Vacuum Referred Binding Energies of the Lanthanides in Transition Metal Oxide Compounds

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The electronic level schemes for divalent and trivalent lanthanide ions in rare earth (La, Gd, Y, Lu, Sc) vanadate, niobate, tantalate, and in alkaline earth (Ba, Sr, Ca, Mg) titanate, molybdate, and tungstate compounds are presented. Use is made of data from luminescence excitation and absorption spectra of lanthanide (mostly Eu^{3+} , Pr^{3+} , and Tb^{3+}) impurities in those compounds. By means of the chemical shift model, binding energies, relative to the vacuum energy, of electrons in the impurity levels and the host bands are obtained. It reveals clear trends in conduction band and valence band energy with changing size of the rare earth or the alkaline earth ion. The bottom of the conduction band is dominated by 3d, 4d, or 5d orbitals, and it is found that the binding energy at the conduction band bottom tends to decrease with higher orbital number.

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The vanadates, titanates, molybdates, niobates, tungstates, and tantalates are widely used in many areas of applied physics and materials science. TiO_2 is famous for its photocatalytic activity used to produce hydrogen in electrochemical cells upon absorption of sunlight. Many other titanates and also vanadates are actively being studied for such applications.¹ It is then crucial that the electron binding energy E_V at the top of the valence band and E_C at the bottom of the conduction band lie closely below and above the redox potentials for hydrogen and oxygen production. Lanthanides in transition metal (TM) based compounds can produce very bright luminescence. For bright luminescence to occur, the location of the emitting impurity level relative to E_C is important. A location too close to E_C will result in poor quantum efficiency or even a total absence of emission because of thermal or autoionization of the excited electron to the conduction band. Whether a lanthanide or a transition metal impurity can trap an electron from the conduction band or a hole from the valence band is also controlled by the impurity level locations in the band gap.² That same location tells us the preferred impurity valence state.³ The above examples demonstrate that knowledge on the electronic structure, i.e., the absolute binding energy of the electrons in impurity states, host band states, or molecules, is crucial for our understanding of the performance of materials.

There is an abundance of data on lanthanide spectroscopy covering many thousands of different compounds. Data that can provide information on the location of lanthanide impurity levels relative to the valence and conduction bands of the host compound. Once the location of the $4f^n$ ground state energy of one particular lanthanide impurity is known, say Eu^{2+} , then it can be predicted for all other divalent lanthanides. This good predictability is caused by the atomic like and well-shielded nature of the inner lanthanide 4f-orbitals.⁴ Host referred binding energy (HRBE) schemes as for GdVO_4 in Fig. 1 where all energies are referred to the top of the valence band, see the right-hand energy scale, can be made routinely. The ground state energies of divalent and trivalent lanthanides follow characteristic double zigzag shapes that are to a good approximation invariant with the type of host compound. Recently the chemical shift model was introduced.⁴ It enables us to convert a HRBE scheme into a vacuum referred binding energy (VRBE) scheme, see the left-hand energy scale in Fig. 1. Since its introduction, the model has been applied successfully for many wide band gap compounds.^{5,6} VRBE means the energy required to extract an electron from the system and to bring it to the vacuum. That electron can be from a host band state or from an impurity ground or excited state. When, for example, an impurity excited state is drawn inside the band gap at two eV above the top of the valence band it means that it requires 2 eV less energy to extract an electron from that excited state and bring it to the vacuum than to extract an electron from the top of the valence band. As matter of

convenience, we will often speak of the VRBE of an electron as if it concerns a single electron. In reality we are always dealing with multi-particle states and systems.

In this work the models and ideas are applied to the following compounds. 1) The rare earth vanadates (REVO_4 with RE = La, Gd, Y, Lu, or Sc), TiO_2 , and the alkaline earth titanates (MTiO_3 with M = Ba, Sr, Ca, or Mg). For these compounds the conduction band bottom is composed of empty 3d-orbitals of V^{5+} and Ti^{4+} . 2) The MMoO_4 and RENbO_4 compounds together with LiNbO_3 and CaNb_2O_6 . Here the bottom of the conduction band is composed of the empty 4d-orbitals. 3) The MWO_4 and RETaO_4 compounds with 5d-orbital conduction band bottoms. PbWO_4 with 6p-orbitals at the conduction band bottom is also included. The above compounds show relatively strong electron binding energy (≈ -4 eV to ≈ -3 eV) at the conduction band bottom, or equivalently they show large electron affinity. It turns out that the lanthanide impurity 5d-level is always located above E_C and consequently 5d-4f emission is never observed. Such a situation favors the observation of intervalence charge (=electron) transfer (IVCT) from for example the Pr^{3+} or the Tb^{3+} $4f^n$ ground state directly to the transition metal cation. These transitions are indicated by arrows 1) and 2) in Fig. 1. Low lying conduction band states also affect the quenching of the emission from the 3P_0 level of Pr^{3+} or the 5D_3 and 5D_4 levels of Tb^{3+} . We will utilize the IVCT band energies and the quenching data to construct the HRBE and VRBE schemes. By comparing the VRBE data of

Figure 1. The host referred binding energy (right hand scale) and vacuum referred binding energy (left hand scale) of electrons in lanthanide impurity and host band states in GdVO_4 . Arrow 1) is the Pr^{3+} IVCT transition, arrow 2) is the Tb^{3+} IVCT transition, and arrow 3) denotes $U(6, \text{GdVO}_4)$.

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the different compounds clear trends are observed with changing size of the rare earth or alkaline earth that will be interpreted with the crystal field splitting of nd -states and the chemical shift model. Also a clear trend is revealed with the type of nd -orbital. Binding is strongest for the compact 3d-orbitals and weakest for the extended 5d-orbitals.

Methodology

With the chemical shift model only a few parameters are required to construct a VRBE scheme for the lanthanides in a compound. The most crucial parameter is the 4f-electron Coulomb repulsion energy $U(n, A)$ which is defined as the Coulomb repulsion experienced by an electron when it is added to the 4f-orbital of a trivalent lanthanide ion in compound A that already contains n electrons. $U(6, A)$ is then the energy difference between the 4f⁶ ground state of Eu³⁺ with the 4f⁷ ground state of Eu²⁺ as indicated by arrow 3) in Fig. 1. Knowledge on $U(6, A)$ alone already defines the location of all the 4f^{*n*} ground and excited state levels of each divalent and trivalent lanthanide impurity relative to the vacuum level.^{4,6,7} It turns out to be difficult to derive accurate values for $U(6, A)$ from spectroscopy. Since $U(6, A)$ is strongly related to the nephelauxetic effect and since that effect is connected with the electronegativity χ of the cations that bind the anion ligands,^{7,8} we took a different approach. We deal in this work with Ba ($\chi = 0.89$), Sr ($\chi = 0.95$), Ca ($\chi = 1.00$), Mg ($\chi = 1.31$) and the rare earths La ($\chi = 1.10$), Gd ($\chi = 1.20$), Y ($\chi = 1.22$), Lu ($\chi = 1.27$), and Sc ($\chi = 1.36$) which all have relatively small electronegativity χ . Table I shows the corrected Pauling electronegativity of the TM cations, which range from 1.50 to 2.36.⁹ Table I also shows the free atom Q^{th} ionization potentials¹⁰ that correlate strongly with the electronegativity.

