^{155}Gd Mössbauer spectroscopic and powder X-ray diffraction study of CeO_2–$GdO_{1.5}$ solid solution

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Abstract Powder X-ray diffractometry and ^{155}Gd-Mössbauer spectroscopy have been applied to $Ce_{1-y}Gd_yO_{2-y/2}$ ($0 \leq y \leq 1.0$) prepared at 1,450°C. The former shows that this system forms a complete solid solution being the disordered defect-fluorite type in the $0 \leq y \leq 0.3$ range and the ordered C-type in the $0.3 < y \leq 1.0$ range. Its marked positive non-Vegardianity was consistently interpreted as a generalized Vegard-law behaviour of this distortion-dilated solid solution having Gd^{3+}—oxygen vacancy associative nature. The latter also clarifies that in the ordered C-type phase with decreasing y the 8b-site ^{155}Gd-Mössbauer intensity steadily diminishes and vanishes at $y \sim 0.50$, indicating that the more distorted minor 8b Gd^{3+} in C-type $GdO_{1.5}$ is being preferentially replaced with Ce^{4+}.

Keywords CeO_2-$GdO_{1.5}$ solid solution · X-ray diffractometry ·
^{155}Gd-Mössbauer spectroscopy · Non-Vegardian lattice parameter behaviour ·
Non-random local structure

1 Introduction

A variety of grossly oxygen-vacancy (V_O) type $M_{1-y}Ln_yO_{2-y/2}$ solid solutions (ss) are formed between fluorite(F)-type MO_2 (M^{4+} =Zr, Hf, Ce, Th, U, etc.) and its V_O-

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ordered superstructure of C-type lanthanide (Ln) sesquioxide $LnO_{1.5}$ (Ln^{3+} =La-Lu, Sc, Y). These so-called defect-fluorite (DF) oxides have been the object of enormous research efforts due to their importance in nuclear, electrochemical and ceramic etc areas. Yet, much remains elusive even today as to their exact nature of complex local structure and its correlations with their key properties such as oxide-ion conductivity (σ(ion)), radiation tolerance and thermal stability, etc. To serve this purpose we have been engaged in their comprehensive coupled Ln ([151]Eu and [155]Gd)-Mössbauer and powder X-ray diffraction (XRD) studies [1–8]. We report here results of one such coupled [155]Gd Mössbauer and XRD study of $Ce_{1-y}Gd_yO_{2-y/2}$ ($0 < y \leq 1.0$). Even in this one, which is one of the most thoroughly studied ceria solid solutions, the reported phase and structure data are often mutually discrepant, needing a more intensive further study over the whole $0 \leq y \leq 1.0$ range.

2 Experimental

Samples with various Gd content (y) in $\Delta y = 0.05$ interval over the entire $0 \leq y \leq 1.0$ range were prepared as follows; the nitrate mixture solution with a given Gd/Ce ratio was dried at 70°C, calcined at 800°C, and after pelletizing finally heated twice at 1,450°C for 12 h with intermediate grinding. These samples are ground into fine powders and are used for the XRD and [155]Gd-Mössbauer measurements. The former was made with a powder X-ray diffractometer (JEOL JDX3530K) using Cu K_α radiation in $10° \leq 2\theta \leq 110°$ range (0.02° step in 1~2 sec). As detailed in previous papers [4–7], the latter was made at 12 K inside a cryostat using a [155]Eu/[154]SmPd$_3$ source and a Mössbauer Doppler-velocity calibrator (Wissel MVC-450). The [155]Gd Mössbauer spectra of almost all the samples with the same ~150 mg Gd/cm^2 were computer-fitted to a quadrupole-split five-line spectrum for 86.5 keV γ-ray ($I_g =$ 3/2, $I_e = 5/2$, $\eta = 0$) using a Lorentz approximation. The value of isomer shift (δ) is referred to the [155]Eu/[154]SmPd$_3$ source.

3 Results and discussion

Figure 1a shows the present XRD lattice parameter (a_0(ss)) data [8] with those of Bevan et al [9] and reveals two important features of phase and a_0(ss) behaviour of this system:

