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The Pr³⁺ and Tb³⁺ ground state locations in compounds obtained from thermoluminescence and intervalence charge transfer studies

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Abstract

The location of the lanthanide ground states with respect to the host valence band or to the vacuum level always follow characteristic zigzag patterns with the number of electrons q in the 4f orbital. The patterns that are used today evolved over the years by combining experimental data from different techniques, and they are in first approximation independent on the type of compound. Here we will demonstrate that the ground state locations for Pr³⁺ and Tb³⁺ in the currently used pattern for trivalent lanthanides appear, when inspected on the ± 0.1 eV accuracy level, not consistent with two independent sets of experimental data. One set is from data on the intervalence charge transfer (IVCT) from Pr³⁺ and Tb³⁺ to the conduction band (CB) observed in luminescence excitation spectra. The other set is from the release of holes from Pr⁴⁺ and Tb⁴⁺ to the valence band observed in thermoluminescence (TL). In addition to the inconsistency, TL based evidence for a slight compound dependence in the characteristic zigzag patterns is found.

I. INTRODUCTION

Figure 1 shows a typical vacuum referred binding energy (VRBE) scheme. It pertains to the electron binding in divalent and trivalent lanthanide levels in LuNbO_4 . The upper zigzag curve connects the binding energy in the ground state of the divalent lanthanides and the lower one in the ground state of the trivalent ones. The chosen shapes for the two zigzag curves have been subject to continual revisions inspired by new knowledge and insight together with new data. One of the first appearance of the divalent lanthanide curve within the band gap of a compound was by Pedrini *et al.* [1] for alkaline earth fluorides. It was based on a tilted version of that of the free divalent lanthanide ions as given by the 3rd ionization potentials. Another version of the divalent zigzag curve was presented in 2003 by Dorenbos [2]. It was based on experimental data on the charge transfer (CT) energy of an electron from the VB to a trivalent lanthanide with the divalent lanthanide 4f ground state as final state. Such data are most abundant for Eu, Sm, Tm, and Yb. To complement the data for lanthanides where CT-band information was missing, a semi-empirical evaluation on how the location of the lowest $4f^{q-1}5d$ -level changes with type of lanthanide was made. Then by subtracting the experimental $4f^q-4f^{q-1}5d$ energy differences, the $4f^q$ -ground state energies were obtained. For trivalent lanthanides also an approach based on a smooth variation with q of the energy in the lowest $4f^{q-1}5d$ -levels was followed.

Since then the shape of the zigzag curves have been corrected [3, 4], refined [5, 6], and verified [7]. The latest, minor, adjustment was made in 2017 [8]. The shape for the divalent lanthanide binding energy curve is now rated to be accurate on the ± 0.1 eV level. That for the trivalent lanthanides has not been tested that well yet. As Fig. 1 shows, most of the trivalent ground state levels are buried in the oxygen valence band and then one cannot use luminescence spectroscopy or thermo-luminescence to determine level locations with respect to the host bands. Ce^{3+} , Pr^{3+} , and Tb^{3+} are however within the band gap. They are able to trap a hole from the valence band and hole release, illustrated by arrows 4) and 5) in Fig. 1, can be probed by thermoluminescence (TL) techniques. One may also excite an electron from the $4f^q$ ground state to the conduction band. Such transition, illustrated by arrows 2) and 3) in Fig. 1, is known as Inter Valence Charge Transfer (IVCT) [9–11].

In this work information on IVCT energies as derived from published spectroscopic data on Pr^{3+} and Tb^{3+} doped compounds is collected. The energy difference between the IVCT

from Pr^{3+} with that from Tb^{3+} is a direct measure for the difference between the Pr^{3+} and Tb^{3+} ground state energies in the band gap. With TL spectroscopy one may relate observed TL glow peaks to the release of a hole from Pr^{4+} and Tb^{4+} to the valence band. The temperature at the maximum of the glow peak is directly related to the hole trapping depth, and information on the location of the Pr^{3+} and Tb^{3+} ground state levels above the valence band is then obtained. We will show that the IVCT data and the TL-data are consistent, and conclude that the VRBE in the Pr^{3+} and Tb^{3+} ground states are within ± 0.1 eV the same. TL-data also reveal a slight compound dependence in the VRBE difference.