Electronegativity is not a unique atomic concept since it depends on the valence of the cation and on the nature of the coordinating anion. Therefore, the electronegativity of the cations in a compound can only provide an indication of the value for $U(6, A)$. Table II compiles the TM compounds studied in this work together with the valence weighted average cation electronegativity χ_{av} in column 2. For CaTiO₃, SrTiO₃, and BaTiO₃ VRBE schemes were already presented in Ref. 7 and a motivation for the chosen value of $U(6, A) = 6.7$ eV was provided there. Since the rare earth tantalates have χ_{av} similar to those titanates, likewise a value of $U(6, A) = 6.70$ eV will be adopted. For MgTiO₃ and ScTaO₄ a slightly larger value of 6.75 eV is used to take into account the higher χ_{av} due to the contribution from the small cations Mg²⁺ and Sc³⁺. χ_{av} for the vanadates and niobates are between 1.4 to 1.5 in Table II, and are larger than those for the titanates and tantalates. They compare well with the χ_{av} for aluminate compounds like YAlO₃ and Y₃Al₅O₁₂ with well established $U(6, A) = 6.8$ eV. We will therefore use $U(6, A) = 6.8$ eV for the vanadates and niobates in this work. The molybdates and tungstates have a higher value again for χ_{av} , i.e., between 1.9 and 2.0 which are typical values for rare earth phosphate compounds with $U(6, A)$ between 7.0 and 7.2 eV. In this work we will adopt a value of $U(6, A) = 7.0$ eV for the molybdates and 7.1 eV for the tungstates.

Table I. Compilation of properties of the transition metals and the values used for $U(6, A)$ in this work. The in-crystal Shannon radius r_S for 6 fold coordinated TM^{Q+} is in pm units. The corrected Pauling electronegativity χ is dimensionless. The free ion Q^{th} ionization potential I and $U(6, A)$ are in eV.

TM^{Q+}	nl	r_S	χ	$I^{Q^{th}}$	$U(6, A)$
V ⁵⁺	3d	68	1.63(2+)	65.3	6.80
Ti ⁴⁺	3d	75	1.54(2+)	43.3	6.70
Mo ⁶⁺	4d	73	2.16(2+)	68.8	7.00
Nb ⁵⁺	4d	78	1.60	50.6	6.80
W ⁶⁺	5d	74	2.36(2+)	64.8	7.10
Ta ⁵⁺	5d	78	1.50	48.3	6.70

With the above values for $U(6, A)$ the VRBE of an electron in all lanthanide states are known, and one only needs to place the host valence and conduction bands relative to those lanthanide states. The most convenient method is to use the Eu³⁺ charge transfer band energy $E^{CT}(6, 3+, A)$ to pin E_V with respect to the divalent lanthanide levels. However for the TM-compounds $E^{CT}(A)$ usually appears too close or even above the host absorption band as in Fig. 1 preventing such pinning. Another method is to pin E_C by using data on Pr³⁺ and Tb³⁺ IVCT energies.^{11,12} After IVCT the electron transferred from Pr³⁺ or Tb³⁺ to the TM is still bonded to either Pr⁴⁺ or Tb⁴⁺ left behind. The VRBE of the transferred electron, indicated by the endpoints of arrows 1) and 2) in Fig. 1, is assumed to be located between E_C and E_X . E_X is then the VRBE of the electron in the host exciton state with an electron-hole binding energy $E_{e-h}^{ex} \equiv E_C - E_X$. The ³P₀ level of Pr³⁺ and the ⁵D₄ level of Tb³⁺ are relatively close to the conduction band in Fig. 1. The emission due to transitions from those levels are then quenched at fairly low temperature, and data on such quenching will be used to estimate the energy difference between the ³P₀ and ⁵D₄ levels and E_X or E_C .

Results and Discussion

HRBE schemes for the lanthanides in various transition metal compounds based on IVCT data were reported already for several of the compounds in this work.^{11–14,17} First VRBE schemes on titanates appeared in Ref. 7. For those and all the other compounds in Table II an extensive literature search was done to derive more and more reliable information on the host exciton creation energy $E^{ex}(A)$. In this work we always use or estimate the value for E^{ex} that pertains to ≈ 10 K. The binding energy of the electron and hole in the exciton is usually not known. For wide band gap oxide and fluoride compounds the binding energy is often estimated at about 8% of E^{ex} .¹⁵ However in small band gap compounds with a high dielectric constant the binding energy is of a smaller percentage.¹⁶ In this work we will adopt, like for the titanates in Ref. 7, an estimated value of 250 meV for all compounds. For each compound spectroscopic data was also collected on Pr³⁺, Tb³⁺ and Eu³⁺ dopants and occasionally Ce³⁺. Ce³⁺, Pr³⁺, Tb³⁺ appear to have the 4f^{*n*} ground state level inside the forbidden band, and then one may observe the IVCT bands or employ the luminescence quenching properties of the characteristic Pr³⁺ and Tb³⁺ emission lines. Whenever the ground state of Eu²⁺ is well below E_C one may also observe the CT-band.

In Appendix A a detailed account with all references is provided on the obtained data used to construct the VRBE schemes. The final results are compiled in Table II and displayed in the stacked band diagram of Fig. 2. The figure shows for each compound in Table II the Tb³⁺ ground state and ⁵D₃ and ⁵D₄ excited state electron binding energies, the ³P₀ excited state of Pr³⁺, and the Eu²⁺ ground state energy. One might equally well construct a scheme with any other level from any other lanthanide but the ones chosen are the most relevant for this work. The energy of charge transfer E^{CT} for Eu³⁺ compiled in column 4 of Table II is for most compounds obtained from Eu³⁺ excitation spectra, but in compounds where the Eu²⁺ ground state appeared too close to E_X it has been inferred from IVCT and luminescence quenching data involving Pr³⁺ and Tb³⁺. E^{CT} is then listed within brackets. With E^{CT} and $U(6, A)$ the values for E_V are obtained with the chemical shift model, and adding E^{ex} (column 3) then provides E_X (column 6) which is shown as a solid data symbol in Fig. 2. E_C is then at 250 meV higher energy. The energy difference ΔE_{X-5D_4} between the Tb³⁺ ⁵D₄ level and E_X is compiled in column 10. Table II also compiles information (when available) on the IVCT band energy E^{IVCT} for Tb³⁺ and for Pr³⁺.

Table II and Fig. 2 reveal various trends. When the size of the rare earth or alkaline earth cation decreases E_X and E_C tend to decrease also. $E_X = -3.0$ eV for BaWO₄ and it decreases to -3.2 eV for SrWO₄ and -3.6 eV for CaWO₄. Similar trends are observed for the vanadates, titanates, molybdates, and the tantalates. The trend is not seen for the niobates. The bottom of the conduction band is dominated by the nd orbitals of the TM cation, and therefore with the

Table II. Data derived from spectroscopy on undoped and Eu^{3+} , Pr^{3+} , or Tb^{3+} doped transition metal based compounds. E_V , E_X , and $\Delta E_{(X-5D_4)}$ are from the vacuum referred binding energy scheme constructed with the chemical shift model. All energies are in eV. The quenching temperature $T_{0.5}$ for the emission from the 3P_0 level of Pr^{3+} or the 5D_4 or 5D_3 levels of Tb^{3+} , if available, are given in K. If $T_{0.5}$ is not known only presence or absence of emission is mentioned. (??) means that assignment is uncertain or tentative.

