Charge transfer bands in optical materials and related defect level location

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A B S T R A C T

Charge transfer (CT)-bands, electron trapping, hole trapping, electron release, hole release, metal-to-metal-charge transfer, CT-luminescence, anomalous emission, impurity trapped exciton emission, inter-valence charge transfer, pair-emission, tunneling, photo-electron spectroscopy, redox potentials, photo-ionization, thermal-ionization. All these phenomena deal with the transfer of an electron from one atom in a compound to either another atom in the compound or to the ambient, i.e., outside the compound. The energy needed for, or released in, such transfer carries information on the electron binding energy in the defect levels with respect to the host band levels or the levels in the ambient. First the different types of charge transfer between a lanthanide and the host bands, and how they can be used to construct a host referred binding energy (HRBE) diagram, are reviewed. Then briefly the chemical shift model is introduced in order to convert the HRBE diagram into a vacuum referred binding energy diagram (VRBE). Next charge transfer between transition metal elements and host bands and between Bi^{3+} and host bands are treated, and finally electron transfer from one defect to another and to the ambient. Illustrating examples are provided.

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1. Introduction

Location of defect levels of the lanthanides, the transition metals, and the $6s^2$ element Bi^{3+} with respect to the valence band (VB) top and conduction band (CB) bottom controls their luminescence properties. It also controls whether those defects can act as electron donor or electron acceptor, or as a hole trap or electron trap. The preferred valence, i.e., whether a lanthanide, transition metal (TM), or Bi prefers to enter the host as 2+, 3+, 4+, or 5+ is also determined by level location [1].

Accurate information on the location of defect levels within the band gap is not easy to obtain and it is has been subject of speculation for a long time. The energy needed for, or released by, the transfer of an electron from a host VB or CB to a defect carries information on binding energy differences. In the field of luminescence spectroscopy a wealth of data has been published during past 70 years; data that comprises 1000nd s of different inorganic compounds doped with the lanthanides, transition metals, and $6s^2$ elements in different charge states. Continuous mining of that data

by the author and co-workers during past 20 years provided trends, and those trends led to semi-empirical models [2–7].

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that of all others.

In 2012 the chemical shift model was published [8] that provides a method to construct a so-called vacuum referred binding energy (VRBE) diagram with the host band states and all lanthanide levels in a routine fashion. In such diagram a level energy is defined as the minimal energy needed to extract an electron from that level and bring it to the vacuum outside the compound with zero kinetic energy. The energy of that extracted electron is then defined as our energy zero, or the vacuum level.

Once that the VRBEs at the top of the VB are known one may search for electron transfer data involving other defects than the lanthanides. This has been done so for the 3d, 4d, and 5d transition metal (TM) elements with empty d-shell. The energy needed for electron transfer provides then information on the VRBE in the transition metal defects. The results will be reviewed in this work. Briefly, charge transfer to TMs with more than one electron in the d-orbital, particularly those involving Cr^{3+} and Mn^{4+}, are discussed and finally charge transfer involving Bi^{3+}.

2. Electron transfer between lanthanides and host bands

In this section the different types of electron transfer between lanthanide dopants and the host bands are reviewed. It deals with VB→Ln and Ln→CB electron transfer which requires energy in the form of photons ($h\nu$) or phonons ($h\Omega$) or a combination of both. The reversed transfer Ln→VB and CB→Ln liberates energy in the form of heat, charge transfer luminescence, or lanthanide luminescence. The systematics in the energy of such transfer with type of lanthanide leads to the so-called divalent $Ln^{2+/3+}$ and trivalent $Ln^{3+/4+}$ zigzag curves, and host referred binding energy diagrams (HRBE).

2.1. VB charge transfer from and to $Eu^{2+/3+}$

The most familiar type of electron or charge transfer (CT) known in luminescence phosphors is that of an electron from the VB to Eu^{3+}. The final state is the $4f^7$ ground state of Eu^{2+} together with a hole left on the neighboring anion ligands. Fig. 1 shows a typical example for $GdAlO_3:Eu^{3+}$ reproduced from data in Ref. [9]. The band at 169 nm (7.35 eV) is due to host exciton creation, and the broad band around 250 nm (4.95 eV) is due to VB + $h\nu$ → $Eu^{2+/3+}$ electron transfer. After excitation the lattice will relax on the ps

time scale and upon the back transfer of the electron to the hole on the ligands, sufficient energy is available to leave Eu^{3+} in an excited state which is then followed by the $^5D_{0,1,2,3} \rightarrow {}^7F_J$ Eu^{3+} emissions with the main intensity in the red (2.1 eV). The most well-known Eu^{3+} CT-band is that of $Y_2O_3:Eu^{3+}$ which is widely used as the red phosphor in tri-color fluorescent tube lighting [10]. The 254 nm (4.88 eV) emission of Hg is then efficiently absorbed via the CT-band.