II. IVCT AND THERMOLUMINESCENCE DATA ON Pr^{3+} AND Tb^{3+}

A. IVCT data

In [8, 12] it was already suggested that transitions from the Tb^{3+} and Pr^{3+} ground state directly to the CB, as indicated by arrows 2) and 3) in Fig. 1, provide information on where to locate their ground state levels. Those transition can be observed as broad excitation and absorption bands in compounds where the CB-bottom is below the lowest $4f^{q-1}5d$ -level. For LuNbO_4 this is seen in Figure 2 where the room temperature host excitation band is at 262 nm (4.75 eV) [13]. At 290 nm and 297 nm the 0.7 eV broad IVCT bands of Pr^{3+} and Tb^{3+} are observed. The higher energy Pr^{3+} IVCT band implies that the Tb^{3+} ground state is about 0.1 eV above that of Pr^{3+} .

To investigate this further, the literature on Pr^{3+} and Tb^{3+} excitation and absorption spectra were carefully screened to obtain information on the energy of the IVCT band of Pr^{3+} and of Tb^{3+} in the same compound. Data are compiled in Table I and shown in Figure 3 where the IVCT band energy of Tb^{3+} is displayed against that of Pr^{3+} . IVCT bands can only be observed when they are not obscured by much more intense $4f$ - $5d$ transitions. The listed compounds in Table I therefore mostly relate to $4d$ and $5d$ transition metal (W, V, Mo, Nb) based compounds where the conduction band is between -3 and -4 eV on the VRBE scale [14]. Compounds with Zn, In, Cd, Sn, and Sb also have a low lying CB-bottom [15, 16]. In all those compounds, the lowest $4f^{q-1}5d$ level is inside the CB.

On average the IVCT band of Tb^{3+} in the data of Fig. 3 is at 0.06 eV higher energy than that of Pr^{3+} with a standard deviation of 0.11 eV. This implies that the Tb^{3+} ground

state energy is about 0.05 eV below that of Pr^{3+} . However, the latest parameter set for the trivalent zigzag curve in [8], places the Tb^{3+} ground state 0.18 eV above that of Pr^{3+} . This already indicates that the trivalent zigzag curve may need for Pr and Tb about 0.24 eV correction. IVCT bands have typical width of 0.8 eV (FWHM) and are often located close to the host excitation band. Figure 2 for LuNbO_4 is an example where the IVCT bands are still separated from the host excitation. For most of the compounds in Table I the separation is less clear, and the bands appear as shoulder peaks or even as a long wavelength tail on the host excitation peak. This all leads to relatively large errors in IVCT band energies. For a better assessment of the indicated correction, an independent and more accurate evaluation on the energy difference between Pr and Tb ground state energies in compounds will be required.

