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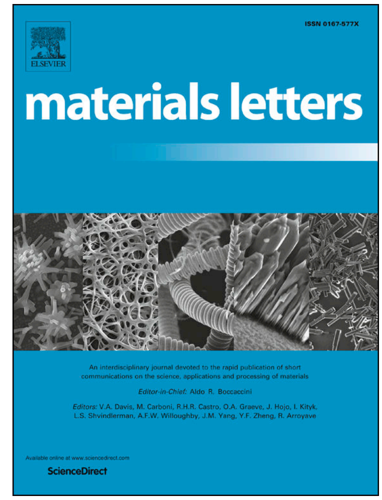

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Serge Vives, David Ramel, Cathy Meunier

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Influence of the defect distribution on the thermal expansion of Gd-doped ceria.

Serge Vives [a,§], David Ramel[a], Cathy Meunier[b]

[a)] *FEMTO-ST Institute, Université de Franche-Comte, CNRS, 2 avenue Jean Moulin 90000 Belfort, France.*

[b)] *Nanomedecine, Imagerie, Therapeutique, Université de Franche-Comte, 4 place Tharradin, 25211 Montbéliard, France.*

[§] corresponding author

serge.vives@univ-fcomte.fr

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Abstract

Molecular dynamics (MD) simulations are performed to obtained the evolution of $Ce_{1-x}Gd_xO_{2-x/2}$ lattice parameter with temperature. Gd^{3+} and $V_O^{\bullet\bullet}$ are distributed randomly (R) or as $Gd'_{Ce}V_O^{\bullet\bullet}Gd'_{Ce}$ trimer (N) inside the fluorite structure. The thermal expansion coefficient (TEC) depends on both the doping ratio and the temperature. Furthermore, MD results evidence the high influence of the defect arrangement on the TEC with the N distribution more in accordance with the experimental published TEC. We also observe that TEC of the two distributions tends to get closer at high temperature.

1. Introduction

An increasing number of works has been devoted to the study of CeO_2 based materials these last decades. In a technological view these materials are of prime importance knowing the large field of their possible energy, environmental and biomedical applications [1]. In a more academic view CeO_2 crystallises in the fluorite structure with modified physico-chemical properties due to introduction of oxygen vacancies. The presence of each oxygen vacancy is concomitant to the reduction of two Ce^{4+} to Ce^{3+} cations (intrinsic defect) or to the introduction of two aliovalent foreign ions (extrinsic defect) generally rare-earth trivalent ions.

There is a general consensus on the room temperature lattice parameter of stoichiometric CeO_2 around the value of 5.41Å [2]. Modification of this lattice parameter is then obtained under doping and thermal solicitation leading to the determination of thermal expansion coefficient (TEC). Classical linear TEC α in the temperature range [T_1-T_2] is defined as:

$$TEC[T_2 - T_1] = \alpha(T_2) = \frac{1}{(T_2 - T_1)} \frac{a(T_2) - a(T_1)}{a(T_1)} \approx \frac{1}{\Delta(T)} \frac{\Delta(L)}{L_1} \qquad (1)$$

with $a(T_i)$ the lattice parameter at the temperature T_i (when diffraction is used) and L_1 the sample length at temperature T_1 (when dilatometry is used). The mismatch existing between the TEC of two materials in contact is the source of stresses which could damage a system as it is the case for a SOFC cell [3]. The knowledge and monitoring of doped fluorite TEC are thus of prime importance for a future technological development in the field of the solid-state electrochemistry.

As it is the case for the ionic conductivity [4] it seems obvious that the thermal expansion of doped ceria is affected by the nature, the rate and distribution of dopant.

2. Simulation procedures and data analysis

To perform the MD simulations, we employ the LAMMPS simulation code [5]. The NPT ensemble with zero external pressure is adopted and the Nosé-Hoover algorithm is used to control temperature and pressure. For each simulation the time step is fixed at 1 fs. The structure is first minimised then an equilibration during 7500 steps is performed at the desired temperature. Lattice parameter is obtained by averaging on the last 250 ps dynamic steps.

