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Awater, Roy H.P.; Dorenbos, Pieter

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Towards a general concentration quenching model of Bi³⁺ luminescence



Roy H.P. Awater*, Pieter Dorenbos

Luminescence Materials Research Group (FAME-LMR), Department of Radiation Science and Technology, Faculty of Applied Sciences, Delft University of Technology, 2629 JB Delft, The Netherlands

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ABSTRACT

The vacuum referred binding energy of the electron in the Bi²⁺ ground state has been determined in 15 different compounds. This shows that the electron binding energy in the ground state of Bi²⁺ is at lower (more negative) energy compared to the electron binding energy in the excited state of Bi³⁺. This means that electron transfer from the excited state of one Bi³⁺ to a neighboring Bi³⁺, forming a Bi²⁺ + –Bi⁴⁺ pair, acts as a quenching route for the Bi³⁺ emission. Electron back transfer in the Bi²⁺ + –Bi⁴⁺ pair is then suggested to be the origin for the frequently observed pair emission. This paper shows that vacuum referred electron binding energy diagrams can provide a unique physical insight in the properties of inorganic compounds.

1. Introduction

Bi³⁺ shows a complex temperature and concentration dependent luminescence quenching [1–3]. The luminescence quenching cannot be explained by multi-phonon relaxation because of a too large energy gap between the ³P₁ excited state and the ¹S₀ ground state. A transfer of an electron from the excited state to the conduction band is often used to describe the quenching, like for example in (In,Lu)BO₃ and Ca(Zr,Sn)O₃ compounds [4,5]. Another possibility for luminescence quenching is via the charge transfer (CT) of an electron in the valence band to a bismuth ion as has been proposed for example in LaOBr [6]. These two quenching routes involving CT apply to isolated bismuth centers. A third type of quenching occurs in Bi-pairs, which becomes important at high concentrations of bismuth or in the case of preferential formation of bismuth pairs or clusters [7–9]. The mechanism of such type of quenching has always remained open.

Recently, we determined the vacuum referred electron binding energies (VRBE) in the Bi³⁺ [¹S₀] and [³P₁] levels in 44 different compounds [10]. The VRBE of Bi³⁺ in a selection of 10 of those compounds is shown in Fig. 1. The VRBE in the ¹S₀ ground state varies between – 5 and – 10 eV and in the ³P₁ excited state between – 2 and – 4 eV in a systematic fashion with the chemical and structural properties of the compound. When Bi³⁺ is doped in compounds with a low lying conduction band, e.g. compounds containing transition metals with d⁰ configuration such as YNbO₄ and YVO₄ in Fig. 1, the ³P₁ excited state appears above the conduction band (CB) bottom. In these cases photoionization to the CB occurs without generating any Bi³⁺ emission. In stead a metal-to-metal charge transfer (MMCT) emission is often observed in these compounds [11,12]. Besides Bi³⁺, also lumi-

nescence from Bi²⁺ has been reported in fluorides, phosphates, sulphates and borates [13–16]. For Li₂BaP₂O₇ and YPO₄, we concluded that the VRBE in the Bi²⁺ ²P_{1/2} ground state is at approximately – 4 eV, which is below the ³P₁ excited state of Bi³⁺ in those compounds [17,18]. This means that electron transfer from the excited state of one Bi³⁺ ion to a neighboring bismuth ion is energetically favorable. Such electron transfer provides then a mechanism for the quenching of the Bi³⁺ emission.

This mechanism is illustrated in Fig. 2. Two Bi³⁺ ions labeled I and II that form a Bi–Bi pair are shown, and after exciting an electron to the ³P₁ excited state of bismuth ion I (arrow 1), energy will be released in the electron transfer to the neighboring bismuth ion II (arrow 2), effectively forming a Bi²⁺–Bi⁴⁺ pair. Recombination of the Bi²⁺–Bi⁴⁺ electron-hole pair (arrow 3) can be radiately or non-radiatively. If the recombination occurs radiatively, a broad emission band with a large Stokes shift typical for CT transitions can be observed. This also provides a quenching route for the Bi³⁺ ³P₁ → ¹S₀ emission. In this paper we will demonstrate that electron transfer between neighboring bismuth ions is a general phenomenon for Bi³⁺-doped compounds when either Bi enters in pairs or cluster or when the Bi concentration is sufficiently high to generate pairs based on statistical grounds. For that we have collected information on Bi²⁺ in the 15 compounds listed in Table 1.

