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Crystallographic properties of the $Ce_{1-x}Lu_xO_{2-x/2}$ system at pressures up to 7 GPa

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ABSTRACT

Synchrotron powder diffraction measurements were performed up to 7 GPa on $Ce_{1-x}Lu_xO_{2-x/2}$ bulk samples in order to elucidate the high pressure structural properties of the system. In the studied pressure range $Ce_{1-x}Lu_xO_{2-x/2}$ does not show any structural phase transition. The bulk modulus as a function of the Lu content is found to broadly fall into two regimes, namely an increasing trend for $0 < x < 0.2$ and a linear decrease for $0.2 \le x \le 0.4$. This twofold compressibility behavior is mostly driven by two competing factors, namely the mean atomic volume for x ranging between 0.2 and 0.4, and the lattice volume at lower Lu content. Present results suggest that oxygen vacancies affect the bulk modulus value mainly above $x \sim 0.2$. Since pressure effects are known to be correlated to the strain acting on a thin film of similar composition, this study contributes to clarify the functional properties of doped ceria systems, such as the increased ionic conductivity of thin films subjected to a tensile strain.

1. Introduction

Among the numerous application fields of rare earth (RE) oxides, such as luminescence [1,2], high temperature superconductivity [3] and thermoelectricity [4,5], solid state ionics plays a key role. Even limiting to solid state electrolytes, in fact, several CeO_2-based oxides behave as optimal systems: in particular, Sm- and Gd-doped ceria provide remarkable ionic conductivity values in the intermediate temperature range [6–8]. The mechanism underlying ionic conductivity is related to the movement of the oxygen vacancies created by the partial substitution of Ce^{4+} by RE^{3+}, such as Sm^{3+}, Gd^{3+}, *etc.*, through the lattice. Yet, the motion is only possible when vacancies present are not associated with RE'_{Ce}, *i.e.* when they are randomly distributed over the fluorite-type structure typical of CeO_2 (hereafter named F, space group: $Fm\bar{3}m$), where RE is coordinated to eight oxygen atoms in the nearest-neighbor shell. The random distribution of vacancies can take place only until the F structure is retained, that is up to a certain substitution range, which depends on the RE identity. The upper compositional boundary of the F phase in $Ce_{1-x}RE_xO_{2-x/2}$ is located, for instance, at $x \sim 0.2$, 0.3 and 0.4 for RE ≡ Gd [9], Sm [10,11] and Lu [12], respectively. What happens at higher RE content is quite complicated and strongly dependent on the Ce^{4+}/RE^{3+} size difference [13]: if a sufficient dimensional resemblance exists, such as in the case of RE ≡ Gd, Sm and Y, an intermediate structure between F and the one typical of sesquioxides RE_2O_3 of the smallest rare earths becomes stable. The latter (hereafter called C) crystallizes in the space group $Ia\bar{3}$, and it is characterized by the coordination number 6 in the first shell. The intermediate or hybrid atomic arrangement (H), widely described in the literature for the aforementioned systems [9,10,14,15], consists in a solid solution of C-structured RE_2O_3 domains embedded within the F matrix, observable by X-ray diffraction in the form of a gradual change of some crystallographic parameters from the values typical of F toward those typical of C. For RE ≡ Lu, the Ce^{4+}/RE^{3+} size difference (r_{Ce4+} [CN8] = 0.97 Å, r_{Lu3+} [CN6] = 0.861 Å, from [16]) is too large to ensure the necessary conditions for the formation of the hybrid atomic arrangement, and for $x > 0.4$ a (F + C) biphasic field is stable [12].

In spite of the validity of the described scenario, it is well known that the maximum ionic conductivity values in bulk RE-doped ceria occur within the F range, *i.e.* at x significantly lower than the one corresponding to the F upper boundary [7,17], as a consequence of the formation of C-based nanodomains trapping vacancies at fixed positions, and therefore hindering their free motion. This interpretation is supported by the results of measurements performed by local

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techniques, such as Raman [10,12] and EXAFS [18,19] spectroscopy, as well as TEM microscopy [20], which are able to detect the presence of the aforementioned nanodomains, at variance with the x-ray diffraction.