host	χ_{av}	E^{ex}	E^{CT}	E_V	E_X	$E^{IVCT}(\text{Pr})$	$T_{0.5} \text{ } ^3P_0$	$E^{IVCT}(\text{Tb})$	$\Delta E_{(X-5D_4)}$	$T_{0.5} \text{ } ^5D_4$	$T_{0.5} \text{ } ^5D_3$
LaVO_4	1.43	4.25	3.95	-7.92	-3.67	≈ 3.6	380	3.81	0.98	230	0
GdVO_4	1.47	4	(4.15)	-8.12	-4.12	3.25	220	3.29	0.53	140	0
YVO_4	1.48	3.95	(4.20)	-8.17	-4.22	3.3	not at RT	no data	0.43	not at RT	0
SrVO_4	1.50	3.85	(4.25)	-8.22	-4.37	3.15	100	no data	0.28	80	0
anatase- TiO_2	1.54	3.45	(3.75)	-7.72	-4.27	no data	≈ 80	no data	0.38	0	0
BaTiO_3	1.32	3.4	(3.33)	-7.25	-3.85	$> E^{ex}$	weak at RT	no data	0.65	not at RT	not at RT
SrTiO_3	1.34	3.46	(3.42)	-7.34	-3.88	$> E^{ex}$	< 200	no data	0.62	not at RT	not at RT
CaTiO_3	1.36	3.85	(4.10)	-8.02	-4.17	3.25	≈ 0	no data	0.33	not at RT	not at RT
MgTiO_3	1.46	4.6	(4.90)	-8.85	-4.25	3.14(??)	not at RT	no data	0.33	no data	no data
BaMoO_4	1.84	4.8	4.3 ± 0.1	-8.37	-3.57	> 4.0	yes at RT	no data	1.4	yes at RT	yes at RT
SrMoO_4	1.86	4.75	4.35 ± 0.15	-8.42	-3.67	4.35(??)	yes at RT	4.25	1.3	yes at RT	yes at RT
CaMoO_4	1.87	4.6	4.4 ± 0.2	-8.47	-3.87	4.0 ± 0.15	430	no data	1.1	450	75
LiNbO_3	1.49	4.7	(4.90)	-8.87	-3.31	3.3	weak at 77K	no data	0.48	200	not at LT
CaNb_2O_6	1.50	4.75	(4.30)	-8.27	-3.52	4	380	3.95	1.1	470	120
LaNbO_4	1.41	4.95	(4.80)	-8.77	-3.82	3.75(??)	yes at 4 K	no data	0.83	yes at RT	yes at LT
GdNbO_4	1.45	5.2	4.86	-8.83	-3.63	no data	no data	no data	1.0	yes at RT	no data
YNbO_4	1.46	5.2	4.8	-8.77	-3.57	4.05	< 370	4	1.1	460	weak at RT
LuNbO_4	1.48	5.2	(4.80)	-8.77	-3.57	no data	no data	no data	1.1	yes at RT	no data
PbWO_4	2.24	4.35	(4.40)	-8.52	-4.17	3.7	> 350	3.75	0.93	yes at RT	weak at RT
BaWO_4	1.99	5.6	4.45	-8.57	-2.97	≈ 4.6	yes at RT	$\approx 4.6(??)$	2.1	yes at RT	yes at RT
SrWO_4	2.01	5.35	4.45	-8.57	-3.22	no data	yes at RT	$\approx 4.8(??)$	1.9	yes at RT	no data
CaWO_4	2.02	5.25	4.7	-8.82	-3.57	no data	yes at RT	no data	1.5	> 600	450
LaTaO_4	1.35	5.1	4.55	-8.47	-3.37	4.6(??)	> 350	4.6(??)	1.1	$< 300(??)$	no data
GdTao_4	1.39	5.8	5	-8.92	-3.12	no data	yes at RT	4.2(??)	1.4	> 300	yes at RT
YTaO_4	1.40	5.8	5.1	-9.02	-3.22	$\approx 4.1(??)$	> 300	$\approx 4(??)$	1.3	750	yes at RT
LuTaO_4	1.41	5.8	5.15	-9.07	-3.27	no data	yes at RT	no data	1.2	yes at RT	yes at RT
ScTaO_4	1.45	5.8	5.2	-9.15	-3.35	no data	no data	4.24(??)	1.2	yes at RT	no data

binding energy of an electron in the nd^1 state. Much information is already available on the VRBE in the $5d^1$ level of Ce^{3+} in compounds. On average it is -1.8 eV, and compound to compound variation by ± 1 eV is almost entirely caused by variation in the crystal field splitting of the $5d$ -level energies.¹⁸ The same was found for the VRBE of the $3d^1$ electron of Ti^{3+} as impurity in wide band gap compounds and semiconductors. It is on average at -4 eV and also with a compound to compound variation of ± 1 eV. Again variations in crystal field splitting were held responsible.¹⁸

The TM cations in the compounds of this work are either 4-fold coordinated in a (distorted) tetrahedron or 6-fold in a (distorted) octahedron. Then, when the size of the rare earth or alkaline earth cation increases not only the lattice parameter increases but usually also the bondlength in the TM-tetrahedron or TM-octahedron. As a result the crystal field splitting will decrease. It translates to less negative E_C . PbWO_4 has E_X at -4.17 eV which is lower than for the alkaline earth tungstates. Here the bottom of the conduction band is formed by $6p$ Pb-orbitals and not by the $5d$ W-orbitals.

Figure 2. Stacked band diagram of TM-compounds showing the energy of the $\text{Pr}^{3+} \text{ } ^3P_0$ level, the Tb^{3+} ground state, 5D_4 , and 5D_3 levels. The solid symbol denotes $E_X(A)$ and the open symbol $E_{4f}(7, 2+, A)$.

Figure 3. Stacked band diagram of TM-compounds showing the energy of the Pr^{3+} 3P_0 level, the Tb^{3+} ground state, 5D_4 , and 5D_3 levels. The solid symbol denotes $E_X(A)$ and the open symbol $E_{4f}(7, 2+, A)$.

Column 10 in Table II shows that $\Delta E_{(X-5D_4)}$ is largest for the tungstates where emission from the 5D_4 level appears very temperature stable. It is small for the titanates where Tb^{3+} emission is not observed at all at room temperature. The smallest value is for LuVO_4 where the 5D_4 emission shows a very low quenching temperature of $T_{0.5} = 80$ K. The 3P_0 level for Pr^{3+} is within our models always at 0.080 eV lower energy than the 5D_4 level of Tb^{3+} , and then the quenching temperature for the 3P_0 emission should strongly correlate with that from the 5D_4 level. This can indeed be seen in Table II. It is also demonstrated in Fig. 3 where the quenching temperature $T_{0.5}$ for the 3P_0 and 5D_4 emission is shown against the energy difference ΔE between the emitting level and E_X . Quenching temperature for both emissions increase with ΔE at about a similar pace. The 5D_3 level is always 0.711 eV above the 5D_4 level, and the data for CaWO_4 , CaNb_2O_6 , and CaMoO_4 fits within the picture.

Assuming that thermal quenching proceeds by thermal activation of the electron in the emitting state to the IVCT state, $T_{0.5}$ is reached when the radiative decay rate Γ_v equals the thermal quenching rate

$$\Gamma_v = \Gamma_0 e^{-\frac{\Delta E}{k_B T_{0.5}}} \quad [1]$$

where k_B is the Boltzmann constant and Γ_0 is the attempt rate which is about equal to the frequency of the main vibrational mode at the luminescence center site. With ΔE in eV one may write

$$T_{0.5} = \frac{11590}{\ln\left(\frac{\Gamma_0}{\Gamma_v}\right)} \Delta E. \quad [2]$$

With typical phonon frequencies of 500–1000 cm^{-1} , $\Gamma_0 \approx 2 \times 10^{13}$ Hz, and with typical Tb^{3+} 5D_4 radiative decay rate $\Gamma_v \approx 10^3$ Hz one obtains $T_{0.5} \approx 500 \Delta E$. The 3P_0 level of Pr^{3+} has larger decay rate of typically $1\text{--}2 \times 10^4$ Hz which leads to $T_{0.5} \approx 550 \Delta E$. It is not too much different from that for the 5D_4 emission. The dashed line in Fig. 3 was drawn with a slope of 500 K/eV, and indeed the data scatter around such a predicted slope. Actually one may not expect better agreement for various reasons; 1) Γ_0 and Γ_v for different compounds are not the same, 2) the VRBE schemes have typical errors of few 0.1 eV which are then also present in ΔE , 3) the $T_{0.5}$ may be reduced by additional quenching processes like multiphonon relaxation or quenching by unknown defects. Nevertheless, the general trend follows the simple predictive equation, and this is regarded as supporting evidence that the VRBE schemes and the entire method of its construction are valid. Note that the dashed line has an intercept at $\Delta E \approx 0.25$ eV. It suggests that the crossing point between the parabola representing the 5D_4 , 5D_3 , or 3P_0 level and the parabola

Figure 4. Illustration of thermal quenching of Tb^{3+} 5D_4 luminescence within a configurational coordinate diagram. The IVCT transition brings the electron to point A in between E_C and E_X . Thermal quenching proceeds via point B located 0.2–0.3 eV below E_X .

representing the IVCT state in a configuration coordinate diagram is about 0.2–0.3 eV below E_X . The situation is illustrated in Fig. 4.

