Thermal conductivity variation in uranium dioxide with gadolinia additions

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Thermal conductivity variation with Gd accommodation in Gd-doped UO₂ using NEMD method


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Abstract

By combining experimental observations on Gd doped fuel with a theoretical understanding, the variation in thermal conductivity with Gd concentration and accommodation mechanism has been modelled. Four types of Gd accommodation mechanisms have been studied. In UO₂−x, isolated substitutional Gd³⁺ ions are compensated by oxygen vacancies and \( \{ 2 \text{Gd}^+_U : V^+_O \}^x \) defect clusters. In UO₂, isolated substitutional Gd³⁺ ions are compensated by U⁵⁺ ions and \( \{ \text{Gd}^+_U : \text{U}^+_U \}^x \) defect clusters. The results indicate that defect clusters can be considered as less effective phonon scatterers and therefore result in less thermal conductivity degradation. The thermal conductivity predicted for UO₂ with \( \{ \text{Gd}^+_U : \text{U}^+_U \}^x \) defect clusters is in good agreement with experimental data for UO₂ with 5 wt% Gd₂O₃. This supports the previous theoretical results that Gd is accommodated through defect clusters \( \{ \text{Gd}^+_U : \text{U}^+_U \}^x \) in UO₂ in the presence of excess oxygen.

Keywords: Gd₂O₃-doped UO₂, Thermal conductivity, Gadolinium accommodation mechanism, Molecular dynamics simulations

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1. Introduction

Neutron poisons are commonly added to nuclear fuels to limit the initial reactivity in specified pellets/rods identified within the reactor core at the beginning of the operational cycle. This limiting of reactivity has a beneficial effect on the overall lifetime of the core by enabling the use of higher enrichment fuel, providing more fissionable material that extends useful residency of the fuel. The effectiveness of burnable poisons purposefully decreases over time as the neutron absorbing elements are transmuted into elements with lower neutron cross sections (i.e. are used up). The burnable poison can take the form of pins or plates in the fuel assembly or as an additive to the fuel pellet itself. Boron [1], erbium [2] and gadolinium [3] have all been chosen as burnable absorbers in the past: boron is used out of the pellet either as a pellet coating (e.g. ZrB₂ [1]) or within the assembly, whilst gadolinium and erbium oxide are used as fuel additives, and create some interesting crystal-chemical and energetic issues with regard to the initial impurity accommodation mechanisms and modifications to the fuel during burn-up.

Gd is added in fuel as a sesquioxide (i.e. Gd₂O₃) [4, 5]. Past work, both experimental and theoretical, has shown that trivalent oxides can be accommodated in large molar volumes within the UO₂ crystal lattice [6]. The accommodation mechanism of the sesquioxides in UO₂ varies significantly with the amount of oxygen available during the solution reaction: in UO₂₋ₓ in the absence of excess oxygen, Gd³⁺ is accommodated by forming a charge compensating oxygen vacancy for every two substitutional Gd ions, resulting in (U,Gd)O₂₋ₓ [7]. In UO₂₊ₓ where excess oxygen is present, substitutional Gd³⁺ ions are charge compensated by U⁵⁺ cations. The solubility of Gd or Er in the presence of excess oxygen is limited by the amount of excess oxygen, whereas in the absence of excess oxygen, solubility is a function of temperature [7].

The thermal conductivity of UO₂ is a key property to understand, for the safe and efficient operation of nuclear fuel [8, 9, 10]. Each fission event produces heat, which is transported through the fuel into the cooling fluid of the power
reactor. Past theoretical work has predicted that temperature [11, 12], radiation
damage induced defects [13] and secondary phases [14] have major impacts on
the fuel's thermal conductivity.