Nevertheless, the composition corresponding to the maximum ionic conductivity, as well as the absolute value of this property, are not necessarily the same in bulk samples and in thin films, due to the presence of heterogeneous interfaces in the latter. Such aspects are for example elucidated both in experimental and theoretical studies regarding Y_2O_3-stabilized ZrO_2- [21,22] and CeO_2-based multilayers [23,24]. In particular, while the presence of a larger amount of defects in thin films with respect to bulk samples determines a remarkable decrease in ionic conductivity [25], the reduction of the layer thickness generally promotes at the same time a significant conductivity increase, which is driven by the controlled interface lattice mismatch between the ionic conductor and the substrate [24,26]. Yet, the difficulty in performing reliable measurements at thin-film interfaces and in correctly evaluating the results by separating the two competing effects (namely the ones deriving from defects and from strain), suggests the possibility to simulate the lattice mismatch effects by following the structural properties of bulk samples subjected to high pressure. Nonetheless, only few high pressure structural studies of solid state electrolytes are currently available in the literature, such as for example Sm-doped ceria [27].

In this work, Lu-doped ceria is taken as a model to study the high pressure structural features of a system where the effect of oxygen vacancies prevails over the Ce^{4+}/RE^{3+} size difference in determining the cell parameters of the F phase; this occurs due to the close similarity of the Ce and Lu ionic radii with coordination number 8 (r_{Ce4+} [CN8] = 0.97, r_{Lu3+} [CN8] = 0.977 Å, from [16]), which strongly reduces the dimensional contribution. Several compositions belonging to the F range of the $Ce_{1-x}Lu_xO_{2-x/2}$ system (nominal $x = 0.1$, 0.2, 0.3 and 0.4) are studied by high pressure synchrotron x-ray diffraction employing a diamond anvil cell (DAC), that is the most commonly used apparatus for high and extremely high pressure diffraction experiments [28]. The applied pressure ranges between 1 and 7 GPa; this choice was operated relying on the evidence that a 1% compressive strain, which is for instance close to the one occurring in a 250 nm thick Gd-doped ceria film deposited on a $MgO/SrTiO_3$ layer [26], roughly corresponds to the application of 5 GPa [27]. Two compositions mainly containing the C phase (nominal $x = 0.8$ and 0.9) are considered too, with the primary aim to check the C/F amount ratio obtained at ambient and at high pressures; moreover, the composition of the F phase in the (F + C) biphasic sample $Ce_{0.2}Lu_{0.8}O_{1.6}$, primarily found by x-ray diffraction [12], could be confirmed through the measurement of the bulk modulus. Data are discussed in terms of the competing factors ruling the bulk modulus of Lu-doped ceria and CeO_2, in comparison to results deriving from other RE-doped ceria systems [27,29].

2. Material and methods

2.1. Synthesis

Six samples belonging to the $Ce_{1-x}Lu_xO_{2-x/2}$ system with nominal $x = 0.1$, 0.2, 0.3, 0.4, 0.8 and 0.9, were prepared by a coprecipitation technique, as described in [30,31]. It consists first of all in the dissolution of due amounts of elemental Ce (Johnson Matthey ALPHA 99.99% wt.) and Lu_2O_3 in HCl (13% wt.), followed by mixing the two solutions and by adding a solution of oxalic acid in large excess, which causes an immediate precipitation of the mixed Ce/Lu oxalate. The so obtained oxalates were filtered, washed using deionized water, dried at 363 K overnight and afterwards treated at 1373 K in air for four days to obtain the corresponding mixed oxides, which form through the mechanism described in [32]. Samples are named Lu10, Lu30 and so on, according to the nominal Lu atomic percent with respect to the total rare earth (Ce + Lu) content.

