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Awater, Roy H.P.; Dorenbos, Pieter

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Vacuum Referred Binding Energies of Bi³⁺ in Insulators Based on the Metal-to-Metal Charge Transfer Energy

Roy H. P. Awater* and 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*

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

Abstract

Introduction

The luminescence of the Bi^{3+} activator ion in a variety of host compounds has been extensively studied over the last 50 years.¹ The Bi^{3+} ion has a $6s^2$ outer electron configuration with the $^1\text{S}_0$ ground state. Optical transitions to the $6s^16p^1$ configuration result in the $^3\text{P}_{0,1,2}$ triplet and $^1\text{P}_1$ singlet excited states (in order of increasing energy). The optical transitions from the $^1\text{S}_0$ ground state to the $^3\text{P}_1$, $^3\text{P}_2$ and $^1\text{P}_1$ excited states are labeled A, B and C, respectively (see Fig. 1). The $^1\text{S}_0 \rightarrow ^3\text{P}_0$ and $^1\text{S}_0 \rightarrow ^3\text{P}_2$ are spin-forbidden, although the transition to the $^3\text{P}_2$ can be induced by coupling with unsymmetrical lattice vibrational modes.² As a result of spin-orbit coupling and mixing with the $^1\text{P}_1$ state, the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ transition becomes allowed. The $^1\text{S}_0 \rightarrow ^1\text{P}_1$ is a spin allowed transition. Therefore, only the A- and C-bands have a high enough absorption strength to be used in phosphor applications. A more detailed discussion on the optical transitions of $6s^2$ ions can be found in the literature.^{3,4}

- Trends in bismuth luminescence as function of h-parameter. Applications: phosphors, scintillators, sensitizer for Eu (and other Ln) emission.

When Bi^{3+} is incorporated into a host lattice an additional absorption band is observed, which is often labeled as the D-band. This absorption originates from a metal-to-metal charge transfer (MMCT) transition, meaning that an electron from bismuth is transferred to the host cation $\text{Bi}^{3+}/\text{M}^{n+} \rightarrow \text{Bi}^{4+}/\text{M}^{(n-1)+}$. Recently, Boutinaud *et al.* developed a model to predict energy of the MMCT transition in d^0 and d^{10} transition-metal oxides doped with Bi^{3+} .^{5,6}

MMCT⁷

Location of energy levels determines optical properties and performance of devices. Com-

parison with lanthanides (Dorenbos model). 6s electrons are not shielded, unlike the 4f, therefore expected that the chemical environment has a critical influence on the location of the optical transitions of the bismuth ion.

In this paper we located the vacuum referred binding energies of the Bi^{3+} ion in a variety of host compounds.

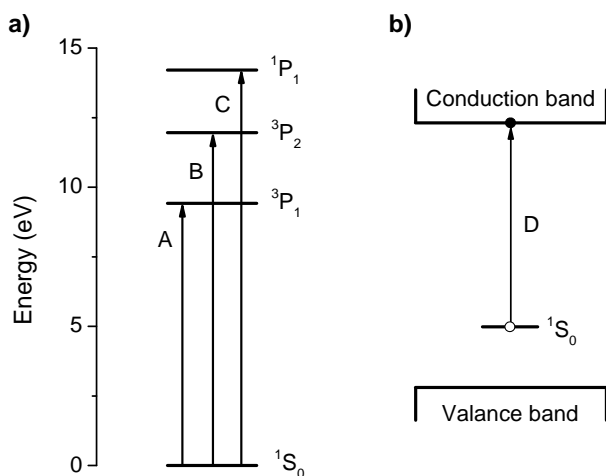


Figure 1: The energy levels of the free Bi^{3+} ion.

- Main focus paper: using MMCT to locate Bi^{3+} energy levels. Show that energy of s2 electron varies considerably with chemical environment.

- Bismuth self-quenching via pair emission as suggestion but focus for different paper. Potentially include bismuth as sensitizer.

Historical overview bismuth doped materials. What has been done: work of Blasse for phosphors, used in glass industry as probe ion,

Electronic configuration Bi^{3+} .

