Defects in hafnium-doped lutetium oxide and the corresponding electron traps: a meta-generalized gradient approximation study

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A number of Lu2O3-based materials were reported to present efficient capability of trapping excited charge carriers in metastable excited states formed either by specific dopants or naturally occurring defects. Over the years, abundant experimental data have been collected, which were taken as a solid ground to treat the problem using computational chemistry. Density functional theory (DFT) calculations with an advanced meta generalized gradient approximation (mGGA) functional were used to analyze electron trapping in cubic Lu2O3 doped with Hf. Individual ions of dopant and nearest-neighbor dopant ion pairs were considered. The effects of interstitial anions such as O2<sup>-</sup> and Cl<sup>-</sup> were analyzed. In most of the analyzed cases the additional electron charge is localized at the dopant site. However, in many of the studied cases, the dopant/defect states overlap with the conduction band and cannot correspond to electron trapping. The Hf<sup>3+</sup> ion in the Lu site of C<sub>3i</sub> local symmetry (Hf<sup>3+</sup>Lu-C<sub>2i</sub>) corresponds to a moderate trap depth of 0.8–0.9 eV. Several composite defects corresponding to deeper (1.1–1.4 eV) traps also exist. Unambiguous deep traps (1.5–1.8 eV) correspond to systems with Hf dopant in the cationic void, accompanied by two interstitial oxygen atoms. The results thus indicate that basic ‘Hf-substitutes-Lu’ doping is unlikely to correspond to the deep traps observed experimentally in Lu2O3:Tb,Hf and Lu2O3:Pr,Hf and more complex defects must be involved.

1. Introduction

Thermoluminescence properties of phosphors based on cubic lutetium oxide (c-Lu2O3) originate from charge carriers (electron and hole) trapping at the relevant impurities or defects (Kulesza et al., 2016). Lanthanide cations (Tb<sup>3+</sup> and Pr<sup>3+</sup>) were shown to act as hole traps in c-Lu2O3 (Ln<sup>3+</sup>Lu,Ln<sup>4+</sup> is formed locally upon hole trapping). The Ln dopants also act as carrier recombination and emission centers. The properties can be fine-tuned via changes in electron traps related to d-metal dopants such as Ti, Nb or Ta (Kulesza et al., 2016; Bolek et al., 2018). This paper is dedicated to analysis of different kinds of Hf-based electron traps in c-Lu2O3 using density functional theory (DFT) calculations.

Several reports on thermoluminescence of c-Lu2O3:Ln,Hf are summarized below. The thermoluminescence measurements in these studies were conducted after preliminary irradiation of the samples with ultraviolet light of about 250 nm, while the trap depths were estimated via fitting the Randall–Wilkins first-order kinetics (McKeever & Chen, 1997) to the thermoluminescence glow curves.

Lu2O3:0.1%Tb,0.1–1.5%Hf samples exhibit a glow curve with an intense peak at about 180 °C (heating rate of
On the basis of the experiments, it was assumed that oxygen vacancies \( V_O \) and d metal dopants in \( \text{Lu}_2\text{O}_3 \) result in additional states below conduction band, that are capable of electron trapping (Kulesza et al., 2016). The advanced DFT calculations for \( \text{Lu}_2\text{O}_3:V_O \) (Shyichuk & Zych, 2020) and \( \text{Lu}_2\text{O}_3:Ta \) (Shyichuk & Zych, 2019) support this assumption. The \( \text{Lu}_2\text{O}_3: \) Hf system was expected to exhibit similar phenomena, albeit with different trap depths. From the experimental papers mentioned above, it is clear that Hf co-doping results in strong enhancement of energy storage properties in \( \text{Lu}_2\text{O}_3: \) Pr and \( \text{Lu}_2\text{O}_3: \) Tb, and the likely reason is Hf-related electron trap formation. From Fig. 1, it is clear that thermoluminescence glow curves of both \( \text{Lu}_2\text{O}_3: \) Tb,Hf and \( \text{Lu}_2\text{O}_3: \) Pr,Hf exhibit the strongest peak at about the same temperature (250 °C), which is not present in the glow curves of the corresponding samples without Hf codopant. Consequently, we have conducted a series of calculations, starting with the simplest structures where Hf substitutes Lu, and concluding with interstitial Hf ions accompanied with two species of interstitial oxygen. The electron trapping in \( \text{Lu}_2\text{O}_3: \) Hf turned out to be by far more complex than the assumed localized formation of Hf\(^{3+}\)(Hf\(_{\text{Int}}\)). This paper presents the results.

2. Computational details

The approach used, the selection of pseudopotentials and functionals, their pros and cons are discussed in our previous papers (Shyichuk & Zych, 2020, 2019), which also present a comprehensive review on the limitations of the applied methodology (Shyichuk & Zych, 2019). There is about 0.5–1 eV underestimation of the band gap, which might translate to about 10–20% error in the calculated trap depth. Thus, we mostly compare the computational results to themselves and look for trends rather than concentrate on specific numbers. Comparison to experiment should be considered as semi-quantitative.

As previously, we have used a two-step procedure. The geometries were optimized using Perdew–Zunger (Perdew & Zunger, 1981) local density approximation (PZ LDA) functional, GBRV (Garrity et al., 2014) ultrasoft pseudopotentials and Quantum Espresso (Giannozzi et al., 2009, 2017) code (at 40 Ry/544 eV plane wave cutoff and mostly default other setting; see Table S1 in supporting information). The valence shells were: O: 2s 2p, Lu,Hf: 5s, 5p, 6s, 5d, 6p and 5f. Before further modifications, the undoped cell geometry has been optimized without restrictions (vc-relax task in the PW module of Quantum Espresso): atomic positions, cell dimensions and principal angles were allowed to vary. This optimized geometry (shown in Table S2 of the supporting information) was used to create the structures with defects, which then underwent the same unconstrained optimization. Next, all-electron full-potential linearized augmented plane wave (FP-LAPW) total energy and properties calculations were performed, using Elk code (Sharma et al., 2014), RPP (Räsänen et al., 2010) meta-generalized gradient approxima-

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1 Note that in Kulesza & Zych (2013) the heating rate was incorrectly given as 4.5 °C min\(^{-1}\) instead of the real rate 4.5 °C s\(^{-1}\).
tion (mGGA, meta-GGA) for exchange and PZ correlation. Muffin-tin radii of the elements were 1.45 bohr for oxygen, 2.0 or 2.3 bohr for the metals. Both calculations used a $3 \times 3 \times 3$ k-point grid. All of the settings are described in detail in the supporting information (Table S4).