2. Results and discussion

For almost all compounds, the listed VRBE at the valence band (VB) top and conduction band (CB) bottom were presented earlier, and together with the VRBE in the Bi³⁺ ground and excited states are taken

* Corresponding author.

E-mail address: R.H.P.Awater@tudelft.nl (R.H.P. Awater).

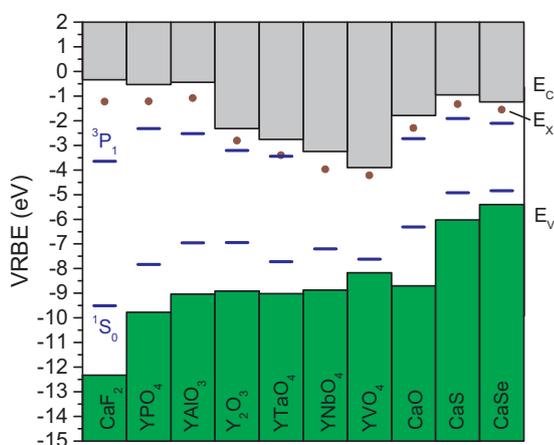


Fig. 1. Stacked VRBE diagrams for 10 different Bi^{3+} doped compounds with E_C the binding energy at the conduction band bottom, E_V the binding energy at the valence band top and E_X the binding energy in the exciton state. The blue bars labeled 1S_0 and 3P_1 indicate the electron binding energy in the Bi^{3+} ground and excited state, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

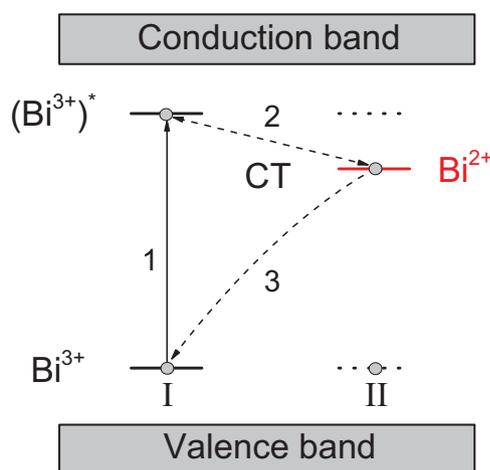


Fig. 2. The proposed quenching model of the Bi^{3+} luminescence and generation of pair emission via electron transfer between neighboring bismuth ions.

Table 1

Spectroscopic and VRBE data on Bi^{2+} in compounds and on pure Bi compounds. All energies are in eV.

Host compound	E_V	E_C	$E_{em}^{\text{Bi}^{2+}}$	$T_{0.9}$	$E_{g.s.}^{\text{Bi}^{2+}}$	Ref.
BiF_3	-9.60	-4.42	-	-	-4.42	-
SrF_2	-12.13	-0.69	2.07	>300 K	-3.66	[13]
CaF_2	-12.33	-0.34	2.25	>300 K	-3.52	[13]
BaSO_4	-8.93	-0.12	1.98	>300 K	-2.91	[14]
SrB_4O_7	-9.59	-0.79	2.1	>300 K	-3.70	[16]
SrSO_4	-8.93	0.12	2.03	>300 K	-2.73	[15]
BaBPO_5	-8.98	-0.29	1.94	>300 K	-3.03	[21]
SrBPO_5	-9.08	-0.21	1.94	>300 K	-2.96	[21]
CaBPO_5	-9.24	-0.01	1.97	>300 K	-2.80	[21]
CaSO_4	-8.94	0.19	2.1	>300 K	-2.73	[15,14]
$\text{Li}_2\text{BaP}_2\text{O}_7$	-9.23	-0.86	1.81	>600 K	-3.95	[17]
BiPO_4	-8.73	-3.83	-	-	-3.83	-
YPO_4	-9.77	-0.53	1.85	350 K	-3.28	[18]
MgGeO_3	-8.70	-2.22	n.a.	n.a.	-3.81	[19]
Bi_2O_3	-7.53	-4.18	-	-	-4.18	-

from Ref. [10]. There are several methods to estimate the VRBE in the Bi^{2+} ground and excited state. One may seek for information on the $\text{VB} \rightarrow \text{Bi}^{3+}$ charge transfer. However, we only found a report on