Bismuth pair formation. General for s2 elements in alkali halide crystals (and possibly all solids).

Incorporation into crystal results in an extra absorption/excitation band, the MMCT transition. Also depression of emission wavelength, very dependent on host lattice due to unshielded outer electrons.

Metal-to-metal charge transfer, useful for determining energy levels. Compare with IVCT of Pr^{3+} and Tb^{3+} .

Heavily-doped and self-activated bismuth compounds will be discussed in future work.

Dorenbos model: chemical shift, optical depression Ce^{3+} , VRBE

Redshift model, charge transfer model

Crystal field splitting and centroid shift only for Ce^{3+} or also applicable for Bi^{3+} ?

- Lanthanide free, which are expensive and only produced in China.
- How does s^2 luminescence work? Electron transitions, quantum mechanical splitting?
- Work of Blasse in the sixties.
- Dorenbos model on lanthanides.
- MMCT model Boutinaud.
- Paper of Wang, quantitative relation bismuth sp energy and host lattice.
- Bismuth as a sensitizer for Eu (and other Ln?) luminescence.
- Paper by Du: Chemical trends of electronic and optical properties of ns^2 ions in halides
- Optical electro negativity (Duffy)

Methodology

- How to locate bismuth energy levels? MMCT, A, C bands. B-band in most compounds too weak to be observed. Therefore excluded in this discussion.
- VRBE model
- Comparison with lanthanide spectroscopy: CT-bands, chemical shift model, redshift model, crystal field splitting, centroid shift.

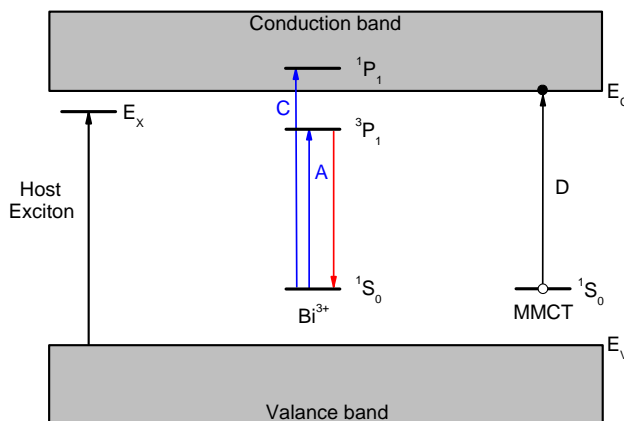


Figure 2: Electronic transitions in Bi^{3+} -doped compounds.

Results and discussion

Controleer toekening A-band en D-band excitaties!

Aim of this paper: show Bi^{3+} energy levels in many compounds. Trends, how do these levels change with respect to chemical environment? Different emission bands, A-, C- and MMCT-band. Different excitations, A-band and MMCT. Difference between MMCT and C-band. In some compounds only MMCT, how to distinguish than between A-band?

- List (table) of all literature data found.
- VRBE schemes of Bi^{3+} in compounds.
- Compare with MMCT-model by Barandiaran *et al.*
- Pieter's model on energy level locations
- MMCT model Boutinaud *et al.*
- Example of concentration quenching (self-quenching/autoquenching)
- Comparison U-parameter and h-parameter: does it work for Bi^{3+} ?
- Stokes shift: calculate and show trends?
- Comparison with Eu and Ce. Eu at -4 eV and almost independent of host. Plot together

as function of U-parameter?

- Paper by Guifang: Y₂O₃ Bi³⁺ with lanthanides, how does sensitization work?
- Nephelauxetic sequence: increasing covalency, large effect on electron energies of 6s² configuration, comparison with lanthanides.
- Shift of peak positions (A-band and MMCT excitations and A-band emission).

-

Data collected for 112 compounds. 7-digit compound identification number⁸

Data VRBE of host compounds from Dorenbos literature.

How does pair or mmct luminescence work? What is the emitting state?

Ju12 gave suggestion for mechanism bismuth sensitization of europium. We show that energy levels of excited state are at around -3.5 eV, matching with europium excited state!