B. TL-data

Recently it was shown that hole release from Tb^{4+} and Pr^{4+} to the valence band can be probed, just like electron release from a divalent lanthanide to the conduction band in [7], by TL studies. TL is a sensitive technique, and it can provide more accurate data on the difference between Pr and Tb ground state energies than IVCT bands do [17]. One of the first observations for hole release from lanthanides was by Bos *et al.* [18] for YPO_4 with Tb-Sm and Tb-Tm combinations. The released hole from Tb^{4+} recombines with the electron trapped on Sm^{2+} or Tm^{2+} to generate Sm^{3+} or Tm^{3+} emission. You *et al.* [20] observed glow peaks for $\text{Y}_3\text{Al}_5\text{O}_{12}$ with the Pr-Eu and Tb-Eu combination but they were not assigned yet to hole release from Pr and Tb. The correct assignment was made by Milliken *et al.* [21]. A more dedicated study on hole release was by Luo *et al.* [22] on GdAlO_3 . Figure 4 shows the TL-glow peaks with glow peak maxima at 416 K for Tb^{4+} hole release and 428 K for Pr^{4+} hole release. The released hole recombines with the electron trapped on Eu^{2+} or on Sm^{2+} yielding Eu^{3+} or Sm^{3+} emission. The hole release from Tb^{4+} and Pr^{4+} in the REPO_4 (RE =La, Gd, Y, Lu) was further studied in Lyu *et al.* [23, 24]. In YPO_4 the glow peak from hole release from Tb^{4+} was observed at 507 K at a heating rate of 1K/s. The hole release from Pr^{4+} takes place at 10K lower temperature of 497 K. In solid solutions of (Y,Lu) PO_4 the glow peaks shift from 497K towards 555K for Pr^{4+} and from 507K towards 570K for Tb^{4+} in LuPO_4 [23]. Data on the temperature T_m at the maximum of the glow

peak for hole release from Tb^{4+} and Pr^{4+} are compiled in Table II.

Inspecting Table II we observe that in LaPO_4 the glow peak from Tb^{4+} appears at 30 K higher temperature than from Pr^{4+} which reduces to 15-12K higher temperature for GdPO_4 , LuPO_4 , and YPO_4 . However, it appears at 5 K lower temperature for LiLuSiO_4 to become 14 K lower for GdAlO_3 . 300-350 K/eV is the typical shift of a TL glow peak maximum with trapping depth [17], and from the glow peak temperatures the energy difference $\Delta E_{\text{Tb-Pr}}$ between the Tb^{3+} and Pr^{4+} ground state can be estimated as listed in column 5 of Table II. It suggests that the Tb^{3+} ground state moves from 0.1 eV above to 0.05 eV below that of Pr^{3+} . These TL data on the one hand confirm that the ground state of Tb^{3+} and that of Pr^{3+} in oxide compounds coincide within ± 0.1 eV as found from the IVCT data, but on the other hand they also indicate that the energy difference between the Pr^{3+} and Tb^{3+} ground states is slightly compound dependent.

III. DISCUSSION

The shape for the divalent zigzag curve is for YPO_4 quite well established particularly because of accurate data from thermoluminescence studies [7, 18]. For other compounds always the same shape is assumed. The shape for the trivalent curve is much less certain. Optical spectroscopy and TL-studies can only provide data on the trivalent lanthanides with ground state level within the band gap. For the oxide compounds we have only Ce^{3+} , Pr^{3+} and Tb^{3+} , and to arrive at a proper shape for all the trivalent lanthanides one has to make use of additional other methods.

For the VRBE $E_{4f}(q, 3+, A)$ of the trivalent lanthanides in a compound A , a shifted and tilted version of the free ion curve was proposed that can be expressed as [4, 19]

$$E_{4f}(q, 3+, A) = E_{4f}(q, 3+, \text{vacuum}) + E(\text{Eu}, 3+, A) + \alpha(3+)[R(\text{Eu}, 3+) - R(q, 3+)] \quad (1)$$

where $E_{4f}(q, 3+, \text{vacuum})$, shown as curve 1) in Fig. 5, is equivalent to the 4th ionization potential of the lanthanide atoms. $E(\text{Eu}, 3+, A)$ is the chemical shift in binding energy in the 4f⁶ ground state of Eu^{3+} due to Coulomb repulsion between the 4f electrons and the negatively charged ligands of the anion surrounding [19]. $[R(\text{Eu}, 3+) - R(q, 3+)]$ is the ionic radius difference of the 3+ lanthanide with 4f^q configuration with that of Eu^{3+} , and $\alpha(3+)$

