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Lattice contraction and lattice deformation of UO_2 and ThO_2 doped with Gd_2O_3

Angela Baena [a, b], Thomas Cardinaels [a], Kevin Govers [a], Janne Pakarinen [a], Koen Binnemans [b], Marc Verwerft [a, *]

[a] Belgian Nuclear Research Centre (SCK•CEN), Institute for Nuclear Materials Science, Boeretang 200, B-2400 Mol, Belgium
[b] KU Leuven, Department of Chemistry, Celestijnenlaan 200F, P.O. Box 2404, B-3001 Heverlee, Belgium

HIGHLIGHTS

- Lattice deformations of $(U_{1-x}Gd_x)O_{2.00}$ & $(Th_{1-x}Gd_x)O_{2-x/2}$ are not identical.
- $(U_{1-x}Gd_x)O_{2.00}$ retains its fluorite structure.
- $(Th_{1-x}Gd_x)O_{2-x/2}$ forms an excess-anion bixbyite structure.
- $(U_{1-x}Gd_x)O_{2.00}$ and $(Th_{1-x}Gd_x)O_{2-x/2}$ contractions were evaluated with high precision.

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ABSTRACT

The lattice deformations in two doped fluorite systems, $(U_{1-x}Gd_x)O_{2.00}$ and $(Th_{1-x}Gd_x)O_{2-x/2}$, have been reassessed by precise X-ray and electron diffraction investigations and the results were interpreted using the *Bond Valence Sum* (BVS) approach. For the $(U_{1-x}Gd_x)O_{2.00}$ system, the experimental findings and theoretical assessment confirm earlier work: the lattice keeps its fluorite structure with a unit cell parameter that contracts linearly with dopant concentration. The lattice contraction in the $(Th_{1-x}Gd_x)O_{2-x/2}$ system has for the first time been analyzed up to the solubility limit. Similar as for $(U_{1-x}Gd_x)O_{2.00}$, the $(Th_{1-x}Gd_x)O_{2-x/2}$ solid solution contracts linearly as a function of dopant concentration but additionally, it develops a superstructure which is closely related to the parent fluorite structure. An excess anion bixbyite trial model is proposed to describe this superstructure.

1. Introduction

Both in Pressurized Water Reactors (PWR) and Boiling Water Reactors (BWR), gadolinium is often used as burnable poison to optimize the core physics by reducing power peaking in fresh assemblies (see e.g. Ref. [1]). The huge neutron capture cross sections in the thermal energy range of both ^{155}Gd and ^{157}Gd isotopes and the low cross sections of the daughter nuclides ^{156}Gd and ^{158}Gd makes Gd_2O_3 an excellent burnable poison. Natural Gd_2O_3 is mechanically blended with UO_2 in small quantities (typically 4–8 wt% Gd) and a limited number of such fuel rods containing Gd_2O_3 as burnable poison are inserted in a fuel assembly [1]. After sintering, the U-rich region of UO_2–Gd_2O_3 forms a solid solution fluorite phase (see Fig. 1a). When sintering is performed under highly reducing conditions, oxygen-to-metal ratios (O/M, with M = U + Gd) less than 2.00 are formed and under moderately reducing conditions the

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* Corresponding author.
E-mail address: marc.verwerft@sckcen.be (M. Verwerft).