2.2. Scanning electron microscopy – energy-dispersive system (SEM-EDS)

The overall rare earth content of monophasic samples was checked by scanning electron microscopy – energy-dispersive system (SEM-EDS, Oxford Instruments, model 7353 with Oxford-INCA software v. 4.07). Powders were pelletized, coated by a graphite layer and analyzed at a working distance of 15 mm, with acceleration voltage 20 kV. EDS analyses were carried out on at least 4 points or areas for each sample.

2.3. High pressure synchrotron x-ray powder diffraction (HP-XRPD)

High pressure X-ray powder diffraction measurements were carried out at the XRD1 diffraction beamline of the Elettra Synchrotron radiation facility located in Trieste (Italy). A monochromatic circular beam of wavelength 0.7 Å and diameter around 50 μm was used; pressure was generated using a gear-driven Boehler-Almax plate diamond anvil cell (plate DAC) with a large X-ray opening containing diamonds of culet size 600 μm. The sample chamber was prepared by pre-indenting 200 μm-thick stainless steel gaskets to about 70 μm using the same plate DAC, and drilling a through hole of diameter 150 μm at the center of the pre-indented region by spark erosion. Finely ground powders of the sample were loaded inside the sample chamber to obtain diffraction data with minimal preferred orientation effects. A tiny piece of oxygen-free Cu was placed inside the chamber along with the sample to have a pressure calibration from the Cu (111) diffraction peak position. The sample chamber was completely filled with silicon oil before bringing the diamonds of the plate DAC in contact with the gasket: within the pressure range covered in the present study (maximum pressure applied ~7 GPa), silicon oil acting as a pressure transmitting medium (PTM) provided good hydrostatic pressure conditions. The experimental station was equipped with a Pilatus2M large area detector; images of the powder diffraction rings were converted into 2θ-intensity plots by means of the fit2D software; 2θ values range between 6° and 36°. The FullProf suite [33] was used to refine structural models by the Rietveld method. High pressure data are discussed in comparison to the ones collected on the same samples at ambient pressure at the MCX beamline, as described in [12].

3. Results

According to the results of the structural investigation described in [12], at ambient pressure samples belonging to the $Ce_{1-x}Lu_xO_{2-x/2}$ system are monophasic and characterized by the fluorite structure up to $x = 0.4$, with only tiny traces of the C phase appearing in Lu40. The amount of C increases with increasing x, until this phase becomes the most abundant one at $x = 0.6$, and the only one from $x = 0.9$. At $x = 0.8$, for instance, the sample is formed by the mixture (88 mol% C + 12 mol% F); this evidence suggests the occurrence of out-of-equilibrium conditions, most probably due to a kinetic effect taking place during the oxalate coprecipitation stage, as elucidated in [12]. No significant changes, neither in the presence of phases, nor in the F/C proportion, were found at high pressure.

The observed compositional extent of the F phase in Lu-doped ceria points at a significantly larger stability field than in Gd- and Sm-doped ceria, where F was found stable up to $x \sim 0.2$ [9] and ~0.3 [10], respectively. EDS analyses, performed on monophasic samples either with the F ($0.1 \le x \le 0.4$) or the C structure ($x = 0.9$), indicate a very good agreement with the nominal Ce/Lu stoichiometry, as evident from Table 1. With regard to the biphasic sample Lu80, the ambient pressure compositions of F and C were differently determined: relying on the interpolation of the refined F lattice parameter to the ones of the $x = 0.1$–0.4 series, the stoichiometry of F results to be $Ce_{0.67}Lu_{0.33}O_{1.83}$; at variance, the composition of C was fixed at $Lu_{1.8}Ce_{0.2}O_{3.1}$, *i.e.* the one corresponding to $x = 0.9$, since the C cell parameter of Lu80 is very close to the one of Lu90.

In agreement with the previous description, three structural models