The simulation supercell contains 8×8×8 CeO_2 fluorite unit cells with periodic boundary conditions. For each system $Ce_{1-x}Gd_xO_{2-x/2}$ (x=0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3) two dopant arrangements are examined. In the first (GdR) dopants and oxygen vacancies are distributed randomly while in the second (GdN) trimers $(Gd'_{Ce}V_O^{\bullet\bullet}Gd'_{Ce})$ are randomly distributed with Gd^{3+} in the nearest neighbour position relative to the oxygen vacancy as it is shown in Fig. 1. For each system the final lattice parameter is averaged over five different structures that are generated [6]. The MD simulations are first carried out at 298 K and then each 100K between 673K and 1373K.

In this work the Buckingham function describes the short-range interaction with parameters given in our previous work [7].

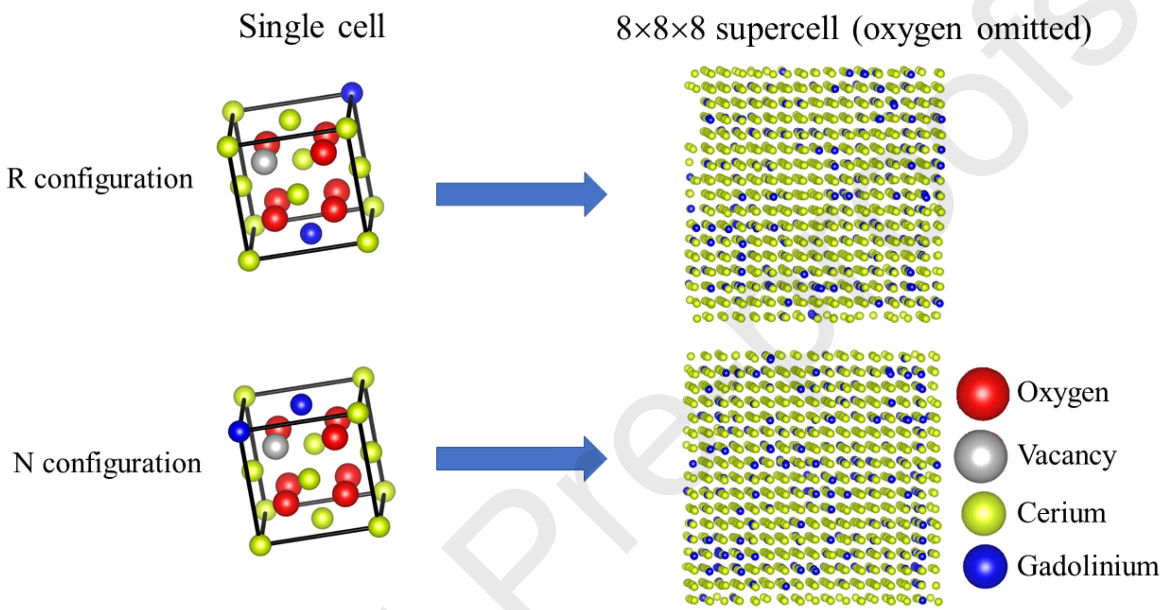

Fig. 1. Example of the two defect configurations on a fluorite single cell and on the 8×8×8 supercell ($Ce_{0.85}Gd_{0.15}O_{1.925}$).

3. Results and discussion

We have already unveiled that the parameter set used here properly describes the evolution of undoped and Gd doped ceria with temperature by comparing the MD results with experimental data extracted from literature [7,8]. We can then admit that this parameter set is adapted for the description of the lattice parameter evolution with temperature at least for the *x* composition range [0-0.3].