Knowing that the absence or presence of 5D_4 , 5D_3 , or 3P_0 emission and the quenching temperatures are connected with the energy difference between the emitting states and conduction band related states one may understand the luminescence properties of lanthanides in solid solutions. In the solid solution of $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$ the VRBE in the exciton state E_X and at the bottom of the conduction band E_C will move upward when the Sr fraction increases. The VRBE of the lanthanide levels are not expected to change significantly. One may then engineer the energy difference between emitting levels of Pr^{3+} and E_C by adjusting the Sr fraction. This will affect the ratio between blue 3P_0 and red 1D_2 Pr^{3+} emission as was indeed observed in Refs. 19–21. Possibly something similar happens when Al^{3+} is added to Pr^{3+} or Tb^{3+} doped SrTiO_3 . The otherwise absent emission from Tb^{3+} starts to appear²² and that from Pr^{3+} is significantly enhanced with increasing Al content.²³

The conduction band bottom of REVO_4 , RENbO_4 , or RETaO_4 is composed of the empty 3d, 4d, or 5d orbitals of V^{5+} , Nb^{5+} , or Ta^{5+} . An electron inside the conduction band then occupies an orbital strongly related to the lowest crystal field split 3d, 4d, or 5d level of V^{4+} , Nb^{4+} , or Ta^{4+} . The VRBE of such electron clearly moves upwards (becomes less negative) in going from 3d to 4d to 5d orbitals. For example, $E_X = -4.12$ eV for GdVO_4 , -3.64 eV for GdNbO_4 , and -3.12 for GdTao_4 . The same applies when the 4d-orbital conduction band VRBE of 6+ TM cations in MMoO_4 are compared with the 5d energies in MWO_4 . For example $E_X = -3.87$ eV in CaMoO_4 and -3.55 in CaWO_4 . This trend for the 5+ and 6+ TM cations was also observed for 4+ cations. Fig. 5 is reproduced from data in Ref. 24 for compounds where the conduction band bottom is composed of the unoccupied nd-orbitals of the 4+ cations Ti^{4+} ($n=3$), Zr^{4+} ($n=4$), Ce^{4+} ($n=5$), or Th^{4+} ($n=6$). When comparing similar types of compounds with nd cations of the same charge, E_X and E_C consistently move up as the principle quantum number n increases. In an accompanying paper we will conclude precisely the same for the TM elements as dopants in wide band gap and semiconducting compounds.²⁵ In that work it will be shown that the trend can be related to the ionization potentials of the free TM atoms.

Finally we will address the clear trends in the binding energy E_V at the top of the valence band in Fig. 2. Generally E_V becomes lower with smaller sized RE or M. The effect is not large, and although the values for E^{CT} that determine E_V were in some cases somewhat tentatively

Figure 5. Stacked band diagram of Ti^{4+} , Zr^{4+} , Ce^{4+} , Hf^{4+} , and Th^{4+} based compounds constructed from data in ⁷. The end points of the up and down pointing vertical bars indicate E_V and E_C .

assigned the effect appears consistent. Similar observations were made for non-TM based compounds like the series Ba-, Sr-, CaF_2 ,⁶ La-, Gd-, Y-, LuAlO_3 ,⁶ and La-, Gd-, Y-, LuPO_4 .⁵ It is explained by the chemical shift of the anion electron binding energy. This shift is negative due to the attractive potential of the surrounding cations, and the magnitude increases with shorter anion to cation bondlength.

Conclusions

The VRBE schemes for the lanthanides in rare earth and alkaline earth transition metal compounds have been constructed using the methods of the chemical shift model. The chosen values for the Coulomb repulsion energy $U(6, A)$ were motivated by the average electronegativity of the cations as listed in Table II. In the selected compounds of this work the bottom of the conduction band E_C falls between about -3 eV and -4 eV. Such a low lying conduction band has consequences for lanthanide luminescence and spectroscopy. The Eu^{2+} ground state, which is always near -4 eV $\pm$ 0.3 eV, is close to E_X . Under such circumstances a Eu^{3+} CT-band cannot be discriminated well from the host excitation bands and VRBE scheme construction cannot be based on CT-band energy data. Another consequence is that the lowest 5d states of the lanthanides are always inside the conduction band. This prevents 5d-4f emission, but it enables us to observe the weak IVCT bands of Pr^{3+} and Tb^{3+} which then forms a basis for VRBE scheme construction. The obtained VRBE schemes as shown in Fig. 2 demonstrate various trends. The binding energy at the conduction band bottom is mainly given by the binding energy of the nd state of the TM cation which is subject to crystal field splitting. A larger sized rare earth or alkaline earth cation tends to reduce that splitting and E_C moves upwards. Also a clear correlation is found with the type of TM. Generally with higher principle quantum number n of the nd conduction band orbital E_C tends to rise. E_C also tends to rise with smaller positive charge state of the TM cation. This implies that E_C is lowest for the V^{5+} 3d compounds and highest for the Ta^{5+} 5d compounds. The obtained VRBE schemes are fully consistent with the absence or presence of and the observed quenching temperature for the Pr^{3+} 3P_0 emission and Tb^{3+} 5D_4 and 5D_3 emission.

Appendix A

Below an account is given on how the data in Table II and used for Fig. 2 were obtained with all the references to the consulted literature. We will start with data to derive $E^{ex}(LT)$ followed by data on Eu^{3+} to determine E^{CT} . Next data on Pr^{3+} and Tb^{3+} to determine IVCT energies and luminescence quenching temperatures are presented. An unambiguous discrimination between host bands, IVCT bands and CT-bands can be difficult or even impossible. Near a defect, the energy for host excitation can be several 0.1 eV different from that of the pure host material which complicates determination of E^{ex} . Whenever E^{ex} in a transition metal compound is near 5.0 eV, the host excitation is likely to overlap with the Eu^{3+} charge transfer band. Also when the Pr^{3+} and Tb^{3+} ground state levels are

less than 1 eV above the top of the valence band, the corresponding IVCT bands tend to merge with the host excitation bands. These all lead to difficulties in discrimination between and proper assignment of bands. All assignments made or suggested in this work were done in such a manner that they are most consistent with all available data and with each other.

The vanadates

LaVO₄. The host luminescence excitation spectrum reveals a band at 307 nm (4.04 eV) that shifts to 291 nm (4.26 eV) when temperature is decreased from 360 K to 8 K.¹³ In addition there is a band at a shorter wavelength of 271 nm (4.58 eV). The two excitation bands are connected with two different broad band host related emissions. The one connected with the 4.26 eV excitation maximum is fully quenched at room temperature.¹³ Similar excitation band energies were observed with Dy^{3+} and with Eu^{3+} doping.^{26,27} Tb^{3+} ,²⁸ Eu^{3+} ,²⁷ Dy^{3+} ²⁶ doped LaVO_4 reveal only the host excitation band near 272 nm (4.55 eV). Apparently at room temperature efficient energy transfer to lanthanide dopants takes place only from the higher energy host band. We will adopt the low energy band to represent $E^{ex}(LT) = 4.25$ eV in this work. There are indications for a Eu^{3+} CT-band as a faint shoulder at 315 nm (3.95 eV) on the long wavelength side of the host excitation band in Refs. 13 and 14 and as a clear shoulder band in Ref. 27 and 29. The energy for the Pr^{3+} IVCT band of ≈ 3.6 eV is estimated from Boutinaud et al.³⁰ The emission from the 3P_0 level shows $T_{0.5} = 380$ K.⁴⁰ Under excitation in the host band there is no emission from the 5D_3 level for all vanadate compounds, and that from the 5D_4 level in LaVO_4 has estimated $T_{0.5} = 230$ K.¹³