The GBRV Hf$^{4+}$ pseudopotential was used in the calculations. The Hf$^{4+}$ pseudopotential passed the Hf$^{3+}$ tests in the uspp-7.3.6 code used to generate it. The alternative GBRV Hf$^{0}$ pseudopotential resulted in shorter Hf—O bonds, while the resulting structures corresponded to no trapping in the following all-electron calculations. The Hf—O bond length from the Hf$^{4+}$ pseudopotential were much more similar to the respective bond lengths from all-electron calculations than the bond lengths from the Hf$^{0}$ pseudopotential.

The experimental cell size of Ia-3Lu$_2$O$_3$ is about 10.4 Å (Zeler et al., 2014). There are 80 atoms in the cell, which is 16 formula units of Lu$_2$O$_3$. The structure resembles a distorted CaF$_2$ lattice, where 16 anions are missing – there are thus 16 anion voids. The remaining anions form rows along the principal directions, with three anions per row. Sixteen of such rows can be seen along either $x$, $y$ or $z$ Cartesian axes of the cell. There are also total of 32 cation voids, which would have been occupied with cations if the material was e.g. Pm3m CsCl. There are eight Lu sites of C3i symmetry, 24 Lu sites of C2 symmetry. The cation voids of the respective symmetries are the same in quantity.

At a first iteration, the study followed the steps of the Lu$_2$O$_3$:Ta (Shyichuk & Zych, 2019) paper: Hf atoms were placed in Lu sites as is (total charge was $+1$ due to Hf$^{4+}$ replacing Lu$^{3+}$), or with a complementary interstitial oxygen in the nearest anion void (total charge $-1$ due to the additional O$^2-$). Another kind of impurity was Lu$_2$O$_2$:Hf(Cl$_2$) (additional interstitial Cl$^-$, the cell total charge was zero). Interstitial Cl$^-$ compensates the additional charge from Hf$^{4+}$ in Lu$^{3+}$ site, and can be unwillingly introduced during synthesis. Next, the following doped structures were analyzed: Lu$_2$O$_2$:2HfO$_i$ (total charge zero) and Lu$_2$O$_2$:2Hf (total charge $+2$). The atoms of the Hf pair were placed in the second-nearest-neighbor Lu sites. Such a choice allowed for the optional O$_i$ in between. The three Hf$\cdots$Hf configurations were: $2 \times C_{3i}$, $2 \times C_2$, $C_{3i} + C_2$. Finally, several structures with Hf dopant in either C$_{3i}$ or C$_2$ cation void and interstitial oxygens in the anion voids were analyzed (Lu$_2$O$_2$:Hf$_i$2O$_h$, total charge zero). Note that Hf does not substitute Lu in the latter case.

For the charged structures, no charge compensation mechanism was explicitly modeled, while the Lu$_2$O$_2$:2HfO$_i$ and Lu$_2$O$_2$:Hf$_i$2O$_h$ were charge-neutral by construction. As discussed previously (Shyichuk & Zych, 2020), we have used a parameter-free approach, meaning no use of empirical or fitted parameters in the density functionals.

Kröger–Vink notation (Kro¨ ger & Vink, 1956) is used in the paper. Bullet superscripts (e.g. Hf$^*_C$) mark additional positive local charge at the defect. Prime superscripts (e.g. O$_i^*$) indicate additional negative local charge. A superscript multiplication sign (e.g. Hf$^*_C$) indicates defects with zero local charge.

3. Results and discussion

3.1. Uni-cell dimensions and bond lengths

The following section concerns the structures optimized using ultrasoft pseudopotentials, unless specified otherwise. In order to get a more complete picture of the defects in question, some of the calculations were also performed using projector-augmented wave (PAW) method, with the respective pseudopotentials (Jollet et al., 2014; Holzwarth, 2019) (which included Lu 4f electrons as a valence shell). While having the numerical cost of only up to several times larger than that of USPP, PAW method accounts for the nodal structure of the valence orbitals and ensures orthogonality between valence and core wavefunctions, resulting in geometries as good as those from all-electron FP-LAPW calculations (Hafner, 2008).

While resulting is slightly larger cells, the PAW calculations lead to the same overall conclusions. Details about the cell dimension dependence on the defect character, as well as the detailed description of bond lengths, are presented in the Supplementary Tables.xls spreadsheet and described in the supporting information.

The optimized pure Lu$_2$O$_3$ cell volume was 1087.5 Å$^3$, while the experimental volume is 1122.7 Å$^3$ (Zeler et al., 2014). Such a difference corresponds to the linear dimensions of the cell (and bond lengths) being about 1% underestimated, which is an acceptable error, and even a good result for LDA. With Hf$^{4+}$ dopant, the cell dimensions were 0.44–0.45% smaller with respect to the optimized Lu$_2$O$_3$ cell. For the structures with a cluster of two Hf$^{4+}$ ions and an interstitial O$^{2-}$ ion, the cell size was almost the same as that of the optimized Lu$_2$O$_3$ cell (differences smaller than 0.05%). The structures with an interstitial Hf$^{4+}$ ion and two interstitial O$^{2-}$ ions were 0.78–0.88% larger than the optimized defect-free cell. In all of the mentioned cases, the change in Hf nominal oxidation state from 4+ to 3+ [i.e. introduction of additional electron(s) to the system] resulted in an increase of the unit-cell size. The Hf$^{4+}$—O bonds were always shorter than Lu$^{3+}$—O bonds, even for the structures where the additional electron did localize at Hf. In many structures, however, the electron did not localize at Hf, and the Hf—O bond lengths were similar to the Hf$^{4+}$—O bond length from the structures with (formally) Hf$^{4+}$. The average Lu—O bonds were also a bit longer in the structures with the additional electrons.