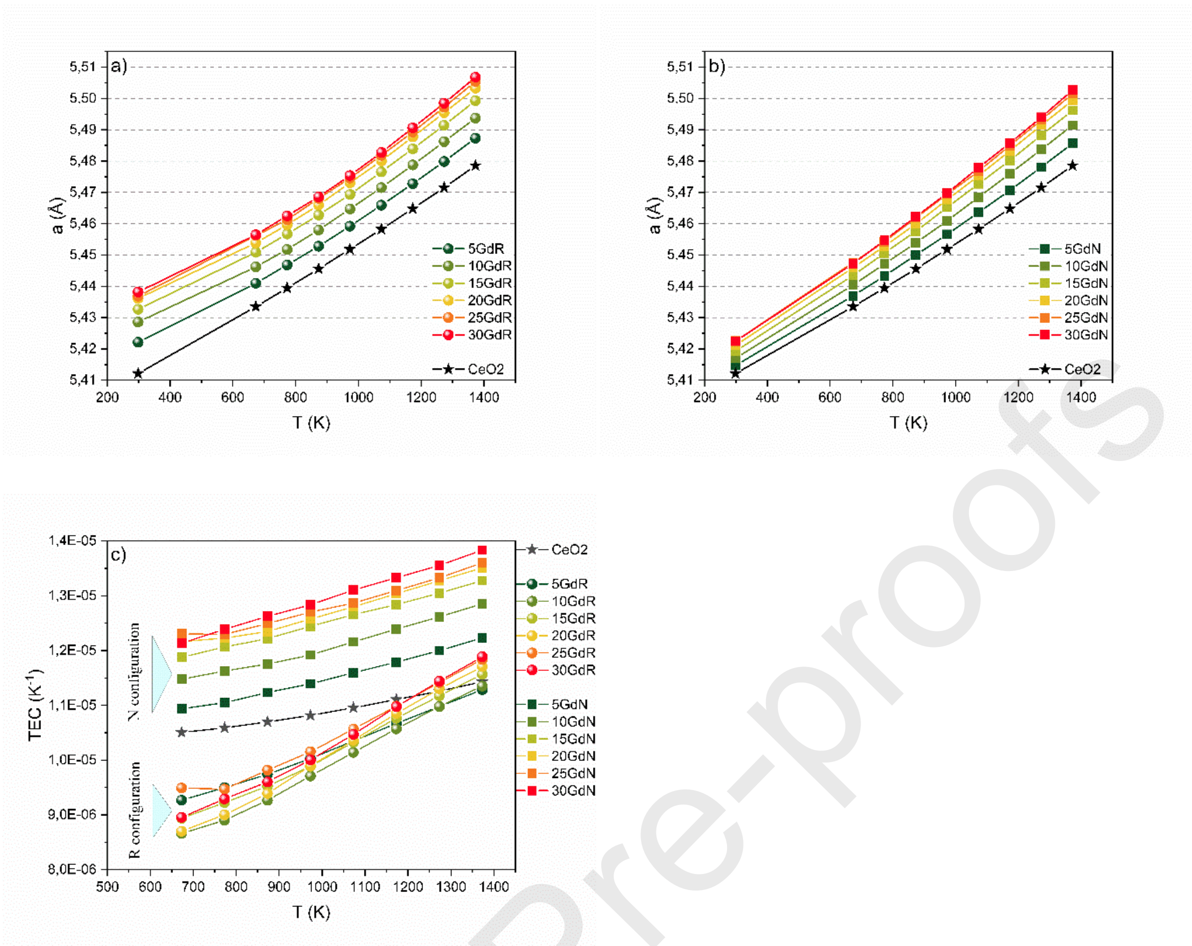

Fig. 2. Evolution of the lattice parameter with temperature a) R configuration, b) N configuration. c) Evolution with temperature of the TEC [T-298K] for both the R and N configurations.

We notice that the evolution of lattice parameter with temperature depends not only on the doping ratio but also on the defect arrangement (GdR or GdN) as it can be seen on Fig. 2, while no noticeable topological difference is manifest between these arrangements considering Fig. 1. As it is the case at room temperature [9] the lattice parameter is always larger for the R distribution than for the N one even though these two distributions tend to get closer with the raise of temperature. In Fig. 2c the average TEC of Gd-doped ceria has been calculated for the two configurations in the temperature range [298-T] with 673K≤T≤1373K using the relation (1). The TEC is highly linked to the temperature range over which it is evaluated and to the defect arrangement mode. Thus, the R configuration leads to TEC lower or equal to undoped CeO_2 in a large temperature range [673K-1173K] and whatever the composition while for the N configuration the TEC is always larger. Some compiled data of Gd-doped ceria TEC have been presented by Nakajo *et al.* [10]. Our simulations are in accordance with these data when we consider the N configuration. We observe an increase of TEC with temperature for a given composition and with the doping level at a given temperature. However, some differences are found in the literature. For instance, for a same composition ($Ce_{0.8}Gd_{0.2}O_{1.9}$) and a similar temperature range [300K-1100K] most of determined TEC are found between 11.8 $10^{-6}K^{-1}$ and 12.6 $10^{-6}K^{-1}$ [11,12,13-15] and even a TEC as high as 18.7 is announced by Fu [16]. These scattered data are commonly explained by the density, the particle size (grain boundary), the presence of impurities, the reduction of Ce^{4+} or the method used (diffraction, dilatometry).