GdVO₄. Many reports on the spectroscopy of lanthanides in GdVO_4 can be found in literature. Irrespective of the type of dopant they always reveal the first host excitation maximum near 323 nm (3.85 eV)³¹ at room temperature.³² report that the luminescence efficiency of Eu^{3+} emission depends on the amount of crystallinity and the best samples show excitation maximum near 312 nm (3.97 eV) at room temperature. The same band at the same wavelength is observed at 15 K in Ref. 14 with Ce^{3+} , Pr^{3+} , Eu^{3+} , or Tb^{3+} doping, and more reports can be found.³³ We will adopt here $E^{ex}(LT) = 4.0$ eV for GdVO_4 . Considering that a separate Eu^{3+} CT band is not observed we conclude that $E^{CT} > E^{ex}$. The IVCT band of Pr^{3+} is reported as a clear shoulder band near 365 nm (3.40 eV) in Ref. 30, and it is even more clearly revealed in the studies by¹⁴ at 382 nm (3.25 eV) which we will adopt as the IVCT energy here. Upon excitation at 480 nm in the 3P levels of Pr^{3+} emission from 3P_0 is observed at 15 K that quenches with $T_{0.5} = 220$ K, and the red emission from the 1D_2 level starts to dominate the spectrum fully. Tb^{3+} in GdVO_4 was studied in detail by.¹⁴ A very clear band at 378 nm (3.29 eV) is observed and attributed to the Tb^{3+} IVCT band. Upon excitation exclusively emission from the 5D_4 state is observed with $T_{0.5} = 140$ K. With these values for the IVCT band one arrives at a VRBE scheme shown in Fig. 1 that predicts the Eu^{3+} CT-band at 4.15 eV which is consistent with the above conclusion that $E^{CT} > E^{ex}$.

YVO₄. The RT host excitation maximum is at 318 nm (3.90 eV) in Dy^{3+} and Pr^{3+} doped samples,^{34,35} at 332 nm (3.75 eV) in Refs. 36 and 37, and at 326 nm (3.80 eV) in Ref. 38. For Ce^{3+} and Eu^{3+} doped samples it is at 325 nm (3.81 eV).³⁹ In this work we will assume for $E^{ex}(LT)$ a value of 3.95 eV. Like for GdVO_4 , see above, a Eu^{3+} CT-band is not observed and $E^{CT} > E^{ex}$. Construction of a VRBE scheme then needs to rely on the values for the Pr^{3+} and Tb^{3+} IVCT bands. That for Pr^{3+} is well established. It is observed as a clear band in Pr^{3+} excitation spectra at 380 nm (3.26 eV) in Refs. 30, 36, and 37 and also clearly at 373 nm (3.32 eV) in.³⁸ Here we will adopt a value of 3.30 eV for the IVCT band of Pr^{3+} . Emission from the 3P_0 is not observed at RT, and the red 1D_2 emission is quenched with $T_{0.5}$ of 345 K⁴⁰ irrespective of whether excitation is in the host (320 nm), the IVCT band (370 nm) or a 4f-state (445 nm). Blasse and Bril have already noticed⁴¹ that $\text{YVO}_4:5\% \text{ Tb}^{3+}$ does not show any emission at all at room temperature.

LuVO₄. The spectroscopy of LuVO_4 with Ce, Eu, Pr, and Tb dopants was studied in.¹⁴ The host excitation maximum for all dopants is consistently observed at 322 nm (3.85 eV) which will be adopted as $E^{ex}(LT)$, and like for GdVO_4 and YVO_4 a Eu^{3+} CT-band cannot be observed and $E^{CT} > E^{ex}$. Again the VRBE scheme must be based on Pr and Tb IVCT and luminescence quenching data.³⁰ reports a clearly resolved IVCT band at 395 nm (3.15 eV) which can be identified also in the spectra by.¹⁴ Upon excitation to the 3P levels of Pr^{3+} the $T_{0.5}$ of the 3P_0 emission intensity is about 100 K which is significantly lower than for GdVO_4 . Information on Tb^{3+} is entirely from.¹⁴ A resolved IVCT band is not observed but excitation at 370 nm in an excitation tail below E^{ex} does produce only emission from the 5D_4 level. Upon excitation at 468 nm the 5D_4 emission shows a low quenching temperature of $T_{0.5} = 80$ K.

The titanates

The VRBE schemes for anatase- TiO_2 , BaTiO_3 , SrTiO_3 , and CaTiO_3 were already presented in Ref. 7 and the references for the values for E^{ex} and the IVCT band energies can be found there. Some additional supporting data is provided below.

anatase-TiO₂ Table II show that χ_{av} for TiO_2 is significantly larger than that for the MTiO_3 compounds, and contrary to⁷ we will adopt $U(6, A) = 6.8$ eV. The adopted value for the Eu^{3+} CT-energy is lowered by 0.05 eV in order to arrive at the same values for E_V and E_X as in ⁷.

BaTiO₃. With 1% Pr^{3+} doping weak emission from the 3P_0 level is observed at RT but that from the 1D_2 level is 20 times stronger.⁴² Information to derive $T_{0.5}$ for Pr^{3+} or for Tb^{3+} emission lines was not found.

SrTiO₃. The emission from the $\text{Pr}^{3+} {}^3P_0$ dominates over that from 1D_2 at 77 K upon excitation in the host band,²⁰ and at 350 K the intensity has reduced by a factor of two compared to RT (0.2% Pr^{3+}). In a study by²³ at 0.2% Pr^{3+} doping concentration 3P_0 dominates at 20 K and it is fully quenched at room temperature which suggests $T_{0.5} < 200$ K. SrTiO₃ does not show Tb^{3+} emission at room temperature.²²

CaTiO₃. The quenching temperature $T_{0.5}$ for the $\text{Pr}^{3+} {}^1D_2$ emission is at 340 K⁴⁰ irrespective whether excitation is in the host (320 nm), the IVCT band (370 nm), or the 4f level at 445 nm. Even down to 77 K emission from the 3P_0 is not observed²⁰ which means that $T_{0.5}$ must be near 0 K.

MgTiO₃. In the work by de Haart et al.⁴³ the optical absorption edge and the onset wavelength for photocurrents is at 335 nm (3.7 eV) and the host absorption maximum is near 280 nm (4.4 eV). In Ref. 44 $E^{\text{ex}}(LT) = 4.05$ eV and absorption reaches maximum value near 4.5 eV. In this work we will assume $E^{\text{ex}}(LT) = 4.6$ eV. Information on the spectroscopic properties of Eu, Pr, and Tb in MgTiO₃ are very scarce. In Ref. 45 weak and broad bands and shoulders are seen at 309 nm (4.0 eV) and 265 nm (4.58 eV) in the excitation spectrum of Eu^{3+} emission. The nature of the bands is not clear yet. Cathode luminescence in Ref. 46 shows at room temperature that the emission from the 1D_2 level of Pr^{3+} is about 20 times stronger than from the 3P_0 level. For BaTiO₃ similar ratio was observed which suggests a similar distance between the Pr^{3+} levels and E_X . In Ref. 30, Pr^{3+} shows weak emission from 1D_2 and no emission from 3P_0 at room temperature and they attribute a band at 394 nm (3.14 eV) to the IVCT of Pr^{3+} . Although that attribution needs further confirmation we tentatively assumed that it is correct and constructed a VRBE scheme accordingly.