Introduction of the Hf$^{4+}$ dopant should result in overall reduction of the unit cell size, as compared to the dopant-free cell. If one interstitial oxygen atom is introduced per two atoms of Hf dopant, no significant change in the cell size is expected. Finally, in the case of the interstitial Hf dopant accompanied by the interstitial oxygen ions, an increase in the cell size is expected.

These changes in bond lengths were utilized when creating Lu$_2$O$_3$:Hf$^{4+}_i$2O$_{3h}$ geometries. With two Hf atoms in the structure, there is a chance that only one of them has a +3 charge (that is, that only one trap of the two is occupied). Setting up the respective calculation with identical surrounds of the two dopant results in magnetization density equally spread between the two ions. The resulting bond lengths turn
out to be somewhat in between the Hf$^{4+}$ and Hf$^{5+}$ lengths. It was not possible to solve the problem using starting magnetization or constrained magnetization options of the PW program. Alternatively, an optimized geometry of Lu$_2$O$_3$:Hf$^{5+}$ was used, where one of the Lu atoms was replaced with Hf in order to create the second dopant site. Such a calculation yet again resulted in a mixed magnetization. As Lu—O bonds are longer than Hf$^{3+}$—O bonds, the second dopant located in the (initially) Lu surround had a stronger tendency to become Hf$^{3+}$, while the (initially) Hf$^{3+}$ dopant becomes Hf$^{4+}$. The successful attempt used optimized geometry of Lu$_2$O$_3$:Hf$^{5+}$ or Lu$_2$O$_3$:2Hf$^{4+}$ calculations can thus be spin-polarized. Alternatively, an optimized geometry of Lu$_2$O$_3$ was not possible to solve the problem using starting magnetization options of the PW program. As Lu$_2$O$_3$ was being optimized, the ‘new’ dopant became Hf$^{3+}$ with the ‘old’ Hf site had a Hf$^{4+}$ surround (and kept it), while the newly added dopant had (initially) a Lu surround. As the geometry was being optimized, the ‘new’ dopant became Hf$^{3+}$ with most of the magnetization localized at itself.

3.2. Density of states – Lu$_2$O$_3$:Hf and Lu$_2$O$_3$:2Hf

The study began with analysis of the empty trap systems. Electronic configuration of Hf$^{5+}$ is the same as that of Lu$^{3+}$. Lu$_2$O$_3$:Hf$^{5+}$ or Lu$_2$O$_3$:2Hf$^{4+}$ calculations can thus be spin-unpolarized (closed-shell), meaning much shorter run times and significantly lower memory requirements. From our Lu$_2$O$_3$:Ta study (Shyichuk & Zych, 2019), it is clear that occupied trap states lie at a bit higher energy than the respective empty traps. Many Hf-related electron traps turned out to be shallow even when empty, and (for the most part) could not explain the experimental depth. The analysis of the filled traps was then limited to the more relevant cases.

In Fig. 2, density of states (DOS) plots of Lu$_2$O$_3$:Hf$^*( Lu_2O_3: Hf^{4+})$ and Lu$_2$O$_3$:2Hf$^*( Lu_2O_3: 2Hf^{4+})$ samples are shown. The cubic Lu$_2$O$_3$ structure provides cation sites of C$_{3i}$ and C$_2$ symmetry. Hf dopant has been analyzed in each of them. Also, placements of two Hf atoms in the second-nearest-neighbor sites were analyzed for Hf$_{C_3}^*$ – Hf$_{C_3}^*$ and Hf$_{C_3}^*$ – Hf$_{C_3}^*$ pairs. The structure with both Hf dopant ions in C$_{3i}$ sites was a furthest-neighbor pair. The atomic positions in question are listed in the supporting information (Table S5).

States below the conduction band are showed in Fig. 2, and this indicates their potential for electron trapping. Strong contribution of the dopant 5$d$ orbitals to the defect bands is clear. The partial DOS plots correspond to the muffin-tin part of Hf states only (i.e. localized inside the atomic sphere of 2.3 bohr/1.127 Å radius). Actual Hf contribution to the states should be significantly larger. The partial DOS plots show total Hf contribution; of that, only 5$d$ orbitals can noticeably contribute to the DOS at the energies close to Fermi level in doped Lu$_2$O$_3$.

When Hf dopant is placed in the C$_2$ site, some of the resulting trap states (bands below the conduction band) are located close to the conduction band, and overlap with it as well as with each other [Figs. 2(b), 2(c) and 2(d)]. It is thus unlikely that long-term electron trapping is possible at Hf atoms in C$_2$ sites. In contrast, Hf in the C$_{3i}$ site might potentially result in a moderately deep trap. Thus, further calculations were performed with Lu$_2$O$_3$:Hf$^{5+}$ and Lu$_2$O$_3$:2Hf$^{4+}$ (described in Section 3.4 below).

The systems with Hf$_{C_3}^*$ – Hf$_{C_3}^*$ and Hf$_{C_3}^*$ – Hf$_{C_3}^*$ pairs exhibit more complex DOS plots [Figs. 2(c) and 2(d)] than a simple sum of the respective single-doped system DOS plots. Apparently, the dopant atoms interact and affect each other energy levels. However, in terms of electron trapping, these pairs do not seem to be much useful. In Lu$_2$O$_3$:Hf$_{C_3}^*$, Hf$_{C_3}^*$, the largest possible depth is similar to that of Lu$_2$O$_3$:Hf$_{C_3}^*$, and is not separated by a gap from the conduction band [Figs. 2(b)].
and 2(b)]. In Lu$_2$O$_3$:Hf$^{1+}$, the maximal trap depth is slightly larger than in Lu$_2$O$_3$:Hf$^{2+}$ [Figs. 2(a) and 2(d)]. In Lu$_2$O$_3$:Hf$^{3+}$, the traps seem to be the same as in Lu$_2$O$_3$:Hf$^{2+}$ [Figs. 2(a) and 2(e)], while the partial DOS peaks of both Hf atoms overlap perfectly.

