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Structural characterization of the CeO_2/Gd_2O_3 mixed system by synchrotron X-ray diffraction

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ABSTRACT

The structural determination of the CeO_2/Gd_2O_3 mixed system is a non-trivial problem because of the close resemblance between the ionic sizes of Ce^{4+} and Gd^{3+} and between the crystal structures of CeO_2 and Gd_2O_3. $(Ce_{1-x}Gd_x)O_{2-x/2}$ powder samples with x ranging between 0 and 1 have been synthesized by coprecipitation of mixed oxalates and subsequent thermal decomposition in air at 1200 °C followed by slow cooling. Synchrotron powder X-ray diffraction data were collected and refined by the Rietveld method. Lattice parameters do not follow Vegard's law and no peak splitting has been observed for any composition, meaning that no biphasic regions exist over the whole compositional range. The same hybrid structural model – a proper mixture of the structures of the two pure oxides – was used for the refinements, allowing to account for the data observed.

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1. Introduction

Rare earth-doped ceria has been extensively studied as electrolyte for solid oxide fuel cells, as it displays an excellent ionic conductivity depending on the dopant type and amount. In particular, Gd-doped CeO_2 shows significantly higher performances than the commonly used Y-stabilized zirconia, as it permits to lower the operating temperature of the fuel cell in the range 400–700 °C thanks to its low activation energy for ionic conduction [1,2]. Despite the importance of this material and the thorough investigations performed on its electrical conductivity, doubts still remain about the crystal structure of the system, due to the close resemblance between the ionic sizes of Ce^{4+} and Gd^{3+} and between the crystal structures of CeO_2 and Gd_2O_3. Actually, a clear understanding of the atomic arrangement is of great importance, as it could provide useful hints to clarify the mechanism of ionic conductivity.

CeO_2 crystallizes in the fluoritic cubic structure (hereafter named F structure) containing four CeO_2 formula units per cell and belonging to the $Fm-3m$ space group [3], with lattice parameter $a=5.411$ Å [4]. This is a highly symmetric atomic arrangement, where Ce is situated in the (0,0,0) position and O in (1/4,1/4,1/4). Ce is coordinated to eight O atoms that build edge-sharing cubes; CeO_8 cubes are connected with each other to form a three-dimensional chess-board. The cubic structure of Gd_2O_3 (hereafter named C structure), belonging to the $Ia-3$ space group, can be considered as a fluorite-related arrangement containing one-fourth O atoms less than CeO_2. Gd is six-coordinated to O, forming corner- and edge-sharing distorted polyhedra (Fig. 1). The removal of the O atoms with respect to CeO_2 causes a displacement of the remaining atoms, so that Gd occupies two different crystallographic positions; the diffractograms differ only for the appearance of some additional peaks in Gd_2O_3, as C is a superstructure of F. Due to the similarity of the ionic sizes of the two rare earths (r_{Ce4+} [C.N.:8]$=0.97$ Å and r_{Gd3+} [C.N.:6]$=0.938$ Å [5]), the lattice parameter of Gd_2O_3 is exactly double with respect to CeO_2, being $a=10.823$ Å [6]. For these reasons the peaks common to the two structures appear to be superimposed and it is not possible by means of a laboratory diffractometer to distinguish whether a biphasic (F+C) region or a solid solution over the whole compositional range exists, or whether other mechanisms take place.

This issue has been often addressed in the literature and the results are contradictory. Bevan and Summerville [7] reported on the existence of a F+C biphasic region in the central part of the CeO_2–Gd_2O_3 pseudobinary phase diagram, while Brauer and Gradinger [8] and more recently Grover and Tyagi [9] asserted the presence of a fluoritic solid solution in the $(Ce_{1-x}Gd_x)O_{2-x/2}$ system for $0 \leq x \leq 0.4$ and a C-type solid solution above $x=0.4$. Jadhav et al. [10] studied the system up to $x=0.30$, Tianshu et al. [2] up to $x=0.4$,

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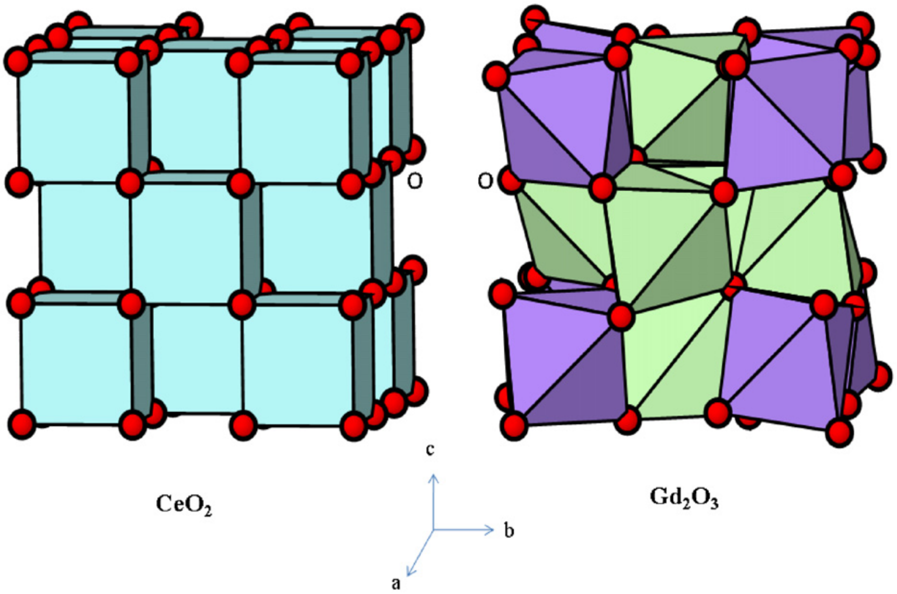