The molybdates

BaMoO₄. The RT absorbance of pure BaMoO₄ reaches a maximum at 4.75 eV (260 nm) in Ref. 47 and the same value is observed in Ref. 49. In this work we will adopt a value $E^{\text{ex}}(LT) = 4.8$ eV. BaMoO₄ with Tb, Dy, or Sm doping shows a common excitation band at 4.45 eV (278 nm) at RT in Ref. 50. The band shifts to 4.3 eV (287 nm) upon Eu^{3+} doping. In Ref. 51 the Eu^{3+} CT maximum is at 285 nm (4.35 eV), in Ref. 52 at 294 nm (4.22 eV), in Ref. 53 at 270 nm (4.59 eV). It seems that $E^{\text{CT}} = 4.3 \pm 0.1$ eV and then with the constructed VRBE scheme the Pr^{3+} and Tb^{3+} IVCT bands are predicted near 4.3 eV. With Pr^{3+} doping a shoulder absorption band develops near 310 nm (4.0 eV) in Ref. 49 which may signal the onset of the Pr^{3+} IVCT band. At room temperature intense emission from the 3P_0 level at 643 nm is observed.^{49,54} With 5% Tb^{3+} doping at RT emission from the 5D_4 level and even from the 5D_3 level is observed.^{50,53} Observation of the emission from the 5D_3 level at room temperature suggests larger separation between that levels and E_X than in the above vanadates and titanates where emission from the 5D_3 is always absent. A clear Tb^{3+} IVCT band is not observed in Ref. 53; it is probably too weak or obscured by the onset of host excitation.

SrMoO₄. Undoped SrMoO₄ shows the optical absorption maximum at 4.65 eV in Ref. 55. With Dy^{3+} doping the RT luminescence excitation maximum is at 268 nm (4.6 eV) in Ref. 56. We will adopt $E^{\text{ex}}(LT) = 4.75$ eV. In Ref. 51 the Eu^{3+} excitation maximum is at 285 nm (4.35 eV), in Ref. 57 at 288 nm (4.30 eV), in Ref. 53 at 270 nm (4.59 eV), in Ref. 58 at 284 nm (4.35 eV), and in Ref. 59 at 295 nm (4.20 eV). The CT band seems to overlap with the host excitation maximum and accurate assignment is not possible. A value of 4.35 ± 0.15 eV will be adopted in this work. The Pr^{3+} emission excitation band at 286 nm (4.35 eV) observed in Ref. 60 suggests the location of the IVCT band. The emission from the 3P_0 level dominates at RT. Data to derive $T_{0.5}$ was not found. With Tb^{3+} a long wavelength shoulder band around 290 nm (4.28 eV) on the rising excitation edge of the host and possibly Tb^{3+} 4f-5d excitation band may signal a presence of a Tb^{3+} IVCT band in Ref. 53. Tb^{3+} emission from the 5D_4 level is observed at room temperature and like in BaMoO₄ even emission from the 5D_3 level is observed with 5% Tb^{3+} concentration.^{53,56}

CaMoO₄. The excitation maximum for the 77 K host emission is at 4.5 eV (275 nm) in Ref. 62. A broad RT excitation maximum near 270 nm (4.6 eV) is observed in Ref. 63. We will adopt $E^{\text{ex}}(LT) = 4.6$ eV. In Ref. 61 with 24% Eu doping the excitation maximum is at 271 nm (4.58 eV) and Eu^{3+} doped nanocrystals in Ref. 64 show maximum excitation at 281 nm (4.41 eV). The Eu^{3+} CT-band apparently strongly overlaps with the host excitation maximum and accurate assignment is not possible. Here we adopt $E^{\text{CT}} = 4.4 \pm 0.2$ eV. With 1% Pr^{3+} a broad luminescence excitation band extending from 250 nm to beyond 300 nm is observed in Ref. 65. The host excitation band near 260 nm is most likely merged with the Pr^{3+} IVCT band on the long wavelength side near 310 nm (4.0 eV). Emission from the 1D_2 and 3P_0 levels of Pr^{3+} are both observed at RT^{65,66} and the 3P_0 emission is quenched with $T_{0.5} = 430$ K.⁶⁶ For Tb^{3+} doping, the excitation maximum is at 289 nm (4.29 eV) in Ref. 67 and like for Pr^{3+} the IVCT band most likely has merged with the host band. The 5D_4 emission from Tb^{3+} shows $T_{0.5} = 450$ K and that from the 5D_3 level has low quenching temperature of $T_{0.5} = 75$ K¹² and at RT the emission is fully absent.¹²

The niobates

LiNbO₃. From^{71–73} the host excitation is found at $E^{\text{ex}}(LT) = 4.7$ eV. The IVCT band for Pr^{3+} is near 375 nm (3.3 eV).^{74–76} The red emission from the 1D_2 level dominates and only at 77 K emission from the 3P_0 level of Pr^{3+} starts to appear.⁷⁶ Emission from the 5D_3 level of Tb^{3+} is not observed at low temperature, and the 5D_4 emission quenches with $T_{0.5} = 200$ K.⁷⁷

CaNb₂O₆. The room temperature host excitation maximum is consistently reported near 265 nm (4.65 eV)^{68,69,78,79,81} from which $E^{\text{ex}}(LT) = 4.75$ eV is estimated. The excitation maximum of Eu^{3+} emission is at 272 nm (4.55 eV) in Ref. 70 which is mostly due to host excitation. A Eu^{3+} CT band cannot be identified. To construct a VRBE scheme one has to use IVCT data for Pr^{3+} and Tb^{3+} . That of Pr^{3+} is at 312 nm (3.97 eV) in Ref. 81 and at 305 nm (4.07 eV) in Refs. 78 and 79. The 3P_0 emission has $T_{0.5} = 380$ K.⁷⁸ The IVCT band for Tb^{3+} is at 3.95 eV in Refs. 68 and 78, and $T_{0.5} = 470$ K for the $\text{Tb}^{3+} {}^5D_4$ emission and 120 K for the 5D_3 emission.⁷⁸ When a VRBE scheme is constructed with this information, the Eu^{3+} CT-band is predicted near 4.3 eV.

LaNbO₄.⁸⁰ shows the host excitation maximum at 258 nm (4.80 eV) for a 100% pure monoclinic phase sample. Another weaker band at 300 nm (4.13 eV) was ascribed to defect NbO₆-groups. Also we observed (unpublished data) a host excitation maximum at 251 nm (4.94 eV) and 302 nm (4.10 eV) in LaNbO₄:Ce³⁺. We will adopt $E^{\text{ex}}(LT) = 4.95$ eV. We also observe (unpublished data) an excitation maximum of Eu^{3+} at 268 nm (4.65 eV). The 0.4 eV width of the band seems too narrow for a CT band and probably it is truncated by competing host absorption. We conclude $E^{\text{CT}} > 4.65$ eV and will adopt a value of 4.8 ± 0.1 eV. 3P_0 emission from Pr^{3+} is observed at 4.2 K in Ref. 82. Boutinaud et al.⁷⁹ report a value of 3.84 eV (322 nm) for the Pr^{3+} IVCT-band but they also write that the value is not very accurate. We observed (unpublished data) a weak broad excitation band near 330 nm (3.75 eV) that will here be regarded as the Pr^{3+} IVCT energy. We also observed $\text{Tb}^{3+} {}^5D_4$ and 5D_3 emission at 15 K. Emission from the 5D_3 level is fully quenched at room temperature⁸³ and evidence for a Tb^{3+} IVCT band is not available.

GdNbO₄. The absorption maximum in undoped GdNbO₄ is at 248 nm (5.0 eV) in Ref. 84. In Ref. 85 an excitation band at 243 nm (5.1 eV) is present for Eu^{3+} and for Tb^{3+} doping that can be attributed to the NbO₄ group excitation. We will adopt $E^{\text{ex}}(LT) = 5.2$ eV. Upon Eu^{3+} doping a characteristic about 0.8 nm FWHM excitation band is observed at 255 nm (4.86 eV) by⁸⁶ which is also observed at the same wavelength in Ref. 85. It is well separated from the host excitation band and it will be assigned to $E^{\text{CT}} = 4.86$ eV. This information is already sufficient to construct a VRBE scheme that predicts the Pr^{3+} and Tb^{3+} IVCT bands near 3.9 eV (318 nm) and 3.7 eV (335 nm), however, data to confirm this was not found. 5D_4 emission is observed at RT in Ref. 85.