3.3. The effect of co-anion

Interstitial oxygen with its $-2$ charge can compensate for the additional charge from two Hf$^{4+}$ ions situated in Lu$^{3+}$ sites. Interstitial chlorine anion can compensate one Hf$^{4+}$. The chlorine ions can be introduced during the synthesis – either from HfCl$_4$ starting material (Kulesza et al., 2016; Wiaterowska & Zych, 2013a, 2012). If the mutual distance between the defects is far enough for them to not interact, the trapping properties should be that of the isolated defects. We have considered an extreme case, where O$_i$ or Cl$_i$ are bound to the dopant Hf atom(s). This is justified as Hf$^{4+}$ can have a coordination number of 6, 7 or 8 (Shannon, 1976), while Lu sites in undoped structure is about 3.4 Å. The intent was to see the effect of O$_i$; bound to both of them (the Lu$_2$O$_3$ undoped structure is about 3.9 Å) have only one oxygen second-nearest-neighbor sites (the Lu$_2$O$_3$ two impurities also justifies such a possibility. In Fig. 3, the respective DOS plots are shown.

On the one hand, some of the Hf empty bands are (almost) overlapped with the conduction band [Figs. 3(c), 3(d), 3(f), 3(g)]. A tiny gap is present in Lu$_2$O$_3$:Hf$^{3+}$, Cl$_i$ DOS [Fig. 3(b)]. On the other hand, the lowest Hf bands are still quite far from the conduction band. It was decided to try Lu$_2$O$_3$:Hf$^{3+}$, Cl$_i$ with one additional electron and see if it is going to be trapped. In contrast, in Lu$_2$O$_3$:Hf$^{3+}$, Cl$_i$ O$_i$ only one of the Hf atoms is bound to the O$_i$, and hence it was expected that one electron can be trapped by such a structure. Noteworthy is the difference in partial DOS of the two dopant ions: there is a clear gap above the lowest defect state [Fig. 3(e)] corresponding to one of the dopant ions, while the state corresponding to the other dopant ion overlaps with the conduction band.

Two more empty-trap systems were considered, where only one Hf$^{4+}$ dopant and one O$_i$ were present in the cell. Such systems were characterized by total charge of $-1$. These calculations were performed in order to find out how the bound interstitial oxygen affects an isolated Hf ion. It was found out that Hf states are located at the proximity of the conduction band and overlap with it [Figs. 3(f) and 3(g)]. Hence, no efficient trapping was expected, and no further effort was taken in this regard.

3.4. Selected filled trap cases

From the empty trap calculations mentioned earlier, it was rather clear that some traps are shallow, while some others seem deeper and were hence worth a more detailed analysis. For such cases, calculations with additional electrons were performed, in order to check the trap depths in a more relevant way, i.e. with the traps being filled. These were Lu$_2$O$_3$:Hf$^{2+}$ (Hf at either the C$_2$ or C$_3$ site), Lu$_2$O$_3$:Hf$^{3+}$, Cl$_i$, Lu$_2$O$_3$:2Hf$^{2+}$ and Lu$_2$O$_3$:Hf$^{3+}$, O$_i$ (the three options for Hf sites: C$_2$, C$_3$; C$_{3i}$, C$_{3i}$, C$_{3i}$, C$_{3i}$), and Lu$_2$O$_3$:Hf$^{3+}$, Hf*$_i$ and Lu$_2$O$_3$:Hf$^{3+}$, Hf*$_i$.

Table 1

<table>
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<tr>
<th>Structure</th>
<th>Trap depth (eV)</th>
</tr>
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<tr>
<td>Lu$_2$O$_3$:Hf$^{3+}$</td>
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</tr>
<tr>
<td>Lu$_2$O$_3$:Hf$^{2+}$-ax</td>
<td>0.85</td>
</tr>
<tr>
<td>Lu$_2$O$_3$:Hf$^{2+}$-unax</td>
<td>0.85</td>
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<tr>
<td>Lu$_2$O$_3$:Hf$^{3+}$-unax</td>
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</tr>
<tr>
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</tr>
<tr>
<td>Lu$_2$O$_3$:Hf$^{3+}$,O$_i$'</td>
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<tr>
<td>(Lu$_2$O$_3$:Hf$^{3+}$,Hf*$_i$)</td>
<td>1.10</td>
</tr>
<tr>
<td>(Lu$_2$O$_3$:Hf$^{3+}$,Hf*$_i$)'</td>
<td>0.62</td>
</tr>
<tr>
<td>(Lu$_2$O$_3$:Hf$^{3+}$,Hf*$_i$)'</td>
<td>0.65</td>
</tr>
</tbody>
</table>

In Fig. 4, densities of states of the structures that exhibited at least some electron trapping potential are shown. In all of them, Hf at C$_{3i}$ Lu site acts as an electron trap of a moderate depth (Table 1).

In Lu$_2$O$_3$:2Hf$^{2+}$, dopant atoms are located at Lu C$_{3i}$ sites and contain one trapped electron each, total of two unpaired electrons in the structure and total cell charge of zero. The respective Hf $d$ partial DOS of both dopant ions overlap.

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Figure 4

Selected cases with filled traps. Fermi level is at zero. Breaks cover the range of $-3.5$–$-0.5$ eV.
completely [Figs. 4(b) and 4(c)]. The overall peak shape of both trap DOS and Hf d PDOS [Figs. 4(b) and 4(c)] are very similar to those of Lu₂O₃:Hf⁺⁴⁺ (Fig. 4a). In other words, two Hf atoms at C₃ sites act as independent Lu₂O₃:Hf⁺⁴⁺ traps.

The structures corresponding to the plots in Figs. 4(b) and 4(c) differ in the dopant ion placement. The first case maintains the overall C₃ rotational symmetry of the cell. With two Hf dopants on the axis, the cell inversion center is at 0.5, 0.5, 0.5, which is a cation void site. The dopants lie 8.858 Å apart, at fractional coordinates 0.25, 0.25, 0.25 and 0.75, 0.75, 0.75, i.e. in the main diagonal, which is also the C₃ axis. The case is thus labeled ‘axial’. The other one does not have such a symmetry, and was labeled ‘unaxial’. The unaxial (off-diagonal) site was at 0.75, 0.25, 0.25; the other one was at 0.25, 0.25, 0.25. These sites lie 5.138 Å apart with two trapped electrons (one per site) or 5.118 Å apart with only one trapped electron in the off-diagonal site.