The present MD results indicate that the defect arrangement could be one of the major sources of the discrepancies noted in published TEC data for a same doping level. The thermal expansion of a solid is a consequence of the anharmonic nature of the atomic vibrations related to the non-symmetric shape of the potential energy/atomic distance curve between two first neighbour atoms in the lattice. Thus, for the undoped ceria the evolution of the lattice parameter with temperature directly reflects the interaction involving cerium and oxygen atoms inside the fluorite lattice. In a perfect CeO_2 single crystal, the interaction is the same between any neighbouring cation/anion (Ce^{4+}/O^{2-}), cation/cation (Ce^{4+}/Ce^{4+}) and anion/anion (O^{2-}/O^{2-}) pair. Even if the average fluorite structure is preserved, the situation becomes more complex when doping has acted on this system. The presence of the foreign rare-earth cations introduces new coulombic and short-range interactions between Gd^{3+}/Gd^{3+}, Gd^{3+}/Ce^{4+} and Gd^{3+}/O^{2-} pairs that did not exist in undoped ceria. Large distortions due the higher ionic radius of Gd^{3+} and to the presence of oxygen vacancies appear at the local level modifying inter atomic distances and the different coordination numbers [9]. We also have to keep in mind that oxide anions diffuse in the structure and that this diffusion enhanced by the thermal energy could participate to the modification of the thermal expansion.

In the R configuration and up to 1200K the system behaves as if the average strength between cations and oxygen raises compared to the undoped CeO_2 leading to lower TEC. Contrariwise in the N configuration the behaviour of the system is opposite. This is illustrated in Fig. 3 where the evolution of TEC with composition is presented for the three temperatures T=673K, 973K and 1373K.

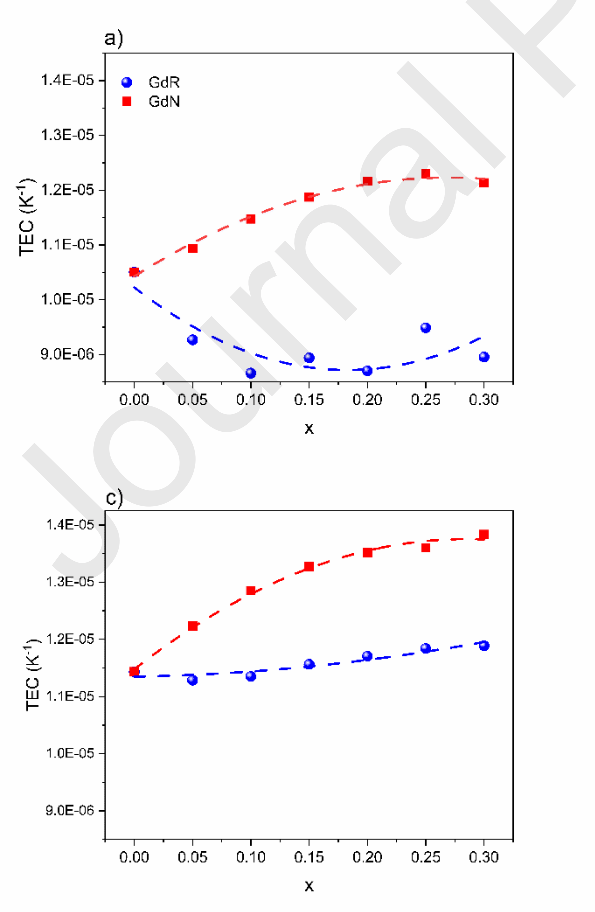

Fig. 3. Doped ceria TEC evolution with the doping rate. a) ΔT [298K-673K], b) ΔT [298K-973K], c) ΔT [298K-1373K]. 2nd order polynomial fits are here to guide the eyes.

