oxygen ion are, in general, taken from the Shannon's compilation.[11]

In this model, the oxygen vacancy radius is assumed to be constant for a given solid solution and can be obtained from the "critical radius". The critical radius is defined as the ionic radius of the dopant whose substitution for the host cation causes neither expansion nor contraction of the fluorite lattice. In the case of ceria solid solutions $r_{V_O^{\bullet\bullet}}$ is 0.1164 nm.[8]

The most used semiempirical equation is, for ceria solid solutions, given by:[9]

$$a = 0.5413 + \sum_k (0.0220\Delta r_k + 0.00015\Delta Z_k)m_k \qquad (3)$$

where Δr_k and ΔZ_k are the ionic radii and valency differences between the host and the dopant cations; m corresponds to the percentual fraction of dopant cation, and is given by:

$$m_k = \frac{h_k u_k}{100 + \sum_k (h_k - 1)u_k} 100 \qquad (4)$$

where h_k is the number of dopant cations and u_k the mol% of the dopant cation, respectively.

In a recent review on pure and doped ceria,[12] the fundamental aspects of Eqs. (2) and (3) were thoroughly discussed. It was point out that both equations may be used within their accuracy limits to calculate the concentration of a given solute in a solid solution, although the different formulae give different values of Vegard's slopes and of critical radius.

These equations have been used to study the variation of the lattice parameter in a number of solid solutions, and the results show that the experimental values, in general, agree with those calculated.[13,14] However, in most of these works the solid solution of yttria-doped ceria was not included.

In this work, the solid solutions of ceria-u mol% yttria were prepared by the conventional mixing of oxides technique to study the variation of the lattice parameter with yttria content in the low yttria region.

2. Experimental procedure

CeO_2 (99.9%) and Y_2O_3 (99.9%) were used as starting materials. Solid solutions of CeO_2: u Y_2O_3 with u = 0, 4, 6, 8, 10 and 12 mol% were prepared by the conventional powder mixing technique. Batches with 10 g of total weight were prepared for each composition in a mixer (Turbula T2C) for 6 h using absolute ethanol and zirconia balls. After drying, the mixed powder was gently ground in an agate mortar. Cylindrical pellets were prepared by uniaxial pressing at 98 MPa. Pressed pellets were sintered at 1600 °C for 6 h in air, with a cooling rate of 5 °C min^{-1} up to 700 °C.

Apparent densities were determined by the immersion technique. Fractured surfaces of sintered pellets were observed in a scanning electron microscope (XL30, Philips).

Lattice parameter determinations were performed on crushed pellets. X-ray diffraction experiments were carried out in a diffractometer (D8 Advance, Bruker-AXS) operating at 40 kV and 40 mA using a Ni filter and Cu K_α radiation. The diffracted X-rays were collected over 2θ range 50–132°, typically using a step width of 0.05° and measuring for 10 s per step. High-quality Si powder was used as standard for the angular correction. The relative amount of Si used in these experiments was adjusted to obtain similar intensities for the peaks of the standard material and ceria-based solid solutions. Three independent determinations of the lattice parameters were performed for each composition in order to avoid errors due to specimen preparation and mounting, Using a peak-search program, and by selecting the average peak width and the significant signal-to-noise ratio, all peaks were determined from the raw data. Then, an output file listing peak positions, the peak widths and relative peak intensity was obtained. The obtained data were fitted using a peak-fitting program, which calculated a theoretical data curve from the original data, assuming a symmetrical peak shape. A Lorentzian function gave the best fit to the experimental data. Lattice parameters were then refined from the fitted data using a least square routine. This procedure allowed for obtaining standard deviations of about 1%.

3. Results and discussion

The relative sintered density was higher than 93% for all yttria-doped pellets. Compacts of nominally pure ceria reached only 80% of the theoretical density value.

Scanning electron microscopy results are in general agreement with density values and demonstrate that yttrium ions act not only as a modifier additive in ceria to improve the electrical properties, but also as a sintering aid enhancing the densification during sintering. Similar observation was previously made in gadolinia-doped ceria.[15]

X-ray diffraction patterns of all studied specimens are shown in Fig. 1. The angular position of peaks for the pure ceria specimen agrees with that in the ICDD 34-394. For doped specimens, a slight peak shift due to the formation of solid solution is observed. In these patterns, peaks related to isolated yttria or to spurious phases are not observed.

In this 2θ range 50–132° a total of five peaks were chosen for lattice parameter determinations. These peaks are marked in the lower part of Fig. 1 according to ICDD 27-1402 and 34-394 for Si and CeO_2, respectively.

The five chosen diffraction peaks in each specimen could be easily distinguished from those of the standard material. Fig. 2 shows an example of the good resolution obtained in the high-angle region.

The X-ray powder pattern for the composition containing 6 mol% yttria in the high-angle region is shown in this Fig. 2. The points stand for the fitting by a Lorentzian function.

The resulting experimental values for the lattice parameter are plotted in Fig. 3 along with those values calculated according to Eqs. (2) and (3).
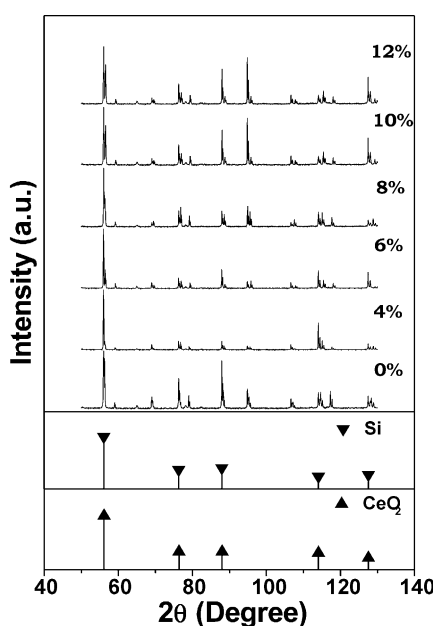
In this case, the ionic radii of Ce^{4+}, Y^{3+} and O^{2-} were taken from the Shannon's compilation.[11] It can be seen that the lattice parameter of the solid solution decreases linearly with increasing the dopant content in agreement with the Vegard's law.