The unaxial structure was also less symmetric at the numerical level: the numbers of the irreducible k-points in the Quantum Espresso calculations were 6 and 10, for the axial and unaxial structures, respectively. In Elk, with its slightly different approach to k-point reduction by symmetry, the unaxial structure had 27 k-points (i.e. the full 3x3x3 grid). Such a difference, however, has a small effect on DOS and the predicted electron trapping. The distance between the sites is apparently too large for them to interact, and they do not share a nearest-neighbor anion void. The significance of this property will be illustrated later in this paper.

The unaxial case was used to populate only one of the two dopant sites with the trapped electron, that is to make a Lu₂O₃:Hf⁺³⁺ structure (total charge +1 on the cell). It was not possible with the axially symmetric structure, as both dopant sites got half-occupied. With the unaxial geometry, starting from pure Lu₂O₃ geometry with the selected Lu atoms replaced with Hf, yet again, both dopant sites were half-occupied by the additional electron. Thus, the optimized geometry was taken, Hf substitution was made at 0.75, 0.25, 0.25, and another geometry optimization was performed. Hf⁺³⁺ has longer bonds than Hf⁺⁴⁺, while Lu⁺⁵⁺ has even longer bonds. The 0.25, 0.25, 0.25 site has been pre-optimized as Hf⁺⁴⁺. The ‘new’ Hf at 0.75, 0.25, 0.25 initially had the Lu³⁺—O bond length, become populated by the additional electron, and converged as Hf⁺³⁺. In the resulting DOS and PDOS (Fig. 4d), the two sites can be distinguished.

In Lu₂O₃:Hf⁺³⁺, the two dopant ions occupy second-nearest-neighbor sites that lie 3.665 and 4.061 Å apart, respectively. The Lu···Lu distance in the undoped structure was 3.889 Å for these sites. In the structures, the contribution of Hf 5d states to the defect peaks is noticeably lower [Figs. 4(e) and 4(f)] than in the C₃,h,C₃,h structures [Figs. 4(a)–4(d)], while the trap depth is higher. This happens due to the fact that the trapped electrons get a strong contribution from the interstitial (void) density. The trap depth is similar to that of the oxygen vacancies (1.4–1.6 eV) (Shyichuk & Zych, 2020). In Lu₂O₃:Hf⁺³⁺, a significant portion of trapped electron occupies an anionic void between the two dopant sites, and is delocalized over both Hf ions.

The presence of unpaired electrons in the studied systems is a natural expectation due to Hf dopant changing its oxidation state from 4+ to 3+ as the trapping mechanism. Hf⁺³⁺ in Lu₂O₃ should contain one unpaired electron, while two Hf⁺³⁺ were expected to contain one unpaired electron each. In order to converge the systems to the respective high-spin states, forced magnetization was used in both Quantum Espresso and Elk. The details are provided in the supporting information (Table S4 and the respective paragraph). In order to force a magnetization, a magnetic field is applied to the system. After Elk calculations with the field converged in their high-spin states, they were restarted from the obtained potentials, this time without the field. Some of the calculations converged to the same high-spin states, without the field. For such cases, the spin-up and the spin-down parts of the DOS plots were not shifted in respect to each other [Figs. 4(a)–4(f), 5(a) and 5(b)]. Some other cases did not maintain the magnetization without the field. Thus, the respective high-spin DOS were calculated with the field, and their spin-up and spin-down parts are mutually shifted [Figs. 5(c)–5(f)].

DOS and PDOS plots of several special cases worthy of a discussion are shown in Fig. 5. The first one is Lu₂O₃:Hf⁺³⁺, where the interstitial oxygen is bound to only one of the dopant atoms: as the C₃,h sites of c-Lu₂O₃ do not share a nearest-neighbor anionic void, a single O cannot bind to both dopant ions. The O₂⁻ free Hf exhibits electron trapping properties (Fig. 5a) similar to Lu₂O₃:Hf⁺⁴⁺. The other Hf does not – the respective states lie too close to the conduction band, even without a trapped electron. Note-worthy, the structure converged to such a state without any

**Figure 5**

Special cases with filled traps. The shifts of the spin-down part in panels (c)–(f) originate from the magnetic field used to stabilize the high-spin cases. Fermi level is at zero. Breaks cover the range of −2.5:−0.5 eV.
special tricks. A similar situation was expected for the Lu₂O₃:Hf/C₂/C₃i; Hf/C₁5/C₂; Oᵢ structure, where the Oᵢ binds to both of the two dopant ions. The Hf/C₁/C₁/C₁ distance in this case is 3.505 Å (shorter than 3.665 Å in Lu₂O₃:Hf/C₂/C₃i; Hf/C₁5/C₂). However, due to the Oᵢ, both sites are locally C₁-symmetric (i.e. asymmetric), which is seen in Fig. 5(b): partial d DOS plots of both dopant ions overlap. The occupied defect peak has a negligible contribution from Hf d orbitals. The trapped electron sits in the nearby anionic void, which will be shown using magnetization density plots. Thus, this structure should rather be labeled (Lu₂O₃:Hf/C₃i; Hf/C₂; Oᵢ)⁺. This kind of defect is characterized by the lowest trap depth among those analyzed in research papers.

Figure 6
Magnetization density plots of the selected impurities and defects. The dashed circles visualize Hf muffin-tin sphere radii. The numbers inside the circles indicate the magnetic moments inside the respective spheres, in the units of negative Bohr magneton.
this work. The depth is about a half of that of an oxygen vacancy (estimated using the same computational methodology). The defect is highly likely to form, as its empty trap form is charge neutral. Thus, out of the analyzed defects, Lu2O3:HF*2, HF*3, O*1/(Lu2O3:HF*2, HF*3, O*1) is the most likely candidate to explain the shallow trap participating in Lu2O3:Ln,Hf fading at room temperature (Kulesza et al., 2010; Kulesza & Zych, 2013).

In Lu2O3:HF*2, HF*3 and (Lu2O3:HF*2, HF*3, O*1), the HF···Hf distance was 3.668 and 3.567 Å, respectively, while in the undoped structure it would have been 3.903 Å. No levels below the conduction band are present; Hf d states overlap with the conduction band, which is clearly seen in the respective PDOS [Figs. 5(c) and 5(d)]. The similar phenomenon is observed in Lu2O3:HF*2, Cl* and Lu2O3:HF*3 [Figs. 5(e) and 5(f)], although Hf d peaks are more distinct for these two. Yet again, strong interstitial character of the trapped electrons is observed. Also, the high-spin states in these four structures were not stable without the magnetic field to enforce them. From Figs. 5(e) and 5(h), it can be concluded that additional coordination anion deteriorates the trapping properties of Hf dopant in c-Lu2O3.