YNbO₄. Abundant information is available on this compound. The pure host luminescence excitation maximum varies between 243 nm (5.1 eV) and 250 nm (5.0 eV) depending on synthesis conditions.⁸⁷ It is at 251 nm (4.95 eV) in Ref. 88, at 243 nm (5.1 eV) in Ref. 85, and at 242 nm (5.10 eV) in Ref. 89. We will adopt $E^{\text{ex}}(LT) = 5.2$ eV which is the same as for GdNbO₄. The Eu^{3+} CT-band appears close to the host excitation band. In Ref. 85 for 5% Eu^{3+} concentration it is observed resolved at 258 nm (4.80 eV) and in Ref. 89 it is seen as a shoulder band near 260 nm (4.75 eV). We will adopt $E^{\text{CT}} = 4.8$ eV which is quite similar as in GdVO₄. The IVCT excitation band for Pr^{3+} is near 306 nm (4.05 eV) and for Tb^{3+} near 311 nm (4.00 eV).^{40,78} These values for the IVCT band are consistent with the VRBE scheme constructed with the Eu^{3+} CT-band energy and E^{ex} . The emission from the 3P_0 level of Pr^{3+} already starts to quench below RT and at 370 K emission has dropped to 50% of the RT value indicating that $T_{0.5} < 370$ K. The emission from the 5D_4 level dominates and is quenched with $T_{0.5} = 460$ K and emission from 5D_3 emission is not observed at RT in Ref. 78. In Ref. 87 5D_3 emission is weakly observed at RT.

LuNbO₄. Like in GdNbO₄ and YNbO₄ a band is observed near 243 nm (5.1 eV) in the excitation spectra of Eu^{3+} and Tb^{3+} doped LuNbO₄ that might be attributed to the host excitation band.⁸⁵ For undoped LuNbO₄ a RT excitation maximum of the host emission is reported at 266 nm (4.66 eV) in Ref. 90 suggesting $E^{\text{ex}}(LT)$ of about 4.8 eV. The same authors find the excitation maximum for Eu^{3+} emission at 268 nm (4.65 eV). On the other hand in Ref. 85 the CT-band can also be located at 245 nm (5.06 eV). At this stage the available information is not conclusive and we will assume the same E^{ex} and E^{CT} as in YNbO₄. Information on Pr^{3+} was not found, and Tb^{3+} shows emission from the 5D_4 level at RT.⁸⁵

The tungstates

BaWO₄. The energy of the RT fundamental absorption onset is at 5.26 eV in Refs. 71 and 95, the ultraviolet absorbance spectrum reaches its maximum at 5.6 eV in Ref. 96, and from low temperature vacuum ultraviolet excitation studies in Ref. 48 the host excitation maximum is at 5.7 ± 0.2 eV. In this work we will adopt the value of 5.6 eV for $E^{\text{ex}}(LT)$. The CT excitation maximum of Eu^{3+} emission is at 258 nm (4.80 eV) in Ref. 104 for 1% doping level, at 271 nm (4.58 eV) in Ref. 98 for 15% Eu doping, at 280 nm (4.43 eV) in Ref. 51, at 283 nm (4.38 eV) in Ref. 99 for 1–9% Eu^{3+} . We conclude that $E^{\text{CT}} = 4.45$ eV which is the same as in SrWO₄. Adding Pr^{3+} creates absorption in the 4.2–5.0 eV region.⁹⁶ It is just below the onset of the host absorption and it suggests a Pr^{3+} IVCT band near 4.6 ± 0.2 eV. In BaWO₄ the Tb^{3+} excitation maximum is at 236 nm (5.25 eV) in Ref. 100. It can be partly the onset of the host excitation and partly the Tb^{3+} 4f-5d excitation. A weak tail extending to about 290 nm might be from the expected IVCT band. In Ref. 51 the Tb^{3+} excitation maximum is at 272 nm (4.55 eV) where the IVCT band is expected. At room temperature emission from both 5D_3 and 5D_4 is observed.

SrWO₄. The RT fundamental absorption onset is at 248 nm (5.08 eV) in Ref. 95, and the RT host excitation maximum is reported at 252 nm (4.92 eV) in Ref. 101. Vacuum ultraviolet studies in Ref. 48 shows that the intrinsic exciton creation peak is around 5.5

± 0.2 eV. We will adopt 5.35 eV for $E^{ex}(LT)$ in this work. Excitation spectra of Eu^{3+} emission shows the CT-band at 286 nm (4.35 eV) in Ref. 102, at 279 nm (4.44 eV) in Ref. 103, at 271 nm (4.58 eV) in Ref. 104, at 281 nm (4.41 eV) in Ref. 101, at 278 nm (4.46 eV) in Ref. 105, and at 280 nm (4.43 eV) in Ref. 105. Altogether we conclude that E^{CT} is near 280 nm or 4.45 eV which is the same as in BaWO_4 . With Pr^{3+} doping intense emission lines from the 3P_0 level are observed at RT,¹⁰⁶ but information to derive the IVCT band energy was not found. The excitation maximum of 5D_4 emission is near 260 nm (4.8 eV) in Ref. 107. It is at lower energy than that for host exciton creation and may suggest the presence of an IVCT band.

CaWO₄. The RT fundamental absorption onset is at 251 nm (4.94 eV) in Ref. 95 which is consistent with the 15 K vacuum ultraviolet excitation studies in Ref. 48 where the exciton peak is at $5.2 \text{ eV} \pm 0.2 \text{ eV}$. Undoped CaWO_4 shows a broad 430 nm emission band at RT with an excitation maximum at 243 nm (5.1 eV).^{97,104,108} In Ref. 109 the excitation maximum is at 238 nm (5.2 eV). In this work we will adopt $E^{ex}(LT) = 5.25 \text{ eV}$. The Eu^{3+} CT-band is at 261 nm (4.75 eV) in Ref. 102, at $267 \pm 10 \text{ nm}$ (4.64 eV) in Ref. 110 shifting to 286 nm (4.35 eV) when 10% Li is added for charge compensation. It is at 266 nm (4.66 eV) in Ref. 104, at 262 nm (4.73 eV) in Ref. 97, and at 268 nm (4.62 eV) in Ref. 111. We conclude that $E^{CT} = 4.7 \pm 0.1 \text{ eV}$. The VRBE scheme then predicts the Pr^{3+} IVCT band at 4.4 eV (282 nm). The excitation maximum of Pr^{3+} emission is at 270 nm (4.59 eV) in Ref. 112 and at 254 nm (4.88 eV) in Ref. 113, but it is not certain at all whether these excitations are related to the IVCT band. They can equally well be related with the host exciton or near defect exciton creation bands. In any case the emission from the 3P_0 level dominates at RT.^{112,113} The emission from Tb^{3+} is very stable and $T_{0.5} > 600 \text{ K}$ for the 5D_4 emission in CaWO_4 and the emission from 5D_4 has $T_{0.5} = 450 \text{ K}$.¹²

PbWO₄. The energy of host exciton creation at low temperature $E^{ex}(LT)$ is found at 4.35 eV from.^{48,91,92} With Pr^{3+} doping an additional broad band is observed between 300 nm and 360 nm and peaking near 335 nm (3.70 eV) which is too low energy to attribute to 4f-5d transitions. Instead an IVCT band is much more likely. The emission from 3P_0 does not yet show any evidence for thermal quenching at room temperature and $T_{0.5}$ is then estimated $> 350 \text{ K}$. With Tb^{3+} a band is observed near 330 nm (3.75 eV) at energy below E^{ex} .⁹³ Like for Pr^{3+} we attribute this band to the IVCT band.^{93,94} report 5D_4 emission at room temperature and also weak emission from 5D_3 is observed.