is the so-called tilt parameter. The parameter values proposed in 2009 were based on Eq. (1) with a tilt parameter of 0.17 eV/pm [3]. The Tb^{3+} ground state is then at 1.06 eV above that of Pr^{3+} . These parameters were not long in use because one year later in 2010 [4] it was realized that the IVCT band energies involving Pr^{3+} and Tb^{3+} provide direct experimental data on level locations within the band gap. For several transition metal based compounds, clear evidence was found that the IVCT band for Tb^{3+} is close in energy to that for Pr^{3+} , and that translates to similar ground state locations for Pr^{3+} and Tb^{3+} . Based on these observations the tilt parameter was reduced from 0.17 to 0.11 eV/pm in [4] which is shown as the dashed curve 2) in Fig. 5. Tb^{3+} appears now 0.56 eV above Pr^{3+} which was still too much, and the Tb data point was lowered somewhat further and that of Pr raised slightly until an acceptable difference of 0.18 eV was obtained as in curve 3). Note that this forced correction leads to a zigzag pattern that deviates from a tilted and shifted version of the free ion curve given by Eq. (1).

The results of Fig. 3 and Table I show that for the oxide compounds $E_{4f}(8, 3+, A) = E_{4f}(2, 3+, A) - 0.06 \pm 0.11$ eV. Going from phosphates, to silicates, to aluminates, the TL-data in Table II show that the Tb^{3+} ground state moves from ≈ 0.1 eV above that of Pr^{3+} in LaPO_4 to ≈ 0.05 eV below in GdAlO_3 . IVCT bands are very clearly observed in the $\text{BaRE}_2\text{ZnO}_5$ (RE= La, Gd, Y) compounds, and the data in Table I even suggest that Tb^{3+} may be 0.11 to 0.26 eV below Pr^{3+} . In the sequence phosphates, silicates, aluminates, $\text{BaRE}_2\text{ZnO}_5$, the bonding strenght in the oxygen ligands decreases which suggests a relationship between the Tb-Pr energy difference and the nephelauxetic effect.

Considering the above findings, the parameter set for the trivalent lanthanide zigzag shape (curve 3 in Fig. 5) with Tb^{3+} 0.18 eV above Pr^{3+} needs to be reconsidered. We also need to add a compound dependence to that shape which requires a theoretical justification. An obvious source for a compound dependence in the Pr-Tb energy difference is the tilt parameter $\alpha(3+)$ of Eq. (1). The chemical shift model predicts already an increase of $\alpha(3+)$ with increasing nephelauxetic effect [19]. However, it will work into the wrong direction and we must seek for another, opposite and stronger, effect. The nephelauxetic effect is a well-known and well-studied phenomenon, and a recent review on how that affects the Pr^{3+} excited state $4f^3$ energy levels was provided by Tanner and Yeung [25]. In forthcoming work the nephelauxetic effect on the VRBE in the $4f^q$ ground states of the lanthanide will be explored, and this indeed will be able to provide an explanation.

Summarizing, we need to redefine the shape of the zigzag curve for the trivalent lanthanides in such fashion that, at least in oxide compounds, the Tb^{3+} ground state has about the same energy as the Pr^{3+} ground state. In addition we need to find a theoretical justification and a model to add a compound dependence to the shape of the zigzag curve. The compound dependence is then a minor effect of at most few 0.1 eV. It can often be ignored when dealing with optical spectroscopy data based on charge transfer bands. However, for the much more sensitive TL-spectroscopy such changes are of significance. Apart from the chemical shift, Eq. (1) does not depend on type of compound, and then also this equation needs to be redefined.