Any degradation in the thermal conductivity of the fuel will have a significant
impact on fuel performance, increasing the centre line temperature in a fuel
pellet at the beginning of life and into operation compared to a standard UO₂
pellet. This will have knock-on effects on fission gas release and fission product
behaviour. Additionally, not only will the margin to melting of the fuel be
reduced as a consequence of the addition of Gd, thereby raising the centre-line
temperature, but also by the lower melting point of UO₂-Gd₂O₃ solid solutions
compared to UO₂ [15].

Past experimental work has measured the change in thermal conductivity
with Gd content [16, 17, 18, 19, 20, 21, 22, 23]. The thermal conductivity was
observed to decrease with increasing Gd content at relatively low temperatures,
but was independent of the Gd content at temperatures close to 2000 K [19].
Simulated burn-up has been taken into account in UO₂ and (U,Gd)O₂ using
soluble fission product elements (Sr, Zr, Y, La, Ce, Nd) [20]. The thermal
conductivity was observed to decrease with an increase in the total amount of
soluble elements at low temperature, but was almost independent of soluble
fission element content at higher temperature [20]. Amaya et al. investigated
the effect of hyper-stoichiometry on the thermal conductivity of 10 wt% Gd₂O₃
doped UO₂₋ₓ, and observed degradation in thermal conductivity with increasing
hyper-stoichiometry [17, 18]. The thermal conductivity of irradiated (U,Gd)O₂
has been studied by Amaya et al. [16] and Minato et al. [23]; the thermal
conductivity decreased with irradiation, and partly recovered after the thermal
diffusivity measurements at high temperatures. The recovery of the thermal
conductivity was due to the recovery of the irradiation-induced point defects
during the measurements. These experimental observations were explained in
terms of phonon-phonon scattering and phonon-point defect scattering [19], as
well as phonon-extended defect scattering [23].

However, the link between the change in thermal conductivity and the spe-
sific defect accommodation mechanism has not been considered. There has been recent work to study the nature of point defects in non-stoichiometric UO₂ [24]. Due to the requirement for large supercells and associated computational costs, it is still impractical to use first-principle calculations to investigate the lattice thermal conductivity of actinide mixtures (or UO₂ with additives) with point defects. In this work, the impact of Gd₂O₃ doping on the thermal conductivity of UO₂ due to accommodation by oxygen vacancies and U⁵⁺ cations is explored using non-equilibrium molecular dynamics simulations and compared to experimentally obtained data.

2. Methodology

2.1. Interatomic potentials

The UO₂ potential form used here [25] combines the Buckingham interatomic potential with a many body embedded atom (EAM) term, so that the energy of an ion i, \( E_i(r_{ij}) \), is given by

\[
E_i(r_{ij}) = \frac{1}{2} \sum_j \phi_{\alpha\beta}(r_{ij}) - G_\alpha \sqrt{\sum_j n_j \frac{n_j}{r_{ij}^2}}, \tag{1}
\]

where \( \phi_{\alpha\beta}(r_{ij}) \) is the pair-wise interaction between two atoms i and j, separated by \( r_{ij} \), and \( G_\alpha, n_\beta \) are parameters associated with the many-body term. The pair-wise interaction has both long-range electrostatic, \( \phi_C(r_{ij}) \), and short-range contributions. The latter are described using Morse, \( \phi_M(r_{ij}) \), and Buckingham, \( \phi_B(r_{ij}) \), potential forms, where \( \alpha \) and \( \beta \) are used to label the species of atom i and atom j, respectively:

\[
\phi_{\alpha\beta}(r_{ij}) = \phi_C(r_{ij}) + \phi_B(r_{ij}) + \phi_M(r_{ij}) \tag{2}
\]

\[
\phi_C(r_{ij}) = \frac{q_\alpha q_\beta}{4\pi\varepsilon_0 r_{ij}} \tag{3}
\]

\[
\phi_B(r_{ij}) = A_{\alpha\beta} \exp\left(-\frac{r_{ij}}{\rho_{\alpha\beta}}\right) - C_{\alpha\beta} \frac{1}{r_{ij}^6} \tag{4}
\]
Table 1: Parameters for the pairwise interactions described by Eq. (1-5) [25, 27, 28].