MgGeO_3 by Katayama et al. from which a Bi^{2+} location at -3.8 eV is derived [19]. Another method is to determine the energy barrier ΔE_q for thermal quenching of Bi^{2+} emission. However, detailed studies on the quenching of Bi^{2+} emission to determine such energy barrier are not available. At best one may find the temperature $T_{0.9}$, the temperature where the intensity has dropped by 10% and the quenching starts to become significant. Using methods similar as described in Ref. [20], the quenching energy barrier ΔE_q is approximately $T_{0.9}/620$ eV. The electron does not need to be transferred as high in energy as the conduction band bottom for quenching to occur. We will assume that $\frac{E_C + E_X}{2} - \Delta E_q - E_{em}^{\text{Bi}^{2+}}$ provides a fair estimate for the VRBE in the Bi^{2+} ground state ($E_{g.s.}^{\text{Bi}^{2+}}$), with E_C the VRBE of the electron at the conduction band bottom and E_X the VRBE of the electron in the exciton state. The relevant values, including the references to the literature we used for $E_{em}^{\text{Bi}^{2+}}$, the Bi^{2+} emission energy, can be found in Table 1.

A final method to obtain indications on the VRBE in the Bi-levels is from pure Bi-compounds. Usable information was found for BiF_3 , BiPO_4 , and Bi_2O_3 . The top of the VB has here a strong Bi^{3+} ground state component and the CB-bottom a strong Bi^{2+} contribution. For BiF_3 the VRBE at the VB-top is found at -9.6 eV and is derived from the X-ray photoelectron spectroscopy studies by Poole et al. [22], and by adding information on the band gap the CB-bottom is found at -4.4 eV. BiPO_4 has been studied for its photo-catalytic activity and from those studies the CB-bottom was found about 0.4 eV above that of TiO_2 [23] which has the CB-bottom at -4.2 eV [24]. Bi_2O_3 has also been studied for its photocatalytic activity and Lin et al. [25] places the CB-bottom at 0.1 eV below the H^+/H_2 redox potential which translates to a VRBE of -4.5 eV. Combined with band gap information, the data as compiled in Table 1 were obtained.

The data from Table 1 are presented as a stacked VRBE diagram in Fig. 3. The Bi^{3+} ground and excited states are indicated by the blue horizontal bars within the forbidden gap. The VRBE in the Bi^{2+} ground state (g.s.) and excited states are illustrated by the horizontal red bars. In the case when only an upper limit VRBE estimation is available, a small down pointing arrow has been added. The true position, depending on the actual emission quenching temperature, can well be 0.5 eV lower. For the pure Bi-based compounds the top of the valence band is regarded as representative for the VRBE in the Bi^{3+} g.s. and the bottom of the CB for the VRBE in the Bi^{2+} g.s. For example, the electron binding energy in the ground state of Bi^{2+} in YPO_4 is located at -3.28 eV, which is only 0.5 eV different from the binding energy in the conduction band bottom of BiPO_4 . Also the electron binding energy in Bi^{3+} ground state located at -8.2 eV in YPO_4 differs only by 0.5 eV from the binding energy in the valence band top of BiPO_4 . The different