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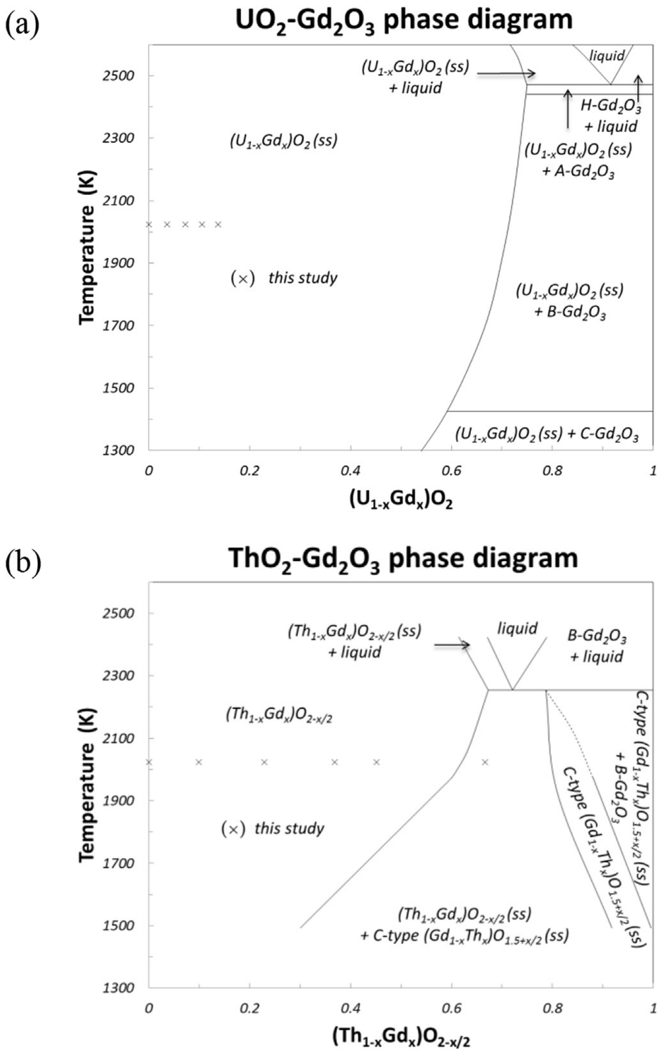

Fig. 1. Sections of the pseudo-binary phase diagrams of UO_2–Gd_2O_3 (a) and ThO_2–Gd_2O_3 (b) with indication of the compositions investigated in the present study. The phase diagrams were redrawn with permission from reference McMurray et al. [14] for UO_2–Gd_2O_3 (Copyright Elsevier 2014) and reference Keller et al. [9] for ThO_2–Gd_2O_3 (Copyright Elsevier 1972).

oxygen-to-metal ratio is 2.00 (O/M = 2.00) [2]. The fluorite lattice parameter decreases with increasing Gd content [3–7] and is also affected by deviation from stoichiometry [2]. The published lattice contraction factors are slightly different from each other. In this paper, we present the lattice contraction of stoichiometric $(U_{1-x}Gd_x)O_{2.00}$. Special attention was paid to the precise determination of the Gd content in solid solution and the avoidance of stoichiometry deviations. Samples were prepared via a dry synthesis route which was optimized towards sample homogeneity [8]. The lattice contraction of stoichiometric $(U_{1-x}Gd_x)O_{2.00}$ was investigated in the range $0 \leq x \leq 0.14$ (see Fig. 1a), which is the range of currently adopted Gd concentrations in nuclear power reactors.

With an O/M ratio equal to 2.00, a fraction of the uranium atoms in the solid solution $(U_{1-x}Gd_x)O_{2.00}$ obviously must shift to higher valences, since Gd has only a single stable valence state (Gd^{III}). In the ThO_2–Gd_2O_3 system, both cations have a single stable valence state (Th^{IV} and Gd^{III}) and hence the charge compensation occurs via anion vacancies. Similar as for $(U_{1-x}Gd_x)O_{2.00}$, the $(Th_{1-x}Gd_x)O_{2-x/2}$ system also forms a broad fluorite-type solid solution in the Th-rich region (see Fig. 1b) [9]. The limiting dopant concentration for the fluorite solid solution to remain stable varies with temperature. At 1250 °C, the solubility limit is reached at $x = 0.31$, while it is as high as $x = 0.66$ at 1900 °C. Similar as for the $(U_{1-x}Gd_x)O_{2.00}$ system, the fluorite unit cell of $(Th_{1-x}Gd_x)O_{2-x/2}$ contracts with increasing dopant concentrations [10–12]. The reported lattice contractions, however, vary by almost a factor of three between the different authors and while it is well established that the $(U_{1-x}Gd_x)O_{2.00}$ contracts linearly with dopant concentration, the studies of the $(Th_{1-x}Gd_x)O_{2-x/2}$ system also disagree on this point. In order to elucidate these disagreements, the lattice contraction was studied in a wide range: $0 \leq x \leq 0.67$ (see Fig. 1b). The end point ($x = 0.67$) of this range is well within the miscibility gap at the sintering temperature (T = 1750 °C).