The experimental points lie between those calculated from Eqs. (2) and (3). The observed deviation between experimental and calculated values is similar for both models and within an acceptable precision ($<5\%$) for this type of determination. This result shows that both the semiempirical and the ion-packing models can account for the observed behavior of lattice parameter in this solid solution range.

In the study[16] of the ionic conductivity and lattice parameter determinations for solid solutions of HfO_2-R_2O_3 (R = lanthanides, Sc^{3+} and Y^{3+}), it was shown that the conduction activation enthalpy increased with the radius of the dopant except for Ho_2O_3 and Y_2O_3. Moreover, the activation enthalpy value was higher for solid solutions containing Ho_2O_3 than Y_2O_3, at the same dopant content. In addition, the lattice parameters were also higher for solid solutions containing Ho^{3+} than Y^{3+}.[17] In a subsequent work[17] a systematic investigation was carried out in ZrO_2 and HfO_2 matrices containing Ho_2O_3 and Y_2O_3 in a broad composition range. From the obtained results, the authors suggested that the ionic radius for Y^{3+} in eightfold coordination proposed by Shannon had been overestimated. A new value was proposed as 0.1011 nm.

Inserting this new value for the Y^{3+} radius in Eqs. (2) and (3) and recalculating the lattice parameter for the ceria-yttria solid solutions, resulted in the curves shown in Fig. 4.

As can be seen in that figure, the equation based on the ion-packing model gave the best fitting for the experimental values especially at low yttria contents. A small deviation between experimental and calculated

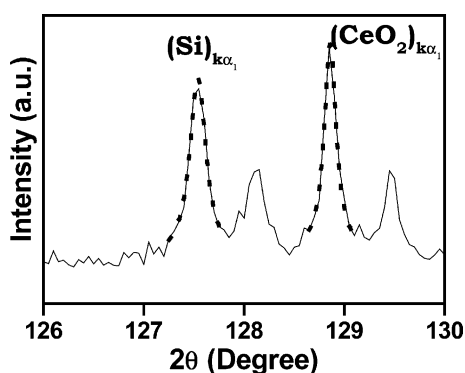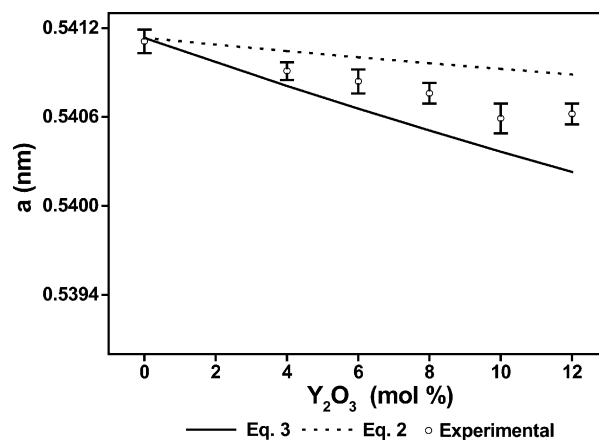Fig. 1. X-ray diffraction patterns of all studied specimens in the 50–132° 2θ region.

Fig. 2. X-ray diffraction pattern of ceria-6 mol% yttria powder on the high angle region. The points show fitting the peaks by a Lorentzian function.

Fig. 3. Experimental (o) and calculated (— and ⋯) lattice parameters in the studied composition range using the Y^{3+} radius proposed by Shannon.[11]
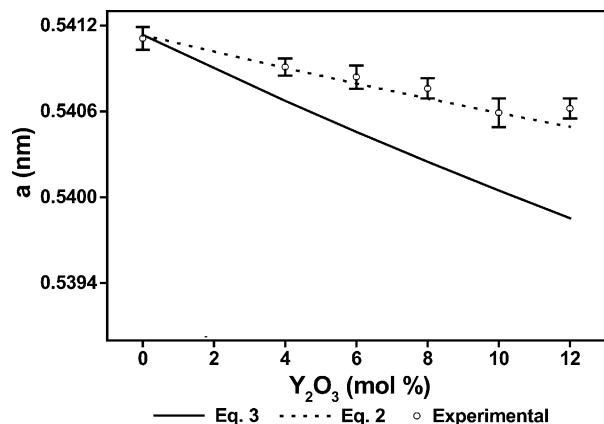
Fig. 4. Experimental (o) and calculated (— and ⋯) lattice parameters in the studied composition range using the Y^{3+} radius proposed in.[17]

values is observed for the high yttria content solid solution. Similar observations for lanthanides-doped ceria were attributed to changes in the anion vacancy radius or to a decrease in the cation coordination number.[8]

4. Conclusions

The doping of ceria with yttria enhances the densification during sintering of the polycrystalline ceramic.

The evolution of lattice parameters of the fluorite structure obeys the Vegard's law, and its behavior with increasing dopant content can be described by the existing models with reasonable precision. However, when an effective ionic radius recently proposed for Y^{3+} is used, the best fitting for the variation of the lattice parameters with composition is accomplished with the ion-packing model.

Acknowledgements

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