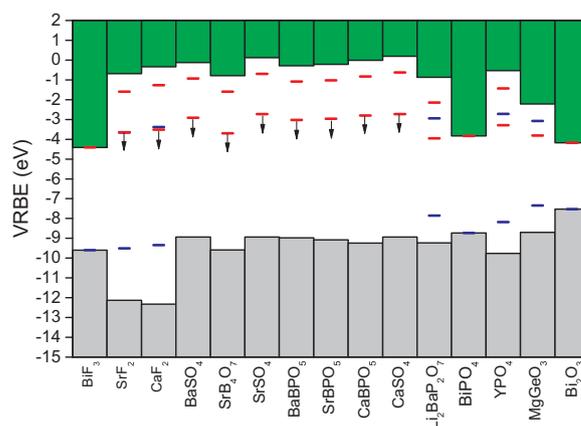


Fig. 3. Stacked diagram with the VRBE at the VB-top and the CB-bottom of various compounds with the Bi^{3+} (blue horizontal bars) and Bi^{2+} (red horizontal bars) levels. Also the VRBE at the CB-bottom and VB-top in BiF_3 , BiPO_4 , and Bi_2O_3 is shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

crystal structures, but also orbital mixing of Bi-states with that of other host atoms may account for such 0.5 eV difference.

The newly added information in this paper is the VRBE in the Bi^{2+} ground state, which appears in the range between -3.5 and -4 eV, and is indeed below the Bi^{3+} excited state usually found near -3 eV in fluoride and oxide compounds. The energy difference between the VRBE in the Bi^{3+} excited state and Bi^{2+} ground state appears to be about 0.7 ± 0.3 eV. If approximately 1 eV lattice relaxation loss is taken into account, the remaining energy for possible pair emission is then expected 1.7 ± 0.5 eV lower than the Bi^{3+} emission energy which is indeed the typical Stokes shift observed. For example, in $\text{YPO}_4:\text{Bi}^{3+}$ the pair emission band at 325 nm is 1.6 eV Stokes shifted from the Bi^{3+} excitation.

Depending on the transition rates, complicated dynamics as in the Bi^{3+} doped garnet systems [26–28] may now occur. It is not the purpose of this paper to enter in too much detail but some general ideas can be launched. The typical luminescence decay rate at room temperature of the Bi^{3+} emission is found near 1 μs and the luminescence decay of the pair emission is typically 100 μs [28,29]. The radiative decay rate of the Bi^{3+} emission (arrow 1 in Fig. 2) has to compete with the electron transfer rate to the neighboring Bi ion (arrow 2 in Fig. 2). In such electron transfer, the above found 0.7 ± 0.3 eV energy difference needs to be emitted as phonons and a temperature dependent rate is to be expected. Once in the $\text{Bi}^{4+}\text{-Bi}^{2+}$ pair state, again different rates apply. With only 0.7 eV energy difference, thermally activated electron back transfer to the higher energy $\text{Bi}^{3+}[^3\text{P}_1] - \text{Bi}^{3+}[^1\text{S}_0]$ pair state is possible (reverse of arrow 2 in Fig. 2). In addition, there are the luminescence decay rates of Bi-pair emission, and its thermal quenching rate.

Srivastava et al. [2] studied the luminescence intensity as function of temperature of the Bi^{3+} emission at 385 nm (3.22 eV) and observed an additional emission band labeled as VIS-band at 514 nm (2.41 eV) when exciting Bi^{3+} at 290 nm (4.27 eV) in 0.5% Bi^{3+} doped $\text{La}_2\text{Zr}_2\text{O}_7$. From 0 K to 60 K the Bi^{3+} emission quenches whereas the VIS-band grows in intensity, and from 70 K to 120 K the process is reversed and the Bi^{3+} emission grows again with decreasing VIS-band intensity. Above 120 K both bands quench until at RT no emission remains. Although the origin of the VIS-band was not clear, one may also interpret it as Bi-pair emission. Intensity first grows at the expense of Bi^{3+} emission, above 70 K electron back transfer to the Bi^{3+} excited state reverses the process, and above 120 K the radiation-less electron transfer to the Bi^{3+} ground state starts to quench both emissions. Energetically such processes are well-possible. More detailed studies on the luminescence dynamics as function of temperature and Bi concentration would be required to verify or falsify such dynamics.