The tantalates

The M-type rare earth tantalates with Gd, Y, and Lu have the fergusonite structure which can be considered as a distorted scheelite structure and Ta^{5+} is tetrahedrally coordinated. There also exists a low temperature phase (M'-type) with octahedral coordinated Ta^{5+} .^{114,115} On the level of accuracy of the VRBE schemes presented in this work we will not make a distinction between the two modifications and the schemes apply approximately to both.

LaTaO₄. Diffuse reflection spectra of undoped LaTaO_4 reaches a maximum near 250 nm (4.96 eV).^{116,117} A vacuum ultra violet study at 10 K on the Pr^{3+} emission shows an excitation band at 242 nm (5.10 eV), and in this work we will attribute this to $E^{ex}(LT)$. The Eu^{3+} CT-band is at 272 nm (4.55 eV) in Ref. 118 at 1% Eu^{3+} doping, at 282 nm (4.40 eV) in Ref. 119 at 3% doping, at 297 nm (4.18 eV) in Ref. 120 at 5–10% doping, and at 307 nm (4.05 eV) in Ref. 121 upon doping with 25% and 40% Eu^{3+} . Apparently the CT-maximum redshifts with higher Eu concentration and here we will adopt the low concentration value of 4.55 eV for E^{CT} . However, one may not exclude the possibility that the Eu^{3+} CT-band is cut-off on the short wavelength side by competing host absorption, and in that case the CT-maximum can be located near 4.7 eV. With the chosen parameters, the VRBE scheme predicts the IVCT bands for Pr^{3+} and Tb^{3+} near 4.0 eV (310 nm). A clear shoulder band near 270 nm (4.6 eV) is observed in the excitation spectrum of Pr^{3+} emission in Ref. 122 and it may be the IVCT band, however, this is not consistent with the prediction. Emission from the 3P_0 and 1D_2 level is observed at 10 K and 300 K in a ratio that remains fixed which suggests no significant quenching of the 3P_0 emission and we tentatively assume $T_{0.5} > 350 \text{ K}$. The excitation maximum of Tb^{3+} emission is at 270 nm (4.6 eV)¹¹⁹ and like for Pr^{3+} this could be the IVCT band but again it is not consistent with the scheme. The luminescence quantum efficiency of Tb^{3+} emission at 3% doping level is 20% whereas for GdTaO_4 and LuTaO_4 it is 70%.¹¹⁹ This suggest that $T_{0.5} < 300 \text{ K}$.

GdTaO₄. Vacuum ultraviolet spectroscopy at 20 K shows the host emission excitation maximum at 217 nm (5.71 eV)¹²³ and at 209 nm (5.93 eV).¹²⁴ Also with Xenon lamp spectroscopy, the RT host excitation maximum is observed in the 5.75 eV to 5.95 eV energy region.^{118,119,125–128} We will adopt in this work $E^{ex}(LT) = 5.80 \pm 0.1 \text{ eV}$. The Eu^{3+} CT in GdTaO_4 is consistently reported near 248 nm (5.0 eV).^{118,123,124,126,128} With these parameters the VRBE scheme predicts the IVCT bands for Pr^{3+} and Tb^{3+} near 4.2 eV (295 nm). Noto et al.¹²² studied Pr^{3+} in GdTaO_4 with VUV-techniques and a clear excitation maximum is observed at 265 nm (4.68 eV) that can be attributed to 4f-5d transitions. Emission from 3P_0 and 1D_2 is stable up to at least RT. Excitation spectra of Tb^{3+} emission shows a clear maximum around 260 nm (4.77 eV).^{119,125,127,129} It was ascribed to the IVCT state in Ref. 119 but in Ref. 129 it was re-assigned to the spin allowed 4f-5d transition in Tb^{3+} . A weak band at 295 nm (4.20 eV) was assigned to the spin forbidden transition.¹²⁹ The energy difference between the spin allowed and spin forbidden transition of 0.57 eV seems too small and considering the prediction from the

VRBE scheme an IVCT band is then more likely. For 3% Tb^{3+} in GdTaO_4 at RT 70% quantum efficiency is reported in Ref. 119 and emission from both the 5D_3 and the 5D_4 level is observed.^{114,125,129} A high quantum efficiency at room temperature implies that $T_{0.5}$ must be well above RT.

YTaO₄. The host excitation maximum is reported at 215 nm (5.75 eV) and in this work a value of $5.80 \pm 0.1 \text{ eV}$ will be used for $E^{ex}(LT)$. The Eu^{3+} CT band is at 238 nm (5.2 eV) in Ref. 89 at 242 nm (5.12 eV) in Ref. 118 at 248 nm (5.0 eV) in Ref. 119. We will adopt a value of 5.10 eV for E^{CT} in this work. The first Pr^{3+} emission excitation band is consistently observed near 271 nm (4.57 eV) in Refs. 40, 88, and 122 and should be attributed to the first 4f-5d transition. 5d-4f emission is not observed for Pr^{3+} and only emission lines from the 3P_0 and 1D_2 levels appear in a ratio that does not change between 10K and RT. It indicates that the quenching temperature $T_{0.5}$ for both emissions are well above RT. The VRBE scheme constructed with above parameters now predicts the Pr^{3+} IVCT band near 4.15 eV (300 nm). Indeed an asymmetry on the long wavelength side of the 4f-5d transition in Ref. 40 might indicate such IVCT. Tb^{3+} has the first excitation maximum at 261 nm (4.75 eV) in Ref. 89, at 264 nm (4.70 eV) in Ref. 119, and at 273 nm (4.54 eV) in Ref. 40. The average of 4.66 eV is about the same as in GdTaO_4 and is attributed to the first spin allowed 4f-5d transition. A long wavelength tail between 300nm and 340 nm to the 273 nm excitation peak of Tb^{3+} emission in Ref. 40 may, like for Pr^{3+} , be related to the IVCT band consistent with the VRBE scheme. Blasse and Bril¹¹⁹ reported a 70% high quantum efficiency at RT for the Tb^{3+} emission together with a very high quenching temperature of $T_{0.5} = 750 \text{ K}$. Under X-ray excitation, the emission from the $\text{Tb}^{3+} ^5D_3$ level is observed at RT for 1% doped YTaO_4 .¹¹⁴

LuTaO₄. Xenon lamp excitation based data show that the host excitation maximum in LuTaO_3 is near 218 nm (5.7 eV) in Refs. 118, 130, and 131 This is the same as observed for GdTaO_4 and YTaO_4 with Xenon lamp excitation and hence the same value for $E^{ex}(LT) = 5.80 \text{ eV}$ will be used. The CT-band for 1% Eu^{3+} doping is at 240 nm (5.15 eV) in Refs. 118 and 131, and at 250 nm (4.96 eV) in Ref. 84 for 5% Eu^{3+} . In this work we will adopt $E^{CT} = 5.15 \text{ eV}$. With 10% Tb^{3+} strong emission from 5D_4 is observed at room temperature with an excitation band near 260 nm (4.77 eV) which is attributed to the first spin allowed 4f-5d excitation of Tb^{3+} . Under X-ray excitation 3P_0 emission is observed at RT,^{118,130} and also under X-ray excitation emission from the 5D_3 and 5D_4 levels of Tb^{3+} are observed at RT.¹³⁰

ScTaO₄. There appears to be not much data on the spectroscopy of the lanthanides in ScTaO_4 . The RT excitation spectrum of Eu^{3+} emission shows the CT band at 238 nm (5.20 eV) for 1% doping in Ref. 118 and a weak band on top of it at 223 nm (5.6 eV) which might be related to the host excitation band. Tb^{3+} shows emission from the 5D_4 level at room temperature with a broad excitation band around 292 nm (4.24 eV) which may be due to either the IVCT transitions or the first spin forbidden 4f-5d excitation band of Tb^{3+} .¹³² With the lack of further data only a tentative VRBE scheme can be made. We will adopt $E^{ex}(LT) = 5.8 \text{ eV}$, i.e., the same value as for Gd-, Y-, and LuTaO_4 , and $E^{CT} = 5.2 \text{ eV}$.

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