Data on MMCT transition is rather scarce for wide band gap compounds because of limitation in excitation energy of most research group (200 nm limit).

Table 1: Spectroscopic data on Bi³⁺ in compounds.

ID number	Compound (A)	Excitation			Emission		Ref.
		A	C	D	A	CT	
0000000	free ion	75980	114610	–	–	–	9
1190010	BaF ₂	46375	63880	75490	38320	–	10
1190020	SrF ₂	46620	65815	73480	44120	–	10
1190030	CaF ₂	47265	66140	73960	44440	–	10
1190404	NaYF ₄	40330	50010	–	–	22745	11
2290002	RbCl	27780	43860	47620	–	–	12
2290003	KCl	30305	47160	49750	–	–	12
2290004	NaCl	30770	47170	50505	–	–	12
2290041	CsMgCl ₃	35250	–	–	–	23875	13
2290101	Cs ₂ NaLaCl ₆	31455	–	–	29280	–	14
2290401	Cs ₂ NaYCl ₆	31000	–	–	30035	–	15
3390003	KBr	27030	42920	46295	–	–	12
3390071	CsCdBr ₃	34925	–	–	17100	–	13
3390401	Cs ₂ NaYBr ₆	27100	–	–	25490	–	14
4490003	KI	26315	41670	44845	–	–	12
5174020	Sr ₃ AlO ₄ F	32050	–	–	23420	–	16
5190400	YOF	37300	–	50000	30300	–	1
5290100	LaOCl	30000	–	37200	29000	22500	1
5290300	GdOCl	29600	–	38875	22500	20165	17
5290400	YOCl	30100	–	39200	25000	–	1
5390100	LaOBr	–	–	36535	27180	20165	18
5532100	LaP ₃ O ₉	42500	–	–	–	21900	19
5532105	LiLaP ₄ O ₁₂	43555	–	–	–	23310	20

Table 1: Continued

ID number	Compound (A)	Excitation			Emission		Ref.
		A	C	D	A	CT	
5532300	GdP ₃ O ₉	41500	–	–	–	–	19
5532400	YP ₃ O ₉	41500	–	–	34100	–	19
5532500	LuP ₃ O ₉	41500	–	–	34600	–	19
5532600	ScP ₃ O ₉	39500	–	–	35000	–	19
5534100	LaPO ₄	40815	–	57145	–	22220	21
5534400	YPO ₄	44445	–	58820	40985	29850	22
5534500	LuPO ₄	44445	–	–	42375	30030	22
5550013	KBaBP ₂ O ₈	41665	–	–	25840	–	23
5552100	LaB ₃ O ₆	38460	–	–	26315	–	15
5552140	LaMgB ₅ O ₁₀	33785	–	–	29760	–	17,24
5552160	LaZnB ₅ O ₁₀	33560	–	–	29760	–	24
5552170	LaCdB ₅ O ₁₀	33900	–	–	30300	–	24
5552300	GdB ₃ O ₆	–	–	–	–	–	15
5552440	YMgB ₅ O ₁₀	37315	–	–	30675	–	17,24
5552460	YZnB ₅ O ₁₀	37040	–	–	30120	–	24
5552470	YCdB ₅ O ₁₀	37315	–	–	30395	–	24
5554000	GaBO ₃	36215	–	–	34520	23630	25
5554000	InBO ₃	35210	–	–	32895	25000	26
5554035	LiCaBO ₃	32895	–	–	26455	–	27
5554100	LaBO ₃	37260	–	–	27910	21695	28
5554300	GdBO ₃	–	–	–	–	–	28
5554400	YAl ₃ B ₄ O ₁₂	38500	–	–	34500	–	1
5554400	YBO ₃	40485	–	54055	34015	31250	29