3. Conclusion

We have shown that in general the VRBE in the Bi^{2+} ground state is located at lower energy as compared to the VRBE in the $\text{Bi}^{3+}^3\text{P}_1$ excited state. In the presence of Bi-Bi pairs, it is then upon excitation of one Bi^{3+} energetically favorable for electron transfer to occur, and to form a $\text{Bi}^{2+}\text{-Bi}^{4+}$ pair. Based on the estimated VRBEs in the Bi^{2+} ground state in 15 different compounds, the electron transfer between neighboring Bi ions appears always energetically possible. The recombination of the electron and hole on the $\text{Bi}^{2+}\text{-Bi}^{4+}$ pair can occur non-radiatively or radiatively, in the later case the resulting visible emission band is often observed and ascribed to pair emission. The proposed mechanism of charge transfer between Bi-pairs can also explain the quenching behavior of Bi^{3+} luminescence when the Bi^{3+} concentration increases.

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References

- [1] A.M. Srivastava, S.J. Camardello, Concentration dependence of the Bi^{3+} luminescence in LnPO_4 ($\text{Ln} = \text{Y}^{3+}, \text{Lu}^{3+}$), *Opt. Mater.* 39 (2015) 130–133.
- [2] A.M. Srivastava, W.W. Beers, On the impurity trapped exciton luminescence in $\text{La}_2\text{Zr}_2\text{O}_7:\text{Bi}^{3+}$, *J. Lumin.* 81 (1999) 293–300.
- [3] A.M. Srivastava, A. Szarowski, On the quenching of Bi^{3+} luminescence in the pyrochlore $\text{Gd}_2\text{GaSbO}_7$, *J. Solid State Chem.* 146 (1999) 494–498.
- [4] V.P. Dotsenko, I.B. Berezovskaya, N.P. Efrushina, Photoionization and luminescence properties of Bi^{3+} in $\text{In}_{1-x}\text{Lu}_x\text{BO}_3$ solid solutions, *J. Phys. Chem. Solids* 57 (1995) 437–441.
- [5] A.M. Srivastava, Luminescence of Bi^{3+} in the orthorhombic perovskites $\text{CaB}^{4+}\text{O}_3(\text{B}^{4+} = \text{Zr}, \text{Sn})$: crossover from localized to D-state emission, *Opt. Mater.* 58 (2016) 89–92.
- [6] A. Wolfert, G. Blasse, Luminescence of Bi^{3+} -activated LaOBr , a system with emission from different states, *J. Lumin.* 33 (1985) 213–226.
- [7] H. Zhiran, G. Blasse, Energy transfer phenomena in luminescent materials based on GdB_3O_6 , *Mater. Chem. Phys.* 12 (1985) 257–274.
- [8] A.M. Srivastava, On the luminescence of Bi^{3+} in the pyrochlore $\text{Y}_2\text{Sn}_2\text{O}_7$, *Mater. Res. Bull.* 37 (2002) 745–751.
- [9] A.M. Srivastava, H.A. Comanzo, The ultraviolet and visible luminescence of Bi^{3+} in the orthorhombic perovskite, GdAlO_3 , *Opt. Mater.* 63 (2017) 118–121.
- [10] R.H.P. Awater, P. Dorenbos, The Bi^{3+} 6s and 6p electron binding energies in relation to the chemical environment of inorganic compounds, *J. Lumin.* 184 (2017) 221–231.
- [11] P. Boutinaud, Revisiting the spectroscopy of the Bi^{3+} ion in oxide compounds, *Inorg. Chem.* 52 (2013) 6028–6038.
- [12] G. Blasse, Optical electron transfer between metal ions and its consequences, *Struct. Bond.* 76 (1991) 153–187.
- [13] R. Cao, F. Zhang, C. Liao, J. Qiu, Yellow-to-orange emission from Bi^{2+} -doped RF_2 ($\text{R} = \text{Ca}$ and Sr) phosphors, *Opt. Express* 21 (2013) 15728–15733.