1. This system, when prepared at a relatively low temperature of 1,450°C (<1,500°C), forms a complete solid solution, being the disordered DF-type in the $0 \leq y \leq 0.30$ range and the ordered C-type in the much wider $0.30 < y \leq 1.0$ range. In contrast, the hitherto most representative Bevan et al's data for samples prepared at a higher 1,600°C show the existence of a clear miscibility gap ($0.52 < y < 0.73$) between conversely the wider DF-type phase in the lower $0 \leq y \leq 0.52$ range and the much narrower ordered C-type phase in the higher $0.73 \leq y \leq 1.0$ range. The present data thus indicate that by adopting a relatively low temperature heating ($1,450 < 1,500°C$) one can prepare the complete solid solution of this system wherein the ordered C-type is the major phase.
2. In reference to there-drawn conventional Vegard-law (VL) baseline (a_0(VL)), this system is markedly positively non-Vegardian; Δa_0(ss)= a_0(ss)-a_0(VL)>>0.
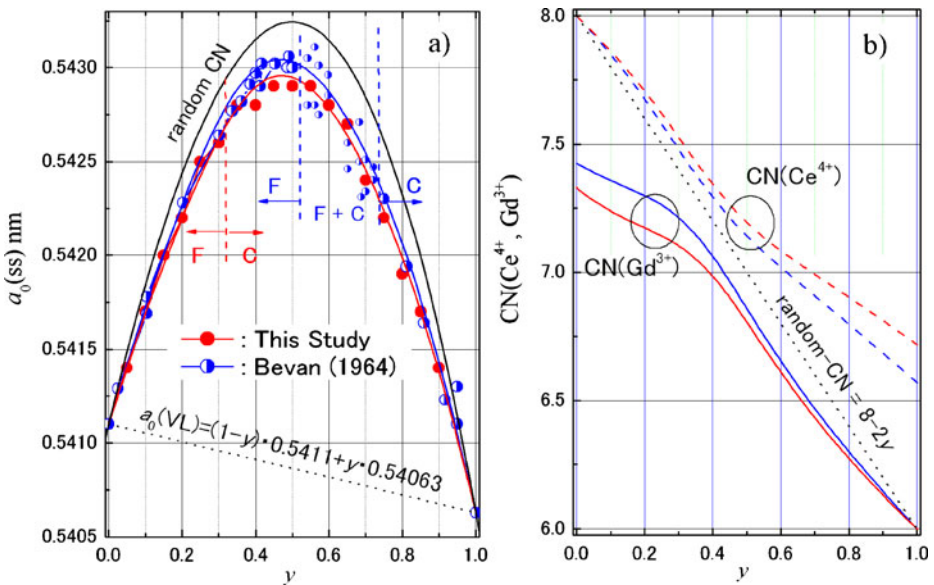
Fig. 1 a_0(ss)(exp) vs. y plot and the model curve of the $Ce_{1-y}Gd_yO_{2-y/2}$ (**a**) (left) and its random and non-random oxygen $CN(Gd^{3+}, Ce^{4+})$ model curves (**b**) (right)

Recently the author proposed a generalized Vegard-law (VL) a_0(ss) model [2] which can give a quantitative account for such marked non-Vegardianity of ceria solid solutions. The model allows to extract quantitative non-random oxygen coordination number data around the cations ($CN(Ce^{4+}, Ln^{3+})$) from the a_0(ss) analysis, by employing the systematized Shannon's ionic-radii $r_C(Ce^{4+}, Ln^{3+})$ expressions as a function of oxygen CN to give the average cation radius of the system; $r_C(av)=(1-y)\cdot r_C(Ce^{4+}) + y\cdot r_C(Ln^{3+})$. As $r_C(Ce^{4+})$ and $r_C(Ln^{3+})$ have mutually different CN dependence, the random→non-random CN change of the system produces the corresponding change of r_C and a_0(ss)$(=(1-y)\cdot f_F(r_C) + y\cdot f_C(r_C))$ in a fully coupled unified manner (where $f_F(r_C) = a_0(F)$ and $f_C(r_C) = a_0(C)/2$ are lattice-parameter functionals of F-type MO_2 and C-type $LnO_{1.5}$, respectively, as a function of r_C; see [2] for details). Applying this generalized VL to total six CeO_2-$LnO_{1.5}$s (Ln^{3+} =Y. Gd, Eu, Sm, Nd and La), the author clarified that with increasing $r_C(Ln^{3+})$ these systems steadily shift from the dopant(Ln^{3+})-V_O associative to the host(Ce^{4+})-V_O associative, the switchover occurring at the $Ln^{3+} \sim$Sm-Nd. Bevan et al's data were used there for the analysis of this system.

Now that our new a_0(ss) data have also become available, we have re-analyzed both sets of a_0(ss) data more deliberately with the model and have drawn the respective most reasonable a_0(ss) model curves in Fig. 1a and non-random $CN(Ce^{4+}, Gd^{3+})$ curves in Fig. 1b. Though the difference between these two sets of a_0(ss) data appears small, in reference to the generalized-VL a_0(random-CN) model curve in Fig. 1a having the random $CN(Gd^{3+})=CN(Ce^{4+}) =8-2y$ curve in Fig. 1b, the more negatively generalized non-Vegardian nature of our samples prepared at the lower