In Table 1, the calculated trap depths are shown for the structures for which distinct traps were found. Hf in Lu C3i of c-Lu2O3 thus corresponds to a moderately deep one-electron trap of 0.8–0.85 eV [the oxygen vacancy trap was estimated to be about 1.4 eV, that is almost as deep (Shyichuk & Zych, 2020)]. If there are two Hf atoms in the nearby C2 sites, but an Oi is bound to one of them – the other one acts as a trap of 1.1 eV depth.

A pair of Hf atoms in the nearest-neighbor C3i and C2 sites would act as a much deeper two-electron trap. The first electron should be released from Lu2O3:HF*2 C3i at 1.21 or 1.07 eV. The second electron is expected to be released upon 1.38 eV stimulation (from Lu2O3:HF*2 C3i). In other words, second-nearest-neighbor clusters of two Hf atoms in different local symmetries exhibit trap depths that can be comparable to that of an oxygen vacancy (Shyichuk & Zych, 2020). Adding an interstitial oxygen to such a pair in between the Hf ions (forming a tightly bound cluster, Lu2O3:HF*2, HF*3, O*1) reduces the one-electron depth to 0.62 eV. With the additional electron, the notation is (Lu2O3:HF*2, HF*3, O*1) as the trapped electron does not localize at Hf. Noteworthy, the defect can hold two electrons, with first-electron depth of 0.65 eV. Low spin (Lu2O3:HF*2, HF*3, O*1) features a DOS practically identical to that of (Lu2O3:HF*2, HF*3, O*1). High-spin (Lu2O3:HF*2, HF*3, O*1) system features two separate Vo-like interstitial magnetization density blobs (see the supporting .xsf files) – i.e. each of the unpaired electrons localizes in a separate anionic void.

Due to the presence of unpaired electrons, the magnetization density plots would not only show where the electron is localized, but also the spatial features of its density. The plots were done using Elk (task 73). As the magnetization (in most cases) was localized at the dopant atom(s) or nearby, only the involved atoms are displayed in Fig. 6. The reader is invited to download the supporting .xsf files that contain the geometries and the said densities, which are much better comprehended with the ability to rotate the structure freely and change the isosurface level.

If Fig. 6, the values of total magnetizations within the atomic (muffin-tin) spheres are given as text. The highest values correspond to about 1/3 of the trapped electron to be localized within the sphere of 2.3 bohr/1.127 Å centered at the dopant ion nucleus. Hf 5d orbitals are much more spatially spread. According to e.g. atomic natural orbitals relativistic core corrected basis (ANO-RCC) (Roos et al., 2008), the portion of radial density of Hf 5d atomic orbitals within the said radius integrates to about 0.371. The last peak of the mentioned radial density lies at about 3.2 Å. Thus, the value of muffin-tin magnetization above 0.3 indicates localization of the trapped electron at the dopant 5d orbitals.

In Fig. 6(a), magnetization density of Lu2O3:HF*2 C3i is shown. It exhibits a characteristic dxy shape, which is located along the C3 rotation axis. The Lu2O3:HF*2 C3i densities exhibit identical shape. So does the Lu2O3:HF*2, HF*3 unaxial site density (Fig. 6b, left); some tiny magnetization is present at the axial site. The Lu2O3:HF*2, HF*3, O*1 trapped electron density shape is similar, although distinctly asymmetrical, and shows contributions from the neighboring atoms [Fig. 6(c)]. A similar asymmetric shape is observed in Lu2O3:HF*2 C3i (Fig. 6d).

Fig. 6(e) presents a peculiar case of Lu2O3:HF*2, HF*3, O*1, where the electron is delocalized among both dopant sites – although the participation of the C3i site is much higher, judging from the muffin-tin magnetization (0.238 versus 0.102 for the C2 site). The space between the dopant ions where the magnetization is localized corresponds to an anionic void, which is occupied by the Oi in (Lu2O3:HF*2, HF*3, O*1) (Fig. 6f).

Addition of the interstitial oxygen forces the trapped electron to occupy a nearby anionic void, in the same fashion as do the trapped electrons in an oxygen vacancy void (Shyichuk & Zych, 2020); both voids are surrounded by LuO in a tetrahedral alignment. No surprise that the Hf—Oi—Hf defect can trap a second electron, with a similar trap depth (Table 1). Despite the trapped electron localization in the anionic void, Hf in C3i site has something to do with it: an analogous structure with both Hf ions in C2 sites exhibits no such localization and no trapping. Noteworthy, the C2 Hf position in the same in both structures.

In (Lu2O3:HF*2, HF*3, O*1), muffin-tin magnetization is quite high – about 1. But, strong overlap of the defect bands with the conduction band is observed (Fig. 5d), while the Hf-localized magnetization is visually much smaller than in the previous cases. Changing isosurface levels results in many magnetization islands spread across the cell, indicating a strong bandlike (delocalized) character of the said magnetization. In (Lu2O3:HF*2, HF*3) the magnetization density yet again occupies an anionic void neighboring to both dopant ions (Fig. 6j), although with strong participation of other atoms nearby. No trapping is observed in this case (Fig. 5e).

Finally, Lu2O3:HF*2, Cl* and Lu2O3:HF*3 exhibit no trapping [Figs. 5(e) and 5(f)] and a different shape of the muffin-tin magnetization [Figs. 6(h) and 6(i)]. The magnetization (judged from the respective partial DOS) corresponds to 5d orbitals of
the dopants, and neither 6s nor 6p. A band-like character of the additional (not-trapped) electrons is observed here.