Table 1: Continued

ID number	Compound (A)	Excitation			Emission		Ref.
		A	C	D	A	CT	
5554500	LuBO ₃	34840	–	–	31850	–	26
5554600	ScBO ₃	34360	–	–	33390	–	28
5555430	CaYBO ₄	35800	–	–	–	–	30
5555430	Ca ₄ YO(BO ₃) ₃	32260	43480	–	26315	–	31
5563400	Y ₂ Sn ₂ O ₇	35715	–	–	30300	19610	32
5564025	Li ₄ SrCa(SiO ₄) ₂	32260	–	44445	32260	–	33
5564040	MgGeO ₃	34480	–	46510	27780	–	34
5564060	Zn ₂ GeO ₄	33330	–	–	–	19420	35
5564300	Gd ₂ GeO ₅	32260	–	42555	22220	–	36
5564405	LiYSiO ₄	35700	–	–	–	–	30
5565400	Y ₂ SiO ₅	36295	–	–	29035	16750	37
5565500	Lu ₂ SiO ₅	33875	40570	47990	27990	18150	38
5570000	ZnGa ₂ O ₄	27780	–	35715	24390	18520	39
5570100	LaAlO ₃	35090	–	–	26670	–	40
5570100	LaGaO ₃	32570	–	41670	26315	–	41
5570100	LaInO ₃	29400	–	–	23810	–	40
5570300	Gd ₃ Al ₅ O ₁₂	36100	–	–	26180	–	42
5570300	Gd ₃ Ga ₅ O ₁₂	34480	–	–	–	21280	43
5570400	Y ₃ Al ₅ O ₁₂	36495	–	49260	32950	21290	44
5570400	Y ₄ Al ₂ O ₉	33875	–	–	25810	–	45
5570400	YAlO ₃	35690	–	52500	29600	–	46
5570400	Y ₃ Ga ₅ O ₁₂	35200	–	–	31250	23810	47
5570500	Lu ₃ Al ₅ O ₁₂	36970	–	49875	33510	20650	44

Table 1: Continued

ID number	Compound (A)	Excitation			Emission		Ref.
		A	C	D	A	CT	
5573300	Gd ₂ GaSbO ₇	34480	–	–	27030	–	48
5581030	CaMoO ₄	–	–	30900	–	17540	5
5582030	CaWO ₄	–	–	34845	–	21370	49
5582060	ZnWO ₄	–	–	29410	–	17860	50
5582070	CdWO ₄	–	–	28570	–	18180	50
5582400	Y ₂ WO ₆	–	–	29300	–	19400	1
5583100	LaVO ₄	–	–	30860	–	18215	5
5583300	GdVO ₄	–	–	30490	–	17985	51
5583400	YVO ₄	–	–	30030	–	17545	51
5583500	LuVO ₄	–	–	29850	–	17360	52
5583600	ScVO ₄	–	–	28170	21505	15750	53
5584030	CaNb ₂ O ₆	–	–	31300	19610	–	5
5584100	LaNbO ₄	–	–	32790	24390	–	54
5584300	GdNbO ₄	–	–	32575	22470	–	55
5584400	YNbO ₄	–	–	31850	22520	18520	56
5585300	GdT _a ₇ O ₁₉	32260	–	–	20835	–	57
5585400	YT _a O ₄	34480	–	40000	23810	–	58
5586030	CaTiO ₃	–	–	27030	–	17240	59
5586400	Y ₂ Ti ₂ O ₇	–	–	31250	–	18180	22
5587030	CaZrO ₃	31250	–	–	25640	–	40
5587100	La ₂ Zr ₂ O ₇	34480	–	40820	25975	19420	60
5588030	CaHfO ₃	32500	–	–	26200	–	47
5589110	BaLa ₂ ZnO ₅	31250	–	37040	24390	–	61