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Figure captions

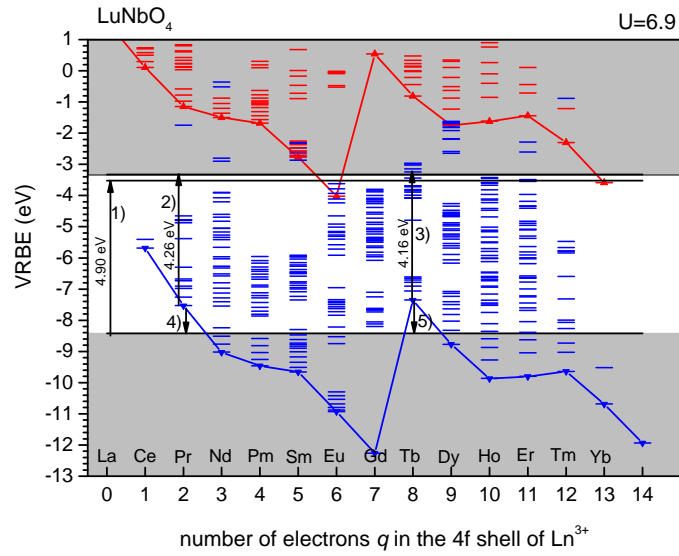


FIG. 1: VRBE scheme for LuNbO₄ constructed with the latest parameter set from Ref. [8]. Arrow 1), 2), and 3) indicate the host exciton transition, and the electron IVCT from Pr³⁺ and Tb³⁺ to the conduction band. Arrows 4) and 5) indicate hole transitions from Pr⁴⁺ and Tb⁴⁺ to the valence band.

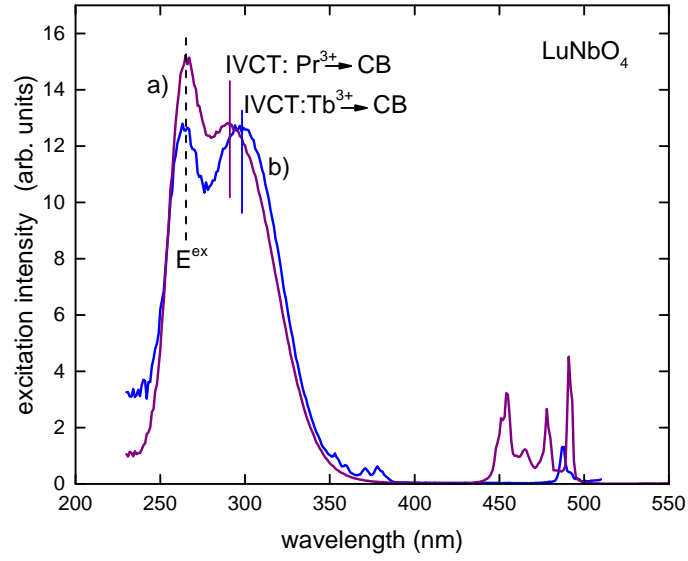


FIG. 2: The excitation spectra of Pr^{3+} and Tb^{3+} emission in LuNbO_4 . Data retrieved from Ref. [8, 13].

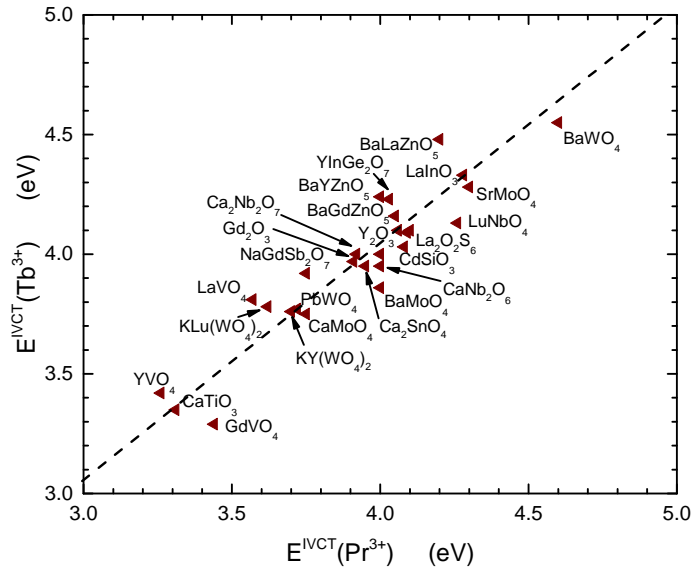


FIG. 3: The energy of the IVCT band of Tb^{3+} against that of Pr^{3+} . The dashed line has unit slope.