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$\Phi_B(r_{ij})$</th>
<th>$\Phi_M(r_{ij})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U^{5+}$-$O^{2-}$</td>
<td>$1155.631$</td>
<td>$0.3465$</td>
</tr>
<tr>
<td>$U^{5+}$-$U^{5+}$</td>
<td>$18600$</td>
<td>$0.2429$</td>
</tr>
<tr>
<td>$U^{5+}$-$U^{4+}$</td>
<td>$18600$</td>
<td>$0.2583$</td>
</tr>
<tr>
<td>$U^{4+}$-$O^{2-}$</td>
<td>$448.7789$</td>
<td>$0.3878$</td>
</tr>
<tr>
<td>$U^{4+}$-$U^{4+}$</td>
<td>$18600$</td>
<td>$0.2747$</td>
</tr>
<tr>
<td>$Gd^{3+}$-$O^{2-}$</td>
<td>$37562.031$</td>
<td>$0.1938$</td>
</tr>
<tr>
<td>$O^{2-}$-$O^{2-}$</td>
<td>$830.2834$</td>
<td>$0.3529$</td>
</tr>
</tbody>
</table>

\[
\phi_M(r_{ij}) = D_{\alpha\beta} \left[ \exp(-2\gamma_{\alpha\beta}(r_{ij} - r_{\alpha\beta}^0)) - 2 \exp(-\gamma_{\alpha\beta}(r_{ij} - r_{\alpha\beta}^0)) \right] \tag{5}
\]

where $A_{\alpha\beta}, \rho_{\alpha\beta}, C_{\alpha\beta}, D_{\alpha\beta}, \gamma_{\alpha\beta}$, and $r_{\alpha\beta}^0$ are empirical parameters describing the Buckingham and Morse potentials between atom $i$ and atom $j$. The total charge of the ions $q_\alpha = Z^{eff}_\alpha |e|$ describes the Coulombic contribution ($Z^{eff}_\alpha = 2.2208$ for $U^{5+}$ ions, $Z^{eff}_\alpha = 2.7760$ for $U^{5+}$ ions, $Z^{eff}_\alpha = 1.6656$ for Gd$^{3+}$ ions, and $Z^{eff}_\alpha = -1.1104$ for oxygen anions). The pairwise potential parameters are summarised in Table 1.

The second term in equation (1) uses the EAM model to introduce a subtle many-body perturbation to the more dominant pairwise interactions [25] with potential parameters reported in Table 2. This potential model has already proven to be excellent for modelling thermal and mechanical properties of UO$_2$ [25, 13]. Additional developments of a Gd-O potential by Rushton and Chronzos [26] and U$^{5+}$ potential by Liu et al. [27, 28] are incorporated in this work.

