Lattice parameters of thoria–yttria solid solutions

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Abstract

ThO$_2$:x mol% Y$_2$O$_3$ (x = 0, 3, 6, 9 and 12) ceramic powders have been prepared by the citrate technique. Dense specimens have been obtained after pressing and sintering at 1550°C/2 h. X-ray diffraction measurements were performed in the sintered pellets for structural phase analysis and lattice parameter determination. The experimental results suggest that an empirical equation, similar to the equation proposed for zirconia–yttria ceramics, is valid for thoria–yttria solid solutions. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Thorium oxide, like other oxides of tetravalent cations (zirconium oxide, cerium oxide) is a material with predominant electrical conduction via $\text{O}^{2-}$ ions [1]. A wide range of applications of these materials, after forming solid solutions with oxides of lower valent cations, is found in modern technology. They are used in oxygen sensors in the steel and in the automotive industries, and in solid oxide fuel cells [2,3]. The role played by the dopants with lower valence ($2^+$ and $3^+$) than the host ($4^+$) is the introduction of oxygen vacancies in the lattice, required for charge neutrality, these vacancies being responsible for the observed high ionic conductivity in these systems. The ionic conductivity of fluorite type oxides, e.g., doped thorium and doped zirconia, depends on the dopant kind and concentration. Maximum conductivity is achieved with dopants having ionic radius close to the ionic radius of the host ion, i.e., the lower is the lattice contraction or expansion, the higher is the ionic conductivity [4]. The effect of dopants on the lattice parameters of the cubic fluorite structure phase is thus important in the study of oxygen-ion conductors [4]. Several equations have been proposed for the dependence of the lattice parameter of fluorite structure MO$_2$ oxide solid solutions on dopant concentration [4–8]. For the determination of lattice parameters in MO$_2$–R$_2$O$_3$ systems ($M = \text{Zr, Hf, Th and } R = \text{La, Pr, Nd, Sm, Sc, Y, Ln}$) as a function of dopant content, the dopant–host radius difference and the contraction of the lattice...
due to the creation of oxygen-ion vacancies was considered [8]. The differences between calculated and experimentally determined lattice parameters were lower than 0.03 Å for Zr and Hf systems. For Th systems, on the other hand, the calculations did not yield good results. Based on the effect of the solute ion size and oxygen-ion vacancies on the geometry of the fluorite unit cell, empirical equations have been proposed for the observed changes in the lattice parameters of MO$_2$ fluorite-type oxides (M = Hf, Zr, Ce, Th, U) due to formation of solid solutions [4]. A critical ionic radius is defined for each system as the hypothetical radius of the dopant whose substitution for the host cation causes neither expansion nor contraction of the fluorite lattice; the closer the dopant ionic radius is to the critical ionic radius, the higher is the ionic conductivity [4]. The changes of lattice parameters of cubic solid solutions, particularly of the ZrO$_2$–Y$_2$O$_3$ system, have been estimated assuming a spherical ion packing [6]. The experimental determination of lattice parameters by X-ray diffraction measurements in ZrO$_2$–Y$_2$O$_3$ single crystals in the 2–5 mol% Y$_2$O$_3$ range gave support to these estimations. That model was considered correct for ZrO$_2$ and HfO$_2$ systems but not for ThO$_2$, CeO$_2$ and UO$_2$ systems. The difference is that these systems can retain the fluorite structure at room temperature without doping, while the other two systems (ZrO$_2$ and HfO$_2$) require aliovalent doping for that purpose [5]. Moreover, oxygen-ion vacancy formation upon doping is not taken into consideration in that model. More recently, an ion packing model was proposed based on cluster of defects in zirconia solid solutions [7].

Thorium oxide is known as one of the structurally more stable oxides. Its structure is cubic fluorite up to the melting point at approximately 3300°C. Yttrium oxide crystallizes with the Th$_2$O$_3$-type, the common structure to the majority of the rare earth oxides [10]. That structure derives from the cubic fluorite structure by an ordered omission of one quarter of the anions and a slight rearrangement of the ions. Based on the similarity of the structure, extensive solid solution can be obtained in the ThO$_2$–Y$_2$O$_3$ system [10].

For the evaluation of the experimentally determined lattice parameters of thoria–yttria specimens, two models previously proposed have been used in this paper [6,14]. The first one, proposed for ZrO$_2$–Y$_2$O$_3$ solid solutions for yttria concentration up to 12 mol% presented the following equation:

$$d_0 = 0.1 A \left( R_{Th} + R_0 + \frac{\sum P_k M_k \Delta R_k}{100 + \sum M_k (P_k - 1)} \right)$$

where $R_0$ is the O$^{2-}$ ionic radius, $R_k$ the ionic radius of the $k$th doping element, $P_k$ the number of ions by unit cell of the $k$th doping element, $A$ a parameter related to the structure geometry.

Considering that yttrium is the doping element, the above equation simplifies to

$$d_0 = 0.1 A \left( R_{Th} + R_0 + \frac{PM \Delta R}{100 + M (P - 1)} \right)$$

Using the Pauling ionic radii for Th$^{4+}$ ($R_{Th} = 1.02 \ Å$), for Y$^{3+}$ ($R_Y = 0.93 \ Å$) and for O$^{2-}$ ($R_0 = 1.40 \ Å$), $A = 4/\sqrt{3}$ for the cubic fluorite structure, and $P = 2$ for the yttrium oxide, the following equation is obtained:

$$d_0 = 0.23094 \left( 2.42 - \frac{0.18 M}{100 + M} \right)$$

That equation is the first one used for calculating the lattice parameter of the thoria–yttria specimens prepared in this work.