Fig. 1. Crystal structures of CeO_2 (on the left) and Gd_2O_3 (on the right). For a better comparison, only one-eighth of the Gd_2O_3 unit cell is drawn. The polyhedra around the rare earth atoms are shown: CeO8 cubes in CeO_2, and the two different six-vertices polyhedra around Gd1 and Gd2 (distorted octahedra) in Gd_2O_3.

Ikuma et al. [11] up to $x=0.5$ and Peng and Zhang [12] up to $x=0.6$; they all found a fluoritic solid solution in the range investigated. Nevertheless, Ikuma et al. [11] recognize that the technique used is not sufficient to determine whether in the range $x=0.4$–0.5 a biphasic region exists or not. Despite the disagreement among the reported data, all the authors that studied the whole compositional range agree on the cell parameters trend that shows a maximum around $x=0.5$ and does not follow Vegard's law. This evidence led some authors to postulate the existence of small microdomains of C structure intergrown in a fluoritic matrix, although the resolution of the technique (powder X-ray diffraction) did not allow to verify this hypothesis [9].

With the aim to find out the structural arrangement of the system, we collected X-ray powder diffractograms on $(Ce_{1-x}Gd_x)O_{2-x/2}$ samples over the whole compositional range at a synchrotron facility, in order to have the necessary resolution to overcome the difficulties described.

2. Material and methods

The $(Ce_{1-x}Gd_x)O_{2-x/2}$ powder samples ($x=0$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, hereafter named C0, C1, …, C10, respectively) were prepared by thermal decomposition of the corresponding coprecipitated mixed oxalates $(Ce_{1-x}Gd_x)_2[C_2O_4]_3 \cdot nH_2O$. The latter were synthesized starting from Ce and Gd_2O_3 (Aldrich, 99.99%), dissolving them in HCl (10% m/V) and mixing the two solutions. The coprecipitation was obtained by addition of an oxalic acid solution in excess. The oxalates powders were filtered and then dried in air at 80 °C for 24 h. A procedure for the compositional control of the samples has been followed, as described in [13]. The oxalates have been subsequently decomposed by thermal treatment at 1200 °C in air and the resulting oxides were then slowly cooled in furnace. A mechanical mixture of the oxides was also prepared by mixing CeO_2 and Gd_2O_3 in 6:4 molar proportion; this sample is hereafter named CM.

All the samples were then analyzed at the powder diffraction beamline (MCX) of the Elettra synchrotron radiation facility located in Trieste, Italy, on a Huber 4-axes X-ray diffractometer equipped with a fast scintillator detector; diffractograms were collected at room temperature for $5^\circ \le 2\theta \le 55^\circ$ with step: 0.006°; the incident beam energy has been chosen at 18 keV, this value being a good compromise between the requirements of the high energy necessary to minimize absorption of the samples, and the spectral characteristics of MCX. The beamline has been designed to work in the range 6–12 keV, exploiting the high brilliance of ELETTRA bending magnets in this spectral region, but photon flux values of interest for specific experiments are available also in the ranges 2.3–6 keV and 12–23 keV. Samples were contained in borosilicate capillary tubes with an inner diameter of 0.5 mm and rotated at a speed of 100 rpm. Data were refined by the Rietveld method by means of the FullProf program [14]. The diffraction data of CeO_2 (C0 sample) were collected on a home powder diffractometer (Philips PW1050/81, Ni-filtered Cu $K\alpha$ radiation), with 0.02° 2θ steps and $10''$ counting time, in the range 4–90°; the refinement was accomplished by the DBWS program [15].

3. Results and discussion

Two main evidences can be noticed analyzing the structural data:

1. For $0 \le x \le 0.3$ only fluorite peaks can be observed, while at higher Gd content weak peaks of the C phase appear; the latter strengthens increasing the Gd amount, up to $x=1$, where only the C phase peaks occur; no peak splitting between C and F structure is visible.
2. The lattice parameters, calculated indexing diffractograms in the $Fm-3m$ space group for $0 \le x \le 0.3$ and in the $Ia-3$ space group at higher x values, do not follow Vegard's law: they show a maximum for $x=0.5$ and a symmetrical trend as a function of composition.

The presence of the only fluoritic peaks up to $x=0.3$ indicates that a certain solubility of Gd^{3+} in the CeO_2 lattice exists; Gd^{3+} enters the structure together with oxygen vacancies that compensate for the valence difference between tetravalent Ce and trivalent Gd.

For $x>0.3$ the situation is much more complex. The increasing height of the C phase peaks with increasing Gd content suggests

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