2.2. Details of the simulation

Five supercell models (UO$_2$, U4-random, U4-bound, U5-random and U5-bound), representing different Gd accommodation mechanisms, were used to
Figure 1: Schematic diagram of a $2\times2\times2$ supercell of UO$_2$ doped with Gd$_4$O$_5$, showing different Gd accommodation mechanisms: (a) isolated Gd$^{3+}$ ions in UO$_2$$_{2-x}$ (U4-random), (b) $\{2\text{Gd}_{U}^{4+} : \text{V}_{O}^{\circ}\}^x$ defect clusters in UO$_2$$_{2-x}$ (U4-bound), (c) isolated Gd$^{4+}$ ions in UO$_2$ (U5-random), (d) $\{\text{Gd}_{U}^{4+} : \text{V}_{U}^{\circ}\}^x$ defect clusters in UO$_2$ (U5-bound). Oxygen is represented as red, U$^{4+}$ - grey-blue, oxygen vacancy - hollow, Gd - purple, U$^{5+}$ - gold.
investigate the effects on the thermal conductivity of UO$_2$. U4-random represents isolated Gd$^{3+}$ substitutional defects in UO$_{2-x}$. It was generated from UO$_2$ by randomly removing $n$ O$^{2-}$ atoms (leaving behind $n$ oxygen vacancies) and randomly replacing 2$n$ U$^{4+}$ atoms with Gd$^{3+}$ atoms (the value of $n$ depends on the doping level). U4-bound represents $(2\text{Gd}'_U : \text{V}_O)^x$ defect clusters in UO$_{2-x}$ and was generated from UO$_2$ by randomly removing $n$ O$^{2-}$ atoms but then replacing the two nearest U$^{4+}$ atoms bounding each removed O$^{2-}$ atom with two Gd$^{3+}$ atoms. Similarly, U5-random also represents isolated Gd$^{3+}$ substitutional atoms in UO$_2$, and was generated from UO$_2$ by randomly replacing $n$ U$^{4+}$ atoms with Gd$^{3+}$ atoms and then randomly replacing $n$ U$^{4+}$ atoms with U$^{5+}$ atoms (i.e. charge compensation by U$^{5+}$ not oxygen vacancy). U5-bound represents $(\text{Gd}'_U : \text{U}_U)^x$ defect clusters in the UO$_2$ lattice. It was generated from UO$_2$ by randomly replacing $n$ U$^{4+}$ atoms with U$^{5+}$ atoms and then replacing randomly one of the nearest neighbour U$^{4+}$ atoms of each U$^{5+}$ atom with a Gd$^{3+}$ atom.

Figure 1 shows the Gd accommodation mechanisms using (conveniently small) 2×2×2 supercells of UO$_2$ doped with Gd$_2$O$_3$.

The Gd-O potential was originally developed for rare-earth doped CeO$_2$. To verify its application in the UO$_2$ system, the lattice parameters of the Gddoped UO$_2$ as a function of the Gd content have been calculated as shown in Fig. 2. The lattice parameter of Gd doped UO$_2$ has been discussed previously with two possible charge compensation mechanisms as the Gd content increases: the creation of the smaller U$^{5+}$ cation and the formation of oxygen vacancies [29, 34, 35]. The smaller U$^{5+}$ cation results in a contraction of the lattice, while the oxygen vacancies were reported to be larger than the O$^{2-}$ ion [34]. The decreasing lattice parameters of U5-bound and U5-random (no oxygen vacancies) with Gd content are consistent with experimental results from Liu et al. [29], Kim et al. [35], Baena et al. [30], and Durazzo et al. [31]. This is due to the smaller U$^{5+}$ cation as compared to the U$^{4+}$ cation. For hypo-stoichiometric (U,Gd)O$_2$ solid solutions of $(U^{4+}_{1-2x+2y}U^{5+}_{x-2y}Gd^{3+}_{x+y})O_{2-y}$ type, it was shown that the lattice parameter increases with a decrease in the O/M ratio or an increase of oxygen vacancy concentration at constant concentration of Gd [34]. Ohmichi
Figure 2: Lattice parameters of $U_{1-x}^{4+}$Gd$_2$O$_{2-x/2}$ or $U_{4-x}^{4+}$U$_2^{5+}$Gd$_3$O$_2$ as a function of Gd content in this work, including comparison with the reference results from Liu et al. [29], Baena et al. [30], and Durazzo et al. [31].

Figure 3: Linear thermal expansion [(L(T)-L(300K))/L(300K)] of UO$_2$+5wt% Gd$_2$O$_3$ with the reference results from IAEA [32].
et al. [34] explained that this increase in the lattice parameter was due to the size of the oxygen vacancy, which is 10% larger than that of the O\(^{2-}\) ion. Kim et al. [35] observed a contraction of the lattice for the hypo-stoichiometric sample, but the contraction factor (the slope of the relationship between the lattice parameter and the Gd content) is smaller than those of the hyper-stoichiometric and stoichiometric samples. The authors also explained this observation with the larger size of the oxygen vacancies. The increasing lattice parameter of U4-random (no U\(^{5+}\) cations, only oxygen vacancies) agrees with this observation and explanation. The lattice parameter of U4-bound (no U\(^{5+}\) cations, only oxygen vacancies), almost constant with Gd content, may indicate smaller oxygen vacancies when bounded with Gd. However, it should be noted that the largest difference in lattice parameters (between U4-random and U5-bound with 8 wt% Gd\(_2\)O\(_3\)) is only about 0.5%.