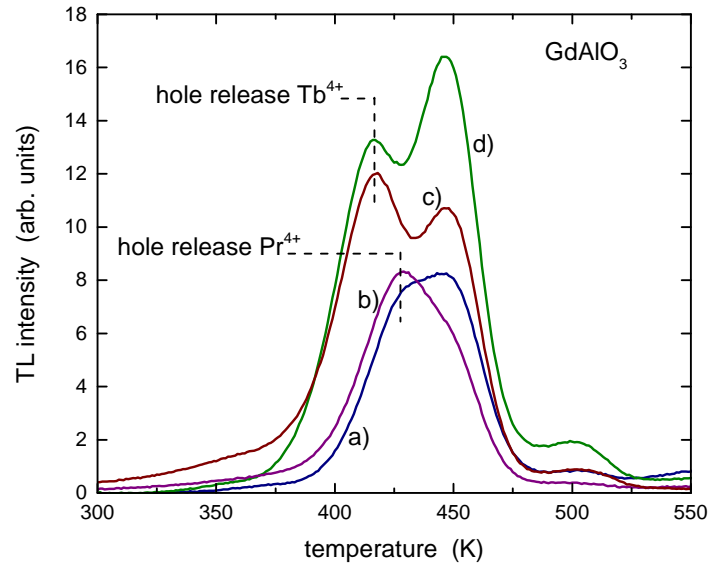


FIG. 4: TL-glow curves for a) Pr³⁺-Eu³⁺, b) Pr³⁺-Sm³⁺, c) Tb³⁺-Sm³⁺, and d) Tb³⁺-Eu³⁺ dopant combinations in GdAlO₃ recorded at a heating rate of 1 K/s. Data were obtained from Luo *et al.*[22].

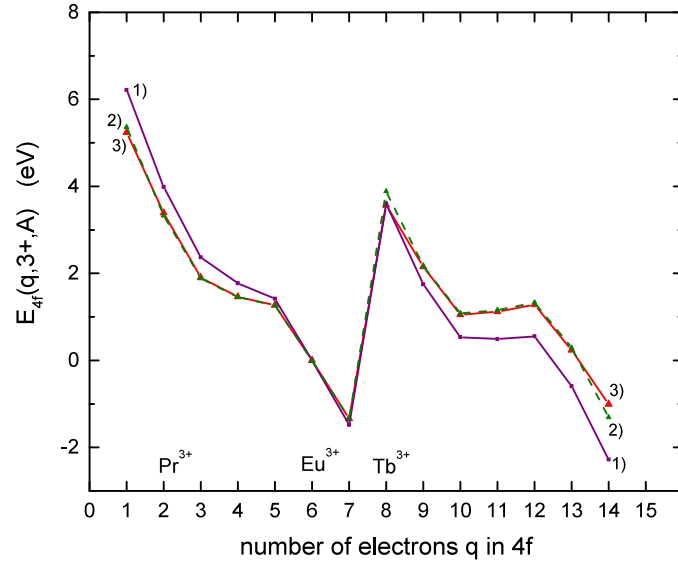


FIG. 5: The variation in VRBE energies in the lowest trivalent lanthanide $4f^q$ and $4f^{q-1}5d$ levels. 1) is for the free trivalent lanthanides derived from the 4^{th} ionization potentials, 2) is obtained when applying a tilt factor $\alpha(3+)= 0.11$ eV/pm, 3) is based on the latest parameters proposed in [4, 8].