Table 1: Continued

ID number	Compound (A)	Excitation			Emission		Ref.
		A	C	D	A	CT	
5590020	SrO	27260	–	37910	22990	–	62
5590030	CaO	28935	–	36455	25445	–	9
5590100	La ₂ O ₃	32470	–	40160	21980	20835	51
5590104	NaLaO ₂	28500	–	–	18000	–	63
5590300	Gd ₂ O ₃	28820	–	–	23530	18450	64
5590304	NaGdO ₂	29100	–	39500	26000	–	63
5590305	LiGdO ₂	30200	–	38900	21700	–	63
5590400	Y ₂ O ₃	30100	–	38000	24400	20800	1
5590404	NaYO ₂	28300	–	39400	26000	–	63
5590405	LiYO ₂	30800	–	–	18000	–	63
5590500	Lu ₂ O ₃	26860	–	30380	24800	19520	51
5590504	NaLuO ₂	28400	–	39100	26100	–	63
5590505	LiLuO ₂	30300	–	–	19500	–	63
5590600	Sc ₂ O ₃	29840	–	37100	24600	19840	65
5590604	NaScO ₂	27700	–	38700	26200	–	63
5590605	LiScO ₂	31600	–	39500	24700	–	63
6690020	SrS	23230	–	30245	20970	12500	62
6690030	CaS	24270	28795	32020	22220	16530	9
6690040	MgS	24035	28550	30890	22885	–	66
7790030	CaSe	22100	25970	29035	20200	15625	9

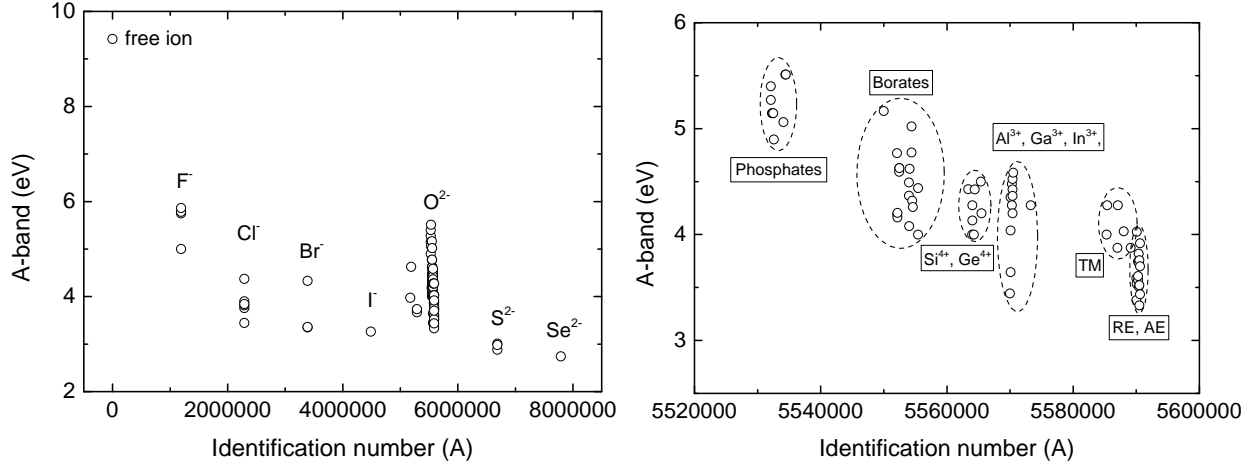


Figure 3: The A-band energies of Bi^{3+} in compounds.

Fig. 3 shows a decrease in the A-band absorption energy as function of the compound identification number (A). The strong decrease in the A-band transition energy from 9.4 eV in the free bismuth ion to 2.7 eV in selenide compounds is caused by a strong crystal field interaction of the 6s-electron with the chemical environment. The decrease follows the nephelauxetic sequence⁶⁷

$$\text{F}^- < \text{O}^{2-} < \text{Cl}^- < \text{Br}^- < \text{I}^- < \text{S}^{2-} < \text{Se}^- \quad (1)$$

$$\text{P}^{5+} < \text{B}^{3+} < \text{Si}^{4+} < \text{Al}^{3+} < \text{RE}^{3+} < \text{AE}^{2+} \quad (2)$$