In the two systems, $(U_{1-x}Gd_x)O_{2.00}$ and $(Th_{1-x}Gd_x)O_{2-x/2}$, the charge compensation mechanisms are different. The lattice contraction was studied in terms of the *Bond Valence Sum* (BVS) concept to evaluate if the observed lattice contractions are compatible with the expected structure and charge compensation mechanisms [13].

2. Experimental

2.1. Sample synthesis and oxygen equilibration

The as-received powder precursors used to prepare the doped pellets were depleted UO_2 (^{235}U content is 0.27 at%), obtained via Integrated Dry Route (IDR) synthesis and supplied by FBFC International (Dessel, Belgium), natural ThO_2 with a purity of 99.99%, supplied by Materion (Arizona, USA), Gd_2O_3 with a purity of 99.999% supplied by Alfa Aesar (Karlsruhe, Germany) and $Gd(NO_3)_3 \cdot 6H_2O$ with a purity of 99.99% supplied by Sigma–Aldrich (Diegem, Belgium). Appropriate mixtures to yield nominal compositions $M_{1-x}Gd_xO_{2-x/2}$ were prepared by co-milling using a Retsch MM200 mixer mill, with ZrO_2 containers of a volume of 25 mL, in combination with one ZrO_2 ball with a diameter of 10 mm. No binder or lubricant was mixed with the powder. The compaction of powder mixtures into pellets was carried out via one-sided pressing in a Carver model M manual press using a die with a diameter of 10.85 mm or an Atlas 8T press using a die with a diameter of 11.07 mm. The pellets were sintered at 1750 °C during 8 h using a mixture of HYTEC (Ar-5 vol.% H_2) (143 mL min^{-1}) and Ar-0.5 vol.% O_2 (7 mL min^{-1}), yielding an H_2–H_2O–O_2 equilibrium with an oxygen potential of −420 kJ mol^{-1}. The sintering was done in a Linn HT 1800 Moly high temperature furnace with an alumina matrix and molybdenum heating elements. The pellets were placed in a ceramic alumina crucible with a molybdenum cover to avoid interactions between the pellets and the crucible [8]. All produced specimens of UO_2–Gd_2O_3 system had good physical stability and achieved a density above 95% of the theoretical density (T.D.) without open porosity. For accurate analysis of UO_2-based systems, it is necessary to avoid stoichiometry variations resulting from air exposure. It was shown by Leinders et al. that samples without open porosity remain stable over several weeks [15]. Most of the ThO_2–Gd_2O_3 specimens reached more than 95% T.D. and had good physical stability. Since stoichiometry variations under ambient conditions do not occur in the ThO_2–Gd_2O_3 system, the level of open porosity is not of a concern here.

After sintering at −420 kJ mol^{-1}, $(U_{1-x}Gd_x)O_2$ is sub-stoichiometric and a post-sintering oxygen equilibration is needed to achieve stoichiometry. The ASTM C 1430-07 guidelines for oxygen-to-metal ratio analysis of UO_2 and UO_2–Gd_2O_3 propose an equilibration by heating the sintered pellets to 800 °C under an oxygen potential of −350 kJ mol^{-1} during 4 h. The mass change is then used to determine the initial stoichiometry of the specimens. To verify the appropriateness of the ASTM C 1430-07 guidelines, a thermogravimetric experiment was performed with a sintered