3.5. Interstitial HfO₂ clusters

After the studies described in the previous sections had been conducted, it was clear that the respective Hf-based traps were, for the most part, too shallow to explain the experimental trap depth of about 1.4 eV in c-Lu₂O₃:Tb,Hf. An alternative option considered clusters of interstitial Hf ions in cationic voids and interstitial oxygen ions in the anionic voids. Introduction of such a Hfₕ₂Oᵢ cluster would be self-charge-compensated by construction, as the dopant Hf oxidation state is 4⁺ at the synthesis stage (Kulesza et al., 2016; Wiatrowska & Zych, 2012, 2013). Calculations with empty traps indeed showed some significant depths, and the respective calculations with filled traps (Lu₂O₃:Hf⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺; 2Oᵢ⁻⁻⁻⁻, total charge −1) were performed.

The Hf dopant was placed at either the C₃i or C₂ cation void. We have tested five options for the interstitial oxygens: both directly coordinated to Hf (making its coordination number 8); one Oᵢ coordinated to Hf and the other Oᵢ in the second coordination sphere of Hf (Hf coordination number was 7); one Oᵢ coordinated to Hf and the other Oᵢ as far from the dopant as possible (Hf coordination number was 7); both Oᵢ as far as possible from the dopant or both in its second coordination sphere (Hf coordination number was 6). A detailed list of positions and the distances between them is given in Table S6. The resulting DOS plots are shown in Fig. 7.

The electron traps from these structures are characterized by rather high depth, which does not seem to depend much on the distances between the defects (although the splitting of Hf 5d orbitals clearly does). In most of the cases, additional hole traps (occupied states above valence band) show up and correspond to the interstitial oxygen atoms. In some other cases, these traps overlap with the band [Figs. 7(b) and 7(g)]. The trap depths corresponding to the Lu₂O₃:Hfᵢ₂Oᵢ clusters are shown in Table 2. Note that the point symmetry subscripts merely label the sites and do not reflect the actual local symmetry, which is specified separately. For the structures with Hf dopant in the C₃i cationic void, the traps are significantly deeper than that of Lu₂O₃:Hf⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺ and are comparable to those of an oxygen vacancy (1.4–1.6 eV) (Shyichuk & Zych, 2020). For the structures with Hf dopant in the C₂ cationic void, the depths were less uniform, although of the similar magnitude (1.2–1.6 eV). The deepest were the traps corresponding to the

Figure 7
DOS plots of Lu₂O₃:Hfᵢ₂Oᵢ. The dopant is located in either C₃i [left, (a)–(d)] or C₂ [right, (f)–(j)] cation void. Position of the Oᵢ’s in respect to the dopant (1st, 2nd coordination sphere, or far) is indicated. The traps are filled with one electron. Fermi level is at zero. Breaks cover the range of −2.5–0.5 eV.
structures with both interstitial oxygens located in the second coordination sphere of the dopant (1.7–1.8 eV).

The magnetization plots (Fig. 8) show only the direct surround of the Hf dopant. The whole structures with the magnetization 3D data can be found in the .xsf files in the supporting information. Some of the cases exhibited very similar magnetization shapes, despite different Hf coordination numbers. Namely, Lu2O3:Hf/C15/C15/C15i-C3i;2O00i with the following Oi location in respect to Hf exhibit the six-point (octahedral-kind) magnetization density shape, as in Fig. 8(a): 1st, 1st; 1st, far; far, far. Lu2O3:Hf/C15/C15/C15i-C2i;2O00i with both Oi in the 1st coordination sphere of Hf, and the one with the Oi in 1st and 2nd coordination spheres exhibit magnetization density shape similar to a d2x2−y2 orbital with some portion of dxz (Fig. 8d). Lu2O3:Hf/C15/C15/C15i-C2i;2O00i with both Oi either in the 2nd coordination sphere, or far from Hf, exhibit a d2−y2 magnetization shape (Fig. 8f). Thus, only the unique shapes were shown.

A principal difference from the previous cases is that the trapped electron is slightly delocalized at several nearby Lu ions, at the same time having a distinctly localized character. The participating orbitals can thus be viewed as a partially bonding Hf–Lu orbitals. Participation of Lu delocalization is likely one of the factors resulting in larger trap depths. Such clusters can be considered as one of the candidates explaining the electron trapping in Hf-doped cubic lutetium oxide.

Most of the magnetization shapes can be approximately attributed to individual d orbitals, either d2x2 or d2−y2 (given their orientation along principal axes). A clear exception is Lu2O3:Hf/C15/C15/C15i-C3i;2O00i with both Oi in the first coordination sphere of Hf, with its octahedron-like shape. The shape is likely a d2x2−y2 hybrid orbital, and originates from the site maintaining its C3i symmetry. The shape is C3i-symmetric as well.

### 3.6. Radial magnetization density

In Fig. 9, plots of radial magnetization density for the selected samples are shown. They show the probability to find the unpaired electron density at distance R from the specified dopant site. The values of the density and R were calculated for each voxel corresponding to the g-point grid in the calculations (i.e. a 108x108x108 grid). The values of R (in Å) were rounded to a single decimal, and the values of density were summed for the corresponding rounded R. In other words, the distance step in the plot is 0.1 Å.

From Fig. 9(a), it is clear that Lu2O3:Hf/C15i magnetization density peaks at about 1 Å from the dopant site. Such a distance is consistent with the peak of radial probability of the Hf 5d wavefunction from e.g. atomic natural orbitals relativistic core corrected (ANO-RCC) basis from Molcas (Roos et al., 2008). Hence, the unpaired electron density is localized at the dopant site. Similarly, for the Lu2O3:Hf/C15i;Hf/C1 unaxial case, the magnetization density mostly occupies the unaxial

## Table 2

<table>
<thead>
<tr>
<th>Oi location</th>
<th>Electron trap depth (eV)</th>
<th>Local symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lu2O3:Hf/C15/C15/C15i-C3i;2O00i</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st, 1st</td>
<td>1.48</td>
<td>C3i</td>
</tr>
<tr>
<td>1st, far</td>
<td>1.45</td>
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<td>1.45</td>
<td>C1</td>
</tr>
<tr>
<td>2nd, 2nd</td>
<td>1.77</td>
<td>S2</td>
</tr>
<tr>
<td>Far, far</td>
<td>1.38</td>
<td>C3i</td>
</tr>
</tbody>
</table>

Figure 8

Magnetization density plots of the Hf2O cluster defects. Locations of the Oi species in respect to Hf site are given under the images.

Figure 9

Radial magnetization density plots for the selected samples.