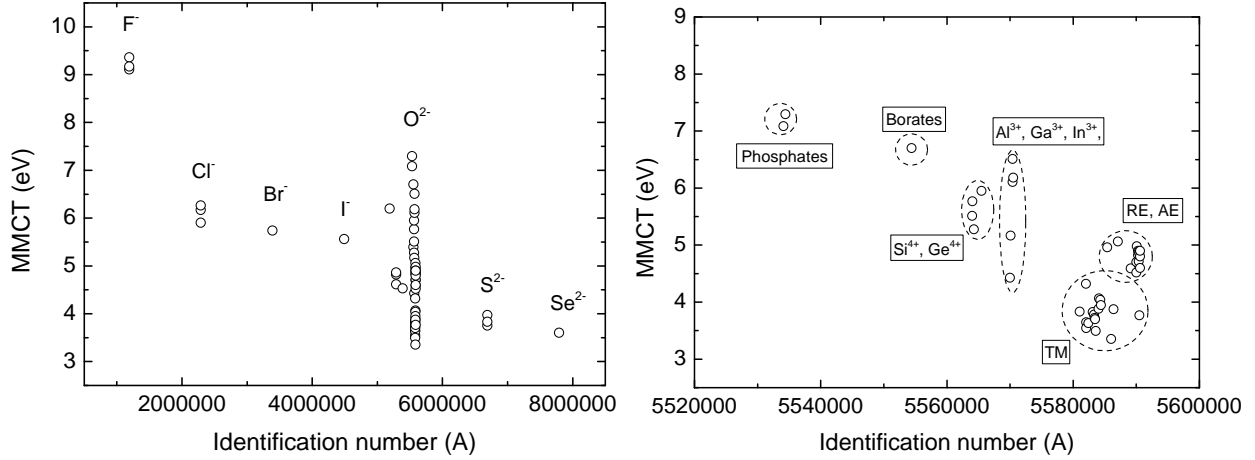


Figure 4: The MMCT energies of Bi^{3+} in compounds.

Eu^{3+} charge transfer energies in compounds⁶⁸

For Bi^{3+} doped in compounds containing transition metals (titanates, vanadates, niobates, tantalates, molybdates and tungstates) broad excitation and emission bands are observed. This is typical for charge transfer type of transition and was also observed by Boutinaud *et al.*⁵ These type of compounds have a low lying conduction band bottom and therefore in most of these compounds no interconfigurational transitions (A- or C-band) are observed, since the $^3\text{P}_1$ state is located inside or close to the conduction band bottom.

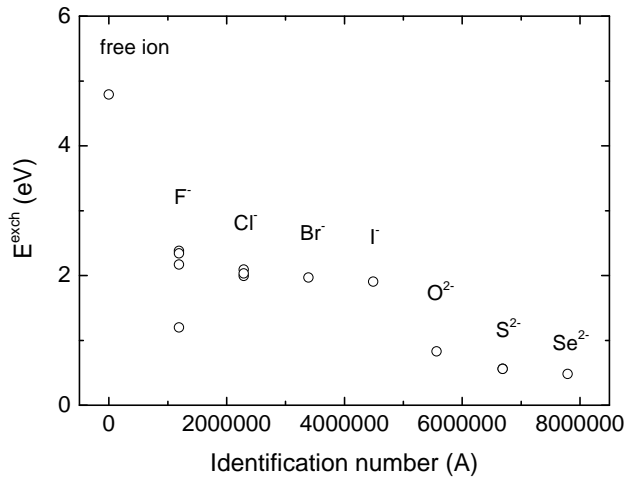


Figure 5: The exchange energies (E^{exch}) of Bi^{3+} in compounds.

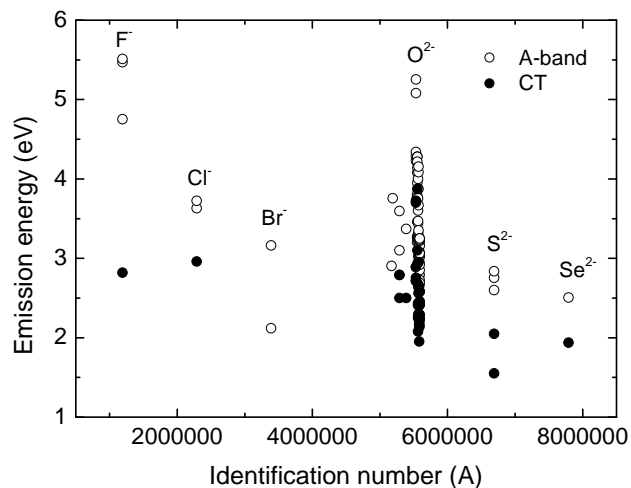


Figure 6: The A-band and CT emission energies in compounds.