Figure 3 shows the linear thermal expansion [L(T) - L(300K)]/L(300K) as a function of temperature calculated for un-doped UO\(_2\) and samples with 5 wt% Gd\(_2\)O\(_3\), as well as reference results from IAEA [32]. The linear expansion of the un-doped UO\(_2\) is slightly larger than the IAEA recommended data at the tem-
temperature range shown in the figure. As the original potential for un-doped UO$_2$
was derived based on the Fink model [36] up to higher temperatures, the small
difference between the calculated linear expansion and the IAEA data (about
2% at 2000 K) is acceptable. It should be noted that recent experimental in-
vestigations on thermal expansion of UO$_2$ [37] using high-energy XRD indicates
a thermal expansion that is systematically slightly higher than the standard
reference data of Fink [36]. As such, the doped samples also show slightly larger
linear expansion than the IAEA recommended data, being largest for the U4-
bound sample (about 10% at 2000 K) and about 5% for the other three samples.
Considering the uncertainties associated with the recommended data (about 4%
at 2000 K for UO$_2$ with 5 wt% Gd$_2$O$_3$ [32]) and recent experimental data show-
ing higher thermal expansion of UO$_2$ [37], this difference is acceptable. Figure
4 shows the enthalpy change $H(T)-H(300K)$ as a function of temperature cal-
culated for all samples with 5 wt% Gd$_2$O$_3$ and reference results from Amaya et
al. [33]. The enthalpy change shows a very small difference and is in excellent
agreement with the experimental results.

It can be seen from Figures 2, 3 and 4 that the incorporation of the Gd-O
potential originally developed for Gd-doped CeO$_2$ can predict the experi-
tentially determined thermophysical properties of Gd-doped UO$_2$, and thus it will
be used in this work to simulate the thermal conductivity of Gd$_2$O$_3$ doped UO$_2$.

Thermal conductivities were computed using the non-equilibrium MD (NEMD)
approach of Müller-Plathe [38] as implemented in the Large-scale Atomic/Molecular
Massively Parallel Simulator (LAMMPS) [39]. A heat flux was imposed along
the longest direction of a $5 \times 5 \times 200$ supercell with a $5 \times 5$ unit cell cross-
section. The mean temperature gradient was measured after the system had
reached steady state (normally at $\sim 100$ps). All simulations were calculated
with periodic boundary conditions and a time-step of 1 fs.
Table 2: Parameters for the many-body interactions described by the second term of Eq. (1) [25, 27, 28].

<table>
<thead>
<tr>
<th>species</th>
<th>$G_\alpha$ (eV Å$^{1.5}$)</th>
<th>$n_\sigma$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U$^{5+}$</td>
<td>1.806</td>
<td>3450.995</td>
</tr>
<tr>
<td>U$^{4+}$</td>
<td>1.806</td>
<td>3450.995</td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>0.690</td>
<td>106.856</td>
</tr>
</tbody>
</table>

Figure 5: Temperature dependent thermal conductivity of five samples with different Gd$_2$O$_3$ contents as indicated in the figure.
3. Results and Discussion