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dopant site, with the slight contribution from the axial site – in line with Fig. 6(b).

In contrast, for Lu$_2$O$_3$:Hf$^{5+}$, Cl$^{-}$ and Lu$_2$O$_3$:Hf$^{5+}$ [Fig. 9(b)], the magnetization density peak at the dopant site is much lower than that of Lu$_2$O$_3$:Hf$^{5+}$. The density is evidently spread to the parts of the cell further from the dopant site, in line with the assumed band-like character of the corresponding electrons.

In the Lu$_2$O$_3$:Hf$^{5+}$, Cl$^{-}$ cell, the unpaired electron is located predominantly near the C$_8$ site [Fig. 9(c)]. However, the peaks at larger distances are more prominent than those in the case of Lu$_2$O$_3$:Hf$^{5+}$, indicating that the Lu$_2$O$_3$:Hf$^{5+}$, Hf$^{5+}$ magnetization density is more sparse. With two additional (both unpaired) electrons in the cell with same dopant positions (i.e. the Lu$_2$O$_3$:Hf$^{5+}$, Hf$^{5+}$ system) significant localization of the magnetization density at both dopant sites can be seen [yet again in line with the magnetization density isosurface plot, Fig. 6(d)]. However, the density between the dopant sites (about 2–2.5 Å from either of them) is higher, indicating a more delocalized character of these electrons.

In Fig. 9(d), the radial magnetization densities of (Lu$_2$O$_3$:Hf$^{5+}$, Hf$^{5+}$, O$^{2-}$) and Lu$_2$O$_3$:Hf$^{5+}$, 2O$^{2-}$ are shown. In the former, the integration centered at the interstitial anionic void site where the magnetization is localized. Despite the lack of atom there, the overall radial distribution is similar to that of Lu$_2$O$_3$:Hf$^{5+}$. The same goes for the (Lu$_2$O$_3$:Hf$^{5+}$, 2O$^{2-}$) cases. However, in the latter, unlike the other examples, the second (small) peak is shifted to the larger distances (2.75–3 Å instead of 2–2.5 Å), indicating the participation of the nearest-neighbor Lu sites in the delocalization of the unpaired electron. In the other systems, this small peak corresponds to the coordination oxygens. This might be interpreted as a sign of some Hf–Lu bonding, also assumed from the magnetization density spatial shape (Fig. 8).

3.7. Potential for intermediate level fading

On the one hand, the electrons trapped at the interstitial Hf ions (Lu$_2$O$_3$:Hf$^{5+}$, 2O$^{2-}$) are separated from the conduction band by a significant gap. On the other hand, in some cases [e.g. Figs. 7(d), 7(e) and 7(f)] there are other Hf levels in between the trap level and the band. An obvious question is: can the electron escape the trap via a multi-step excitation process involving the intermediate levels, at temperatures lower than that corresponding to the full depth? i.e. can the electron ‘climb a ladder’ while being thermally excited only one step at time?

The question was analyzed in terms of rate equations, via an extended single trap model. A simplified approach was used, where only one intermediate level is present. No retrapping was assumed. We have considered a case where full depth is 1 eV, while the intermediate level is at 0.5 eV. In such a system, the electron needs to take a step to the intermediate level, and then another step to the conduction band, both of 0.5 eV. While 0.5 eV traps usually result in afterglow at room temperature, 1 eV trap would require the temperature to be at least 100–150 K higher in order to get efficiently cleared.

The respective rate equations were constructed, and solved numerically using odeint module of SciPy Python library. Different values of excitation and relaxation rates have been tested. It turned out that the higher the equilibrium population of the intermediate level is, the higher would be the rate of the actual detrapping. If the relaxation rate of the intermediate level is high, the system effectively behaves as a single trap model and is expected to follow the first-order kinetics in a thermoluminescence experiment. However, if the relaxation rate is slow, some portion of the intermediate population has a chance to get promoted to the conduction band, meaning the electron release – at the temperature corresponding to only half of the full trap depth. Such a process might not be enough for efficient thermal detrapping at room temperature (i.e. afterglow), but it might be enough for fading.

On the one hand, the intermediate levels are clearly characterized by Hf 5d character (Fig. 7), as well as the lowest trap state. The transitions between them are intraconfigurational and thus forbidden. Additionally, in many of the deeper-trap geometries, local inversion symmetry is maintained, reducing the intrinsic transition probabilities even further. Thus, the electric dipole relaxation rates of the intermediate levels might happen to be of the microsecond order of magnitude, which would be enough for fading. However, multiphonon relaxation must be efficient for the small energy gaps in question. It is thus hard to speak with certainty on the likelihood of the ladder process. But, it is possible in principle, and provides an explanation for the experimentally observed fading.

4. Conclusions

It was shown that, in order for Hf-based defect in c-Lu$_2$O$_3$ to exhibit at least some electron trapping, the said defect must involve a Hf dopant in the C$_8$ site of Lu. Interstitial anions bound to the dopant atom would result in no electron trapping. Simple defects involving one Hf ion provide shallow electron traps at best (0.8–0.9 eV). More complex defects involving a pair of dopant ions (one in C$_8$ site and the other one in C$_3$ site) can result in deeper traps of 1.1–1.4 eV. Adding interstitial oxygen to said pair reduces the trap depth to about 0.6–0.7 eV. Even deeper traps are possible if the dopant ion is placed in a cationic void with two interstitial oxygens in the nearby anionic voids, resulting in trap depth up to 1.8 eV. These depths can be arranged by their depths into three groups, which correspond to roughly three kinds of glow curve peaks observed experimentally in Hf-codoped c-Lu$_2$O$_3$ phosphors. However, these results are not exclusive: other kinds of traps are likely possible. This study also shows a possibility for room temperature fading of the charged (irradiated) persistent phosphors, via a ladder mechanism involving states above the main electron trap state and below the conduction band.

Acknowledgements

Kevin F. Garrity from the National Institute of Standards and Technology, NIST, is acknowledged for the provided Lu$^{3+}$...

Funding information

Funding for this research was provided by: Narodowe Centrum Nauki (grant No. 2017/26/D/ST3/00599 to Andrii Shyichuk); Wroclawskie Centrum Sieciowo-Superkomputerowe, Politechnika Wrocławska (award No. 300).

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