The fact that the MMCT/pair emission is rather constant could indicate that the emission is not from cation-Bi³⁺ luminescence transition but from bismuth pairs (IVCT).

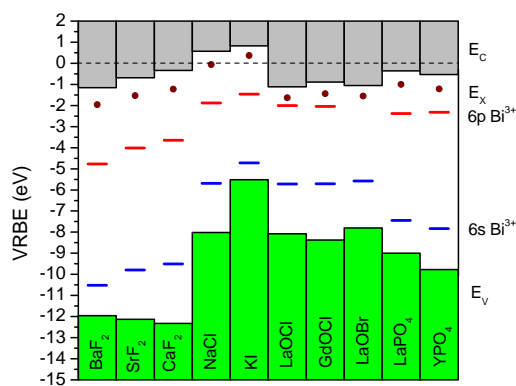


Figure 7: The vacuum referred binding energies of Bi³⁺ in compounds.

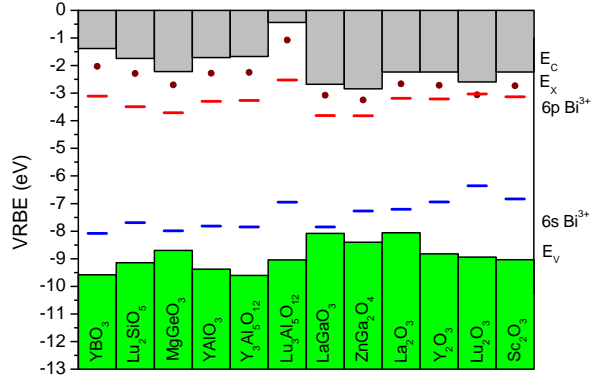


Figure 8: The vacuum referred binding energies of Bi^{3+} in compounds.

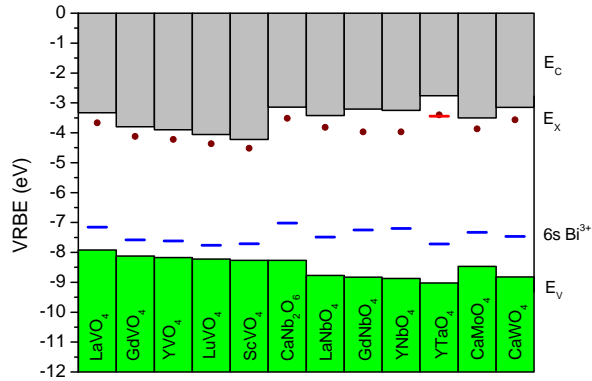


Figure 9: The vacuum referred binding energies of Bi^{3+} in compounds.

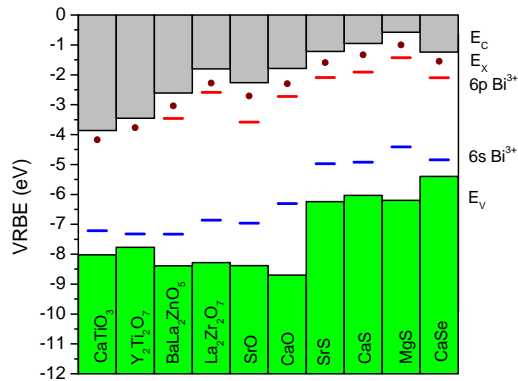


Figure 10: The vacuum referred binding energies of Bi^{3+} in compounds.

The chemical shift of the 6s-electron binding energy towards higher energy (less binding) as compared to the binding energy in the gaseous bismuth ion (free ion) is introduced by the crystal field of the host compound.

Conclusions

Acknowledgments

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Graphical TOC Entry