Fig. 2 ^{155}Gd-Mössbauer δ (**a**), QS (**b**) and 24-d site area fraction data (**c**) vs. y plots of the $Ce_{1-y}Gd_yO_{2-y/2}$
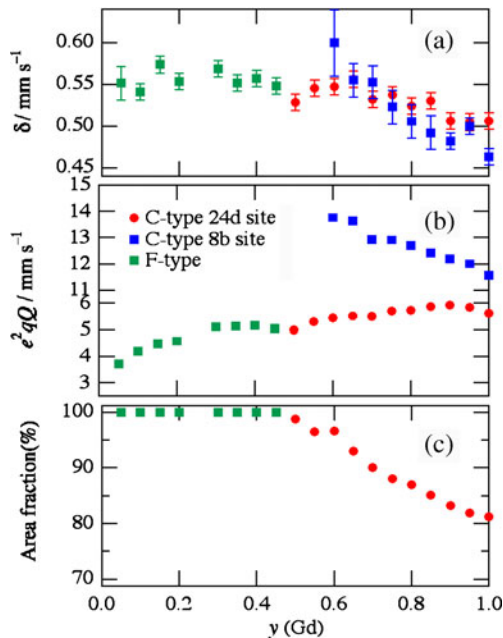
1,450°C than Bevan et al's samples prepared at the higher 1,600°C (i.e. a_0(this study)$< a_0$(Bevan)$< a_0$(random-CN)) in Fig. 1a and the corresponding more Gd^{3+}-V_O associative nature of our samples than Bevan et al's (i.e. $CN(Gd^{3+})$(this study)$<$ $CN(Gd^{3+})$(Bevan)$< CN(Gd^{3+})$(random)$=8-2y$) in Fig. 1b seem clear enough. This thus provides a first direct a_0 evidence for this system that the system is becoming more non-random with decreasing the preparation temperature.

The ^{155}Gd-Mössbauer results are summarized in Fig. 2a, b and c as δ, quadrupole splitting (QS) and 24d-site absorption area fraction (%) vs. y plots, respectively: In Fig. 2a the δ value exhibits a steady increase with decreasing $y = 1.0 \rightarrow 0.50$ in the ordered C-type phase, suggesting the increase in ionic character of the Gd^{3+}-O^{2-} bond with increasing oxygen-CN of the system (Fig. 1b). As is well known, in the ideal C-type structure of $GdO_{1.5}$ (CN = 6 at $y = 1.0$) two O^{2-}s out of eight around the Gd^{3+} are regularly missing either face- or body-diagonally for the three-fourth (3/4) 24d or the one-fourth (1/4) 8b Gd site, respectively, giving apparent two-doublet ^{155}Gd spectra composed of the more distorted minor 8b doublet and the less distorted major 24d doublet in 1:3 ratio, as seen in Fig. 2b and c. Their most notable and obvious trend is the sharp diminishment of the minor 8b-site ^{155}Gd^{3+}-Mössbauer intensity with decreasing y in Fig. 2c and its final disappearance at $y \sim 0.50$ fairly before the XRD macroscopic order-disorder (C→DF) phase change is observed at $y \sim 0.30$ in Fig. 1a. The QS data in Fig. 2b even indicate that the local distortion around this vanishing 8b Gd^{3+} is being increasingly enhanced with decreasing y. These data thus clearly demonstrate that with decreasing y the more distorted minor 8b Gd^{3+} site in C-type $GdO_{1.5}$ at $y = 1.0$ is being preferentially replaced with the Ce^{4+}, and therefore below $y \sim 0.50$ basically the major 24d-site based Gd^{3+} local structure only persists in the disordered DF phase. The $CN(Ce^{4+}, Ln^{3+})$ data in

Fig. 1b indicate that when y decreases from 1 to zero (=0) and the CN(average)=8–2y increases from 6 to 8, the CN(Ce^{4+}) increases from ∼6.6–6.7 at $y \sim 1.0$ to ∼7.2 at $y \sim 0.50$ and finally to 8 at $y = 0$, always maintaining the Gd^{3+}-V$_O$ associative nature (CN(Gd^{4+}) <CN(Ce^{4+})) over the entire $0 \leq y \leq 1.0$ range. Accordingly, one can reasonably guess that in the ordered C-type solid solution the minor 8b site preferentially replaced with the Ce^{4+} should be more oxygen rich than the major 24d site, i.e. CN(8b)> CN(24d)> 6 as whole, thereby driving the locally less oxygen-rich 8b Gd^{3+}-O^{2-} configuration to the increasingly more-distorted metastable or even unstable vanishing state.

4 Conclusion

The Ce$_{1-y}$Gd$_y$O$_{2-y/2}$ solid solution ($0 \leq y \leq 1.0$) prepared at 1,450°C has been studied with powder X-ray diffractometry and ^{155}Gd-Mössbauer spectroscopy. Contrary to our conventional knowledge of this system, the XRD results show that the relatively low-temperature (1,450°C) heating can lead to the formation of its complete solid solution wherein the ordered C-type is the major solid solution phase ($0.3 < y \leq 1.0$). Its marked positive non-Vegardianity could also be consistently analyzed with the proposed lattice-parameter model [2, 3] as a generalized Vegard-law behaviour of this distortion-dilated non-random solid solution having dopant (Gd^{3+})—oxygen vacancy (V$_O$) associative non-randomness. The^{155}Gd-Mössbauer results further clarified that in the ordered C-type phase with decreasing y the 8b-site ^{155}Gd-Mössbauer intensity sharply diminishes and finally disappears at $y \sim 0.50$, evidencing that the more distorted minor 8b Gd^{3+} site in C-type GdO$_{1.5}$ at $y = 1.0$ is being preferentially replaced with Ce^{4+}.

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