It can mainly be appreciated the large gap existing between the R and N distributions unveiling the importance of the defect arrangement on the thermomechanical behaviour of doped ceria. As indicated by the dashed lines (2nd order polynomial fit) different trends can be clearly noticed for the two configurations. For the R configuration the TEC first decreases till x=0.15-0.2 and then seems to slightly increase remaining close to the TEC of the undoped CeO_2 in all the composition range. The N configuration reveals an important increase for low doping ratio (x=0.05-0.15) which lessen for higher x values. The gap between the TEC obtained for the R and N arrangements decreases when the coefficient is calculated for the highest temperatures in correlation with the non-linearity of the TEC=f(T) curves (Fig. 2c).

While the TEC evolution discussed above is deduced from relation (1) some authors propose, due to the non-linearity of the curve a=f(T), an empirical polynomial equation to fit the data. Thus Sameshima et al. [17] used a third-degree polynomial function to approximate the experimental dilatation measurements ($\Delta L/L_0$, $\Delta a/a_0$) an obtained the TEC ($\alpha(T)$) differentiating this function.

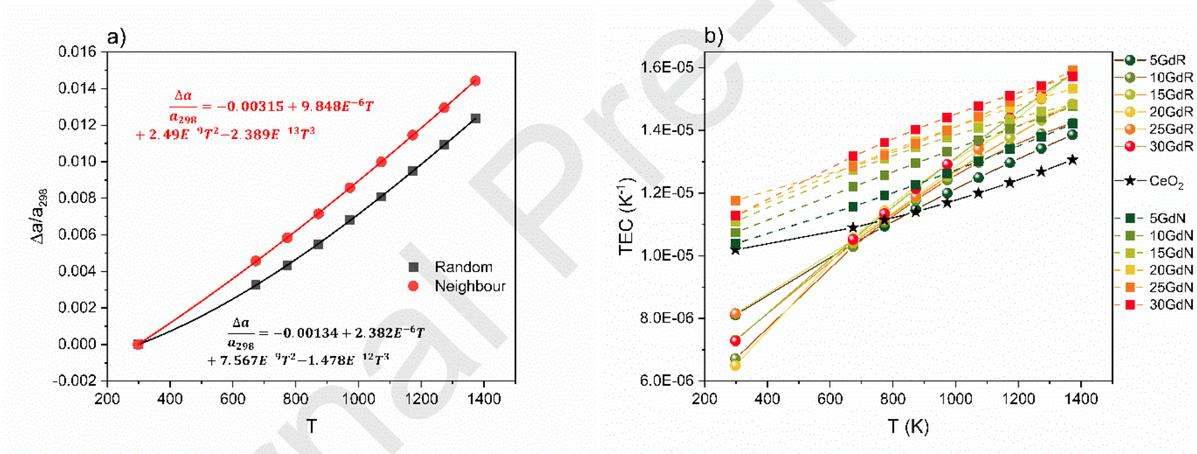

Fig. 4. a) Lattice thermal expansion fitted by a third-degree polynomial function for x=0.2, b) TEC obtained from a) (see text for details).

On Fig. 4 is presented an example a third-degree polynomial fit of ($\Delta a/a_{298}$) for the $Ce_{0.85}Gd_{0.2}O_{1.9}$ simulations and the evolution of the deduced TEC for all the doping ratio. The trend observed on this figure is obviously similar to the Fig. 3c one with the GdR TEC becoming higher than the CeO_2 TEC till 873K and coincidence of the two distribution curves at high temperature. Shameshima explained the increase of TEC with temperature by the asymmetry of the cation-O potential interaction. However, as it is also observed on this figure, the raise of the TEC depends to a large extent on the dopant and oxygen vacancies distribution which will influence the expansion of the defected fluorite structure.

4. Conclusion

Two defect arrangements, the random and the neighbour one, were tested on the lattice parameter evolution with temperature. It was noted that the defect distribution largely influences the TEC of the doped ceria with the neighbour distribution giving rise to the highest TEC then more in accordance with the published experimental coefficients. The TEC of the two distributions tend to get closer at high temperature. The same behaviour could be expected for other systems.

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Serge VIVES: Conceptualization, Validation, Writing - Original Draft

David RAMEL: Conceptualization, Validation, Writing - Original Draft

Cathy MEUNIER: Conceptualization, Validation, Writing - Original Draft

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

- Doping atoms and oxygen vacancies are distributed randomly or as trimers

- Thermal expansion largely depends on the defect distribution

- The neighbour distribution (N) lead to thermal expansion in accordance with literature data

- The thermal expansion of the two distributions (R and N) get closer with the increase of temperature