Figure 5 summarizes the calculated thermal conductivities as a function of temperature, K(T), for samples incorporating different accommodation mechanisms and for different Gd$_2$O$_3$ concentrations: 0 wt%, 1 wt%, 2 wt%, 5 wt% and 8 wt%. The thermal conductivity functions K(T) are grouped into four groups according to their respective accommodation mechanism, U4-random, U4-bound, U5-random, or U5-bound, which are then shown in separate subfigures. We make the following observations and conclusions: (1) Each thermal conductivity function K(T) decreases with increasing temperature, and would seem to asymptotically approach a (lower) limit, as T increases. As a corollary, as T increases, the rate of decrease of K(T) decreases. (2) The thermal conductivity is a decreasing function of Gd content for all temperatures and all accommodation mechanisms. Consequently, the rate of decrease in K(T) as T increases is smaller for higher Gd contents.

To understand the effects of the Gd accommodation mechanism more clearly, we again show in Figure 6 the thermal conductivities as a function of temperature. However, this time the thermal conductivity curves K(T) are grouped according to the samples’ Gd content, so that samples with the same Gd content but different Gd accommodation mechanisms are shown on the same plot. Our main observation is that at low Gd content (1 wt% Gd$_2$O$_3$), the difference in the thermal conductivity for the different Gd accommodation mechanisms is relatively small, the largest difference being between U5-bound and U4-random at 300K (about 23%). However, as the Gd content increases, the difference increases (29% and 39% between U5-bound and U4-random at 300K at Gd contents of 2 wt% and 5 wt%, respectively), and becomes quite distinct at a Gd content of 8 wt% (41% between U5-bound and U4-random at 300K).

For all Gd$_2$O$_3$ concentrations, the U5-bound sample (i.e. UO$_2$ containing \(\{\text{Gd}_1^2 : \text{U}_1^2\}\times\) defect clusters) shows the highest thermal conductivity, while the U4-random sample (UO$_{2-x}$ containing isolated Gd$^{3+}$) shows the lowest thermal conductivity, and the thermal conductivities of U5-random (UO$_2$ containing iso-
lated Gd$^{3+}$) and U4-bound ($\text{UO}_2$-$z$ containing $\{2\text{Gd}^{3+}_\text{U} : \text{V}_{\text{O}}\}^x$ defect clusters) are in between and very close to each other. It can be seen from Figure 6 that samples with defect clusters ($\text{U5}$-bound and U4-bound) show higher thermal conductivity than those corresponding samples with isolated defects ($\text{U5}$-random and U4-random). The U4-random and U4-bound samples ($\text{UO}_2$-$z$) contain extrinsic charge balancing oxygen vacancies due to the Gd$_2$O$_3$ doping. The oxygen vacancies are effective phonon scatterers and will reduce the thermal conductivity [13], however, the thermal conductivity of U4-bound is very close to that of U5-random (no oxygen vacancies). Thus, the defect clusters are less effective phonon scatterers and will reduce thermal conductivity degradation in UO$_2$.

The experimental thermal conductivity data shown in Figure 6 were measured for a ($\text{U}_{0.372}\text{Gd}_{0.073}$)O$_2$ sample of 5 wt% Gd$_2$O$_3$ concentration [19]. These were thermal conductivity measurements of samples corrected to a theoretical density of 100% $K_{th}$, by normalising the measured thermal conductivity $K_M$ using the modified Loeb equation [40],

$$K_{th} = \frac{K_M}{1 - P\eta},$$  \hspace{1cm} (6)

where $P$ (0.0443) is the porosity and $\eta$ an experimental parameter,

$$\eta = 2.6 - 5 \times 10^{-4}(T - 273.15),$$  \hspace{1cm} (7)

where $T$ is the temperature in K, as reported by Brandt & Neuer [10].