- [14] R. Cao, M. Peng, J. Qiu, Photoluminescence of Bi^{2+} -doped BaSO_4 as a red phosphor for white LEDs, *Opt. Express* 20 (2012) A977–A983.
- [15] M.A. Hamstra, H.F. Folkerts, G. Blasse, Red bismuth emission in alkaline-earth metal sulfates, *J. Mater. Chem.* 4 (1994) 1349–1350.
- [16] G. Blasse, A. Meijerink, M. Nomes, J. Zuidema, Unusual bismuth luminescence in strontium tetraborate ($\text{SrB}_4\text{O}_7:\text{Bi}$), *J. Phys. Chem. Solids* 55 (1994) 171–174.
- [17] R.H.P. Awater, P. Dorenbos, X-ray induced valence change and vacuum referred binding energies of Bi^{3+} and Bi^{2+} in $\text{Li}_2\text{Ba}_2\text{P}_2\text{O}_7$, *J. Phys. Chem. C* 120 (2016) 15114–15118.
- [18] R.H.P. Awater, L.C. Niemeijer-Berghuijs, P. Dorenbos, Luminescence and charge carrier trapping in $\text{YPO}_4:\text{Bi}$, *Opt. Mater.* 66 (2017) 351–355.
- [19] Y. Katayama, J. Ueda, S. Tanabe, Effect of Bi_2O_3 doping on persistent luminescence of $\text{MgGeO}_3:\text{Mn}^{2+}$ phosphor, *Opt. Mater. Express* 4 (2014) 613–623.
- [20] P. Dorenbos, Thermal quenching of $\text{Eu}^{2+}5d\text{-}4f$ luminescence in inorganic compounds, *J. Phys.: Condens. Matter* 17 (2005) 8103–8111.
- [21] M. Peng, L. Wondraczek, Bi^{2+} -doped strontium borates for white-light emitting diodes, *Opt. Lett.* 34 (2009) 2885–2887.
- [22] R.T. Poole, J. Liesegang, R.C.G. Leckey, J.G. Jenkin, J.B. Peel, Photoelectron valence-band spectra of PbF_2 , SbF_3 and BiF_3 , *Phys. Rev. B* 13 (1976) 896–899.
- [23] C. Pan, Y. Zhu, New type of BiPO_4 oxy-acid salt photocatalyst with high photocatalytic activity on degradation of dye, *Environ. Sci. Technol.* 44 (2010) 5570–5574.
- [24] P. Dorenbos, The electronic structure of lanthanide impurities in TiO_2 , ZnO , SnO_2 , and related compounds, *ECS J. Solid State Sci. Technol.* 3 (2014) R19–R24.
- [25] X. Lin, J. Xin, W. Wang, Z. Shan, F. Xu, F. Huang, Photocatalytic activities of heterojunction semiconductors $\text{Bi}_2\text{O}_3/\text{BaTiO}_3$: a strategy for the design of efficient combined photocatalysts, *J. Phys. Chem. C* 111 (2007) 18288–18293.
- [26] Y. Zorenko, V. Gorbenko, T. Voznyak, V. Jary, M. Nikl, Luminescence spectroscopy of the Bi^{3+} single and dimer centers in $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Bi}$ single crystalline films, *J. Lumin.* 130 (2010) 1963–1969.
- [27] V. Babin, V. Gorbenko, A. Krasnikov, A. Makhov, M. Nikl, K. Polak, S. Zazubovich, Y. Zorenko, Peculiarities of excited state structure and photoluminescence in Bi^{3+} -doped $\text{Lu}_3\text{Al}_5\text{O}_{12}$ single-crystalline films, *J. Phys.:Condens. Matter* 21 (2009) 415502.
- [28] V. Babin, V. Gorbenko, A. Krasnikov, A. Makhov, E. Mihokova, M. Nikl, S. Zazubovich, Y. Zorenko, Origin of Bi^{3+} -related luminescence centres in $\text{Lu}_3\text{Al}_5\text{O}_{12}$ and $\text{Y}_3\text{Al}_5\text{O}_{12}$ single crystalline films and the structure of their relaxed excited states, *Phys. Status Solidi B* 249 (2012) 1039–1045.
- [29] G. Blasse, A. Brill, Investigations of Bi^{3+} -activated phosphors, *J. Chem. Phys.* 48 (1968) 217–222.