The second model is the one recently proposed for determining lattice parameters in fluorite (MO$_2$) and C-type (MO$_{1.5}$) solid solutions [14]. According to the authors, it can be applied in the full composition range and it also shows that for relatively large M$^{4+}$ substituting cations (Th, Ce), there is a positive (convex) deviation from the Vegard’s law; for M$^{4+}$ relatively small (Zr, Hf) cation ionic radii, on the other hand, the deviation is (concave) negative. The basic equation to evaluate the lattice parameter $a_0$ of the M$_{1-x}$M$_x$O$_{2-y/2}$ (0 < $y < 1$) solid solution is:

$$a_0(y) = (1 - y)f_b + yf_c$$

$y$ is the molar fraction of the cubic oxide, $f_b$ ($r_b$) the curve fitting of the lattice parameter of the fluorite-type oxides (MO$_2$) as a function of the corresponding (M$^{4+}$) cationic radius, and $f_c$ ($r_c$) the curve fitting using lattice parameter values for cubic (MO$_{1.5}$) oxides as a function of the corresponding (M$^{4+}$) cationic radius.
2. Experimental

Thoria–yttria reactive (high surface area) powders have been prepared according to the citrate technique [11–13] for yttria contents 3, 6, 9 and 12 mol%. The powders were pressed to pellets and sintered at 1550°C/2 h. Finishing of the pellet surfaces has been achieved by polishing. X-ray diffraction analysis has been performed in the parallel pellet surfaces in the 25–95° 2Θ range (0.02° angle step size, 5 s time per step). Bruker-AXS D8 Advance and Philips 3710 diffractometers were used at 40 kV and 40 mA.

3. Results and discussion

The X-ray diffraction patterns of the sintered ThO₂–Y₂O₃ specimens are shown in Fig. 1. The diffraction lines of pure ThO₂ and Y₂O₃ from JCPDS files are also shown. The diffraction patterns of the specimens correspond to that of pure ThO₂, no diffraction lines of Y₂O₃ being detected. As far as X-ray diffraction experiments are concerned, thoria–yttria solid solution has been attained in all doped specimens. Impedance spectroscopy experiments on these yttria-doped specimens described elsewhere [12,13] provided further evidence of solid solution formation.

The lattice parameters were determined for each composition after indexing all diffraction lines. Table 1 shows these values.

There is a decrease in the lattice parameter values for increasing Y₂O₃ addition. The same behavior has already been reported for thoria–yttria ceramics for

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ThO₂</td>
<td>5.5921</td>
</tr>
<tr>
<td>ThO₂:3 mol% Y₂O₃</td>
<td>5.5845</td>
</tr>
<tr>
<td>ThO₂:6 mol% Y₂O₃</td>
<td>5.5725</td>
</tr>
<tr>
<td>ThO₂:9 mol% Y₂O₃</td>
<td>5.5626</td>
</tr>
<tr>
<td>ThO₂:12 mol% Y₂O₃</td>
<td>5.5543</td>
</tr>
</tbody>
</table>

Table 1

Lattice parameter values for sintered. ThO₂:x mol% Y₂O₃ (x = 0, 3, 6, 9 and 12)

JCPDS file 42-1462.
Fig. 2. Lattice parameter of ThO$_2$:m mol% Y$_2$O$_3$ (m = 0, 3, 6, 9 and 12) sintered pellets as a function of Y$_2$O$_3$ content: ● — experimental, ○ — according to model 1 Ref. [6], □ — model 2 Ref. [14].

Yttria concentrations in the 0–33% range [10]. The substitution of Y$^{3+}$ for Th$^{4+}$ in the crystal lattice promotes local contraction due to the difference in ionic radius (1.02 Å for Th$^{4+}$ and 0.93 Å for Y$^{3+}$). An opposite behavior is found in zirconia–yttria systems, the lattice parameter increasing for increasing yttria content due to a local expansion of the crystal lattice (the ionic radius of Zr$^{4+}$ is 0.80 Å).

Fig. 2 shows the dependence of the lattice parameter of ThO$_2$–Y$_2$O$_3$ on the Y$_2$O$_3$ content. The theoretical values of the lattice parameter, determined using the equation corresponding to the first model, are plotted for comparison with the experimentally determined values. A good agreement is found. As expected, the values determined experimentally by X-ray diffraction are higher than the calculated ones. Even though there are no Y$_2$O$_3$ diffraction lines in the X-ray diffraction patterns, probably not all added yttrium ions are soluble in the ThO$_2$ matrix. The larger the Y$_2$O$_3$ content added to the ThO$_2$ matrix, the larger the difference between the experimental and the calculated lattice parameters.

In the same figure, the values determined using the second model, proposed recently by Otobe and Nakamura, are also shown. A good agreement is also found. The main difference between both models is that the first shows large deviation for increasing yttria content, while for the second the deviation is at low yttria concentrations.

4. Conclusions

One model developed for the dependence of the lattice parameter on the dopant content of zirconia ceramics was successfully applied to thoria–yttria ceramic solid electrolytes in the 0–12 mol% yttria composition range. The model, proposed by Ingel and Lewis, fits the experimentally determined decrease of the lattice parameter of thoria–yttria for increasing yttria content in that range. In this case, the larger the dopant concentration, the larger the deviation between experimental and calculated lattice parameters. Another model, recently proposed by Otobe and Nakamura, also fits the experimental data. In this case, the larger the dopant concentration, the smaller the deviation.
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References