The oxygen-to-metal ratio (O/M) of the experimental sample was determined to be 2.00 within an experimental error of ±0.003. Therefore the oxygen vacancy concentration was very low and no more than 0.15 at%, which is negligible compared to the ~ 7.3 at% of U$^{5+}$ ions present in the sample acting as charge compensation for Gd$^{3+}$. It can be seen from Figure 6, the experimental thermal conductivity (5 wt% Gd$_2$O$_3$ concentration) is in excellent agreement with the thermal conductivity of the U5-bound ($\{\text{Gd}^{3+}_\text{U} : \text{U}_{\text{U}}\}^x$ defect clusters in the UO$_2$) sample. This result is in agreement with previous modelling predictions that the Gd is accommodated by associating itself with a U$^{5+}$ cation.
to form stable defect clusters \{
Gd_{\text{U}}^{2+} : \text{U}_{\text{U}}^1\}^x
in \text{UO}_2 with excess oxygen [7].

Thermal conductivity calculated using the FRAPCON-4.0 fuel code [41] is also shown in Figure 6 for comparison (neither burn-up nor irradiation effects were considered for a direct comparison with MD results). At low \text{Gd}_2\text{O}_3 concentrations (1 wt\% and 2 wt\%), the thermal conductivity calculated using the FRAPCON-4.0 fuel code is slightly smaller than the MD results. As the \text{Gd}_2\text{O}_3 concentration is increased to 5 wt\%, it becomes larger than the MD results for U4-bound, U4-random and U5-random, but is consistent with the experimental results, and is very close to the MD result for U5-bound. This is even more obvious as the \text{Gd}_2\text{O}_3 concentration is increased to 8 wt\%, for which at temperatures below \sim 700K, the thermal conductivity calculated using the FRAPCON-4.0 fuel code is very close to the MD result for U5-bound, but much larger than the MD results for U4-bound, U4-random and U5-random.

Figure 6: Temperature dependent thermal conductivity of four types of samples, representing different \text{Gd} accommodation mechanisms (see text for details), and with different \text{Gd}_2\text{O}_3 contents. The experimental data were obtained by scaling the measured data to the theoretical value by Hirai and Ishimoto [19].
4. Summary

The effects of Gd accommodation mechanisms and concentration on the thermal conductivity of UO$_2$ doped with Gd$_2$O$_3$ have been investigated using molecular dynamics simulations for four types of Gd accommodation mechanisms: in (U,Gd)O$_{2-x}$, isolated Gd$^{3+}$ substitutional defects, charge compensated by isolated oxygen vacancies or \{2Gd$^{3+}_U$ : V$^-_O$\}$^\times$ defect clusters; and in (U,Gd)O$_2$, isolated Gd$^{3+}$ substitutional defects, charge compensated by U$^{5+}$ or \{Gd$^{3+}_U$ : U$^+_U$\}$^\times$ defect clusters. The thermal conductivity was observed to decrease systematically with increase in Gd$_2$O$_3$ concentrations and temperature. The samples with \{Gd$^{3+}_U$ : U$^+_U$\}$^\times$ defect clusters show the highest thermal conductivity, while the samples with isolated Gd$^{3+}$ ions forming (U,Gd)O$_{2-x}$ exhibit the lowest values.

This result indicates that defect clusters are less effective phonon scatterers than their corresponding isolated defects, and would therefore result in less thermal conductivity degradation. The reduction in phonon scattering is likely due to a combination of the reduced number of scattering points (as clusters are expected to act as a single scattering point) and the specific effectiveness of the scattering centre.

The experimental thermal conductivity of a UO$_2$ sample with 5 wt% Gd$_2$O$_3$ content was in good agreement with that of the sample with \{Gd$^{3+}_U$ : U$^+_U$\}$^\times$ defect clusters (U5-bound), which is consistent with previous theoretical results for the Gd accommodation mechanism of defect clusters \{Gd$^{3+}_U$ : U$^+_U$\}$^\times$ in UO$_2$ with excess oxygen.

The thermal conductivity calculated using the FRAPCON-4.0 fuel code was also in good agreement with that of the material with \{Gd$^{3+}_U$ : U$^+_U$\}$^\times$ defect clusters (U5-bound) at high Gd$_2$O$_3$ concentrations.

5. Acknowledgements

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