TABLE I: The energy of the IVCT bands for Pr^{3+} and Tb^{3+} in compounds. Data with an asterisk are tentative because the IVCT band appears as a weak shoulder and one may not exclude a 4f-5d transition origin.

| compound | $E^{IVCT}(\text{Pr}^{3+})$ | Ref. | $E^{IVCT}(\text{Tb}^{3+})$ | Ref. |
|------------------------------------|----------------------------|-------------|----------------------------|--------------|
| $\text{NaGdSb}_2\text{O}_7$ | 3.75* | [27] | 3.92 | [28] |
| CdSiO_3 | 4.08 | [29] | 4.03 | [30] |
| CdGeO_3 | 4.00 | [31] | 4.00 | [32] |
| YInGe_2O_7 | 4.03 | [33] | 4.23 | [34] |
| CaSnO_3 | 4.10 | [35–37] | 4.10 | [35, 37, 38] |
| Ca_2SnO_4 | 3.95 | [39] | 3.95 | [40] |
| LaInO_3 | 4.28* | [41] | 4.33* | [41] |
| BaMoO_4 | 4.00* | [42] | 3.86 | [43] |
| SrMoO_4 | 4.30 | [44, 45] | 4.28* | [46] |
| CaMoO_4 | 3.75 | [47] | 3.75 | [47, 48] |
| BaWO_4 | 4.60 | [49] | 4.55 | [50] |
| PbWO_4 | 3.72 | [51–53] | 3.77 | [54] |
| $\text{KY}(\text{WO}_4)_2$ | 3.70 | [55] | 3.76 | [56] |
| $\text{KLu}(\text{WO}_4)_2$ | 3.62 | [55] | 3.78 | [55] |
| LaVO_4 | 3.57 | [57] | 3.81 | [58] |
| GdVO_4 | 3.24 | [57, 59] | 3.29 | [59] |
| YVO_4 | 3.26 | [9] | 3.42 | [60, 61] |
| CaNb_2O_6 | 4.00 | [10, 62] | 3.95 | [10] |
| $\text{Ca}_2\text{Nb}_2\text{O}_7$ | 3.92 | [63, 64] | 4.00 | [65] |
| YNbO_4 | 4.06 | [11, 66] | 4.10 | [11, 67–69] |
| LuNbO_4 | 4.26 | [13] | 4.13 | [8] |
| CaTiO_3 | 3.31 | [10, 70–72] | 3.35 | [11, 37] |
| $\text{BaLa}_2\text{ZnO}_5$ | 4.20 | [73] | 4.48 | [73–75] |
| Gd_2O_3 | 3.91 | [76] | 3.97 | [77–79] |
| $\text{BaGd}_2\text{ZnO}_5$ | 4.05 | [16, 80] | 4.16 | [81] |
| BaY_2ZnO_5 | 4.00 | [82, 83] | 4.24 | [81, 83, 84] |
| $\text{La}_2\text{O}_2\text{S}$ | 4.09* | [85] | 4.09* | [86] |

TABLE II: Temperature T_m in K at the maximum of the glow peak for hole release from Pr^{4+} and Tb^{4+} in compounds recorded at a heating rate of β . Using an approximate 300 K/eV relation between T_m and trap depth, the energy difference ΔE_{Tb-Pr} was obtained.

| compound | $T_m(\text{Pr}^{4+})$ | $T_m(\text{Tb}^{4+})$ | β (K/s) | ΔE_{Tb-Pr} (eV) | Ref. |
|--------------------------------------|-----------------------|-----------------------|---------------|-------------------------|------|
| LaPO_4 | 210 | 240 | 1 | 0.1 | [23] |
| GdPO_4 | 265 | 280 | 1 | 0.05 | [24] |
| LuPO_4 | 555 | 570 | 1 | 0.05 | [23] |
| YPO_4 | 497 | 509 | 1 | 0.04 | [23] |
| LiLuSiO_4 | 582 | 577 | 1 | -0.02 | [26] |
| $\text{Y}_3\text{Al}_5\text{O}_{12}$ | 590 | 578 | 2 | -0.04 | [20] |
| GdAlO_3 | 428 | 416 | 1 | -0.05 | [22] |