The energy of the CT-band carries information on the location of the Eu^{2+} ground state level above the top of the valence band. However, one should take lattice relaxation effects into account and also the still remaining binding energy between the transferred electron and the hole left on the ligands to arrive at the Eu^{2+} ground state location. In Ref. [6] it was concluded that both tend to cancel each other out, and then the energy at the maximum of the CT-band provides a good measure for the location of the Eu^{2+} ground state level above the top of the VB.

In literature, one may find 1000^{nd}s of papers on VB + $h\nu \rightarrow Eu^{2+/3+}$ CT-band energies, and large part of it was collected and analyzed in 2003 [6]. Fig. 2 shows data on these energies in many different compounds. There are clear trends visible. Within the halides, chalcogenides, and pnictides, the CT-band energy decrease with higher atomic number of the anion. The data show that in fluoride compounds the Eu^{2+} ground state is 7–8 eV above the VB. It decreases to about 4, 3, and 2 eV in Cl-, Br-, and I-compounds. In oxides the spread in energy is quite large (from 3 to 6.5 eV) and decreases when moving to S-, Se-, and Te-compounds. In the nitrides the CT-band is between 3 and 4 eV and decreases towards the phosphides.

Immediately after CT-band excitation of Eu^{3+}, the transferred electron will back transfer to the hole left on the neighboring anions and the excitation energy will be released again. Part of the energy is lost as heat in lattice relaxation and other part appears in a $^5D_{0,1,2,3}$ excited state of Eu^{3+} leading to the emission as seen in Fig. 1. From those excited states the electron can also return radiation less via the charge transfer state, i.e., Eu^{3+} (^5D_J) + $h\Omega$ → Eu^{2+}(g.s.) + V_h → Eu^{3+}(g.s.) + $h\Omega$, where V_h denotes a hole in the VB. This is the so-called thermal quenching of Eu^{3+} emission via the charge transfer state [11–14].

The temperature T_k where the thermal quenching starts (becomes significant) appears to lower with lower energy of the CT-band [14]. In Fig. 3 data are collected to demonstrate this, and a more or less linear relation can be seen (see also [15]). Extrapolating the data towards zero quenching temperature, the CT-band
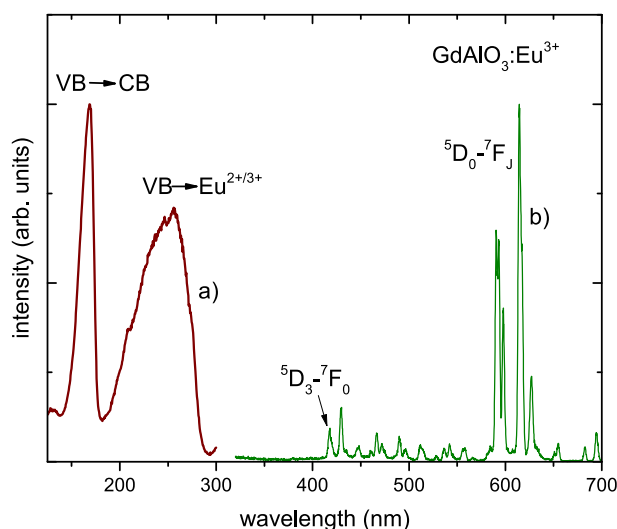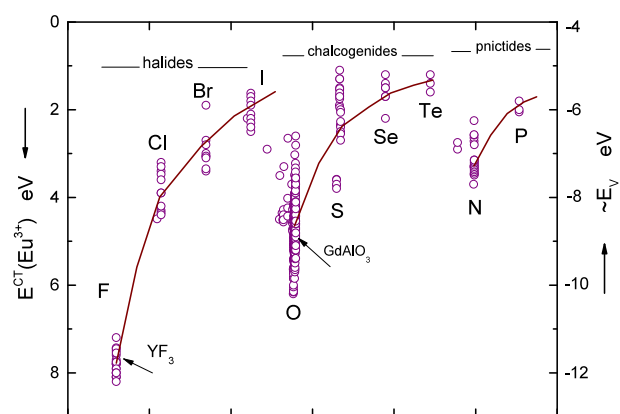

Fig. 1. Excitation spectrum a) of 592 nm emission and emission spectrum b) at 250 nm excitation of $GdAlO_3:Eu^{3+}$ at 10 K. Data are obtained from Luo et al. [9].

Fig. 2. Collected data on Eu^{3+} CT-band energies (left hand scale) in compounds. The right hand scale shows the electron binding energy at the VB-top assuming an approximate VRBE of −4 eV in the Eu^{2+} ground state. Data for $E^{CT} \leq 3$ eV are often derived values from the E^{CT} to other lanthanides than Eu.