The Bi^{3+} 6s and 6p electron binding energies in relation to the chemical environment of inorganic compounds

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Vacuum Referred Binding Energies of Bi^{3+} in Insulators Based on the Metal-to-Metal Charge Transfer Energy

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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 $^1S_0$ ground state. Optical transitions to the $6s^16p^1$ configuration result in the $^3P_{0,1,2}$ triplet and $^1P_1$ singlet excited states (in order of increasing energy). The optical transitions from the $^1S_0$ ground state to the $^3P_1$, $^3P_2$ and $^1P_1$ excited states are labeled A, B and C, respectively (see Fig. 1). The $^1S_0 \rightarrow {}^3P_0$ and $^1S_0 \rightarrow {}^3P_2$ are spin-forbidden, although the transition to the $^3P_2$ can be induced by coupling with unsymmetrical lattice vibrational modes.[2] As a result of spin-orbit coupling and mixing with the $^1P_1$ state, the $^1S_0 \rightarrow {}^3P_1$ transition becomes allowed. The $^1S_0 \rightarrow {}^1P_1$ 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 $Bi^{3+}/M^{n+} \rightarrow Bi^{4+}/M^{(n-1)+}$. 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]

MMCT[7]

Location of energy levels determines optical properties and performance of devices. Comparison 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.

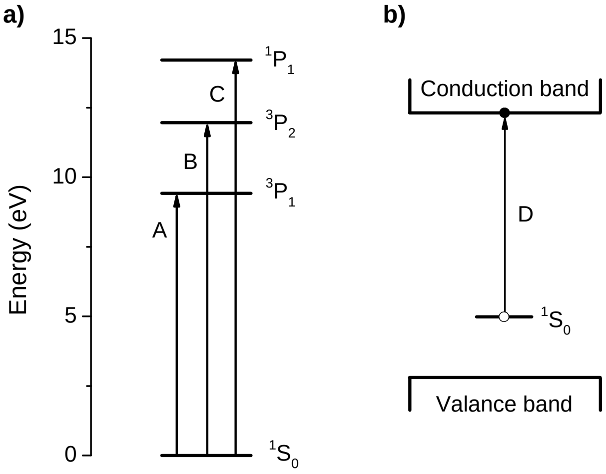

Figure 1: The energy levels of the free Bi^{3+} ion.

- Main focus paper: using MMCT to locate Bi3+ 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 Pr3+ and Tb3+.

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

Dorenbos model: chemical shift, optical depression Ce3+, VRBE

Redshift model, charge transfer model

Crystal field splitting and centroid shift only for Ce3+ or also applicable for Bi3+?

- Lanthanide free, which are expensive and only produced in China.
- How does s2 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 ns2 ions in halides
- Optical electro negativity (Duffy)

Methodology

- How to locate bismuth energy levels? MMCT, A, C bands. B-band in most compounds to 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.

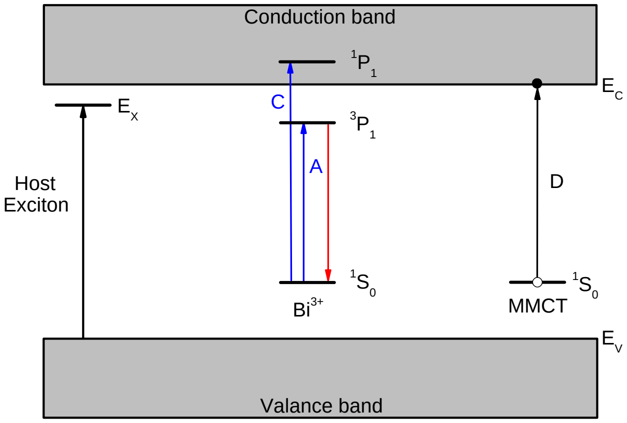

Figure 2: Electronic transitions in Bi^{3+}-doped compounds.

Results and discussion

Controleer toekenning A-band en D-band excitaties!

Aim of this paper: show Bi3+ 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 Bi3+?
- 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 covalancy, 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 number[8]
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 scars for wide band gap compounds because of limitation in excitation energy of most research group (200 nm limit).

Table 1: Spectroscopic data on Bi^{3+} in compounds.

ID number	Compound (A)	Excitation A	Excitation C	Excitation D	Emission A	Emission CT	Ref.
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	$Cs_2NaLaCl_6$	31455	–	–	29280	–	14
2290401	Cs_2NaYCl_6	31000	–	–	30035	–	15
3390003	KBr	27030	42920	46295	–	–	12
3390071	$CsCdBr_3$	34925	–	–	17100	–	13
3390401	Cs_2NaYBr_6	27100	–	–	25490	–	14
4490003	KI	26315	41670	44845	–	–	12
5174020	Sr_3AlO_4F	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_3O_9	42500	–	–	–	21900	19
5532105	$LiLaP_4O_{12}$	43555	–	–	–	23310	20

Table 1: Continued

ID		Excitation			Emission		
number	Compound (A)	A	C	D	A	CT	Ref.
5532300	GdP_3O_9	41500	–	–	–	–	[19]
5532400	YP_3O_9	41500	–	–	34100	–	[19]
5532500	LuP_3O_9	41500	–	–	34600	–	[19]
5532600	ScP_3O_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	$KBaBP_2O_8$	41665	–	–	25840	–	[23]
5552100	LaB_3O_6	38460	–	–	26315	–	[15]
5552140	$LaMgB_5O_{10}$	33785	–	–	29760	–	[17,24]
5552160	$LaZnB_5O_{10}$	33560	–	–	29760	–	[24]
5552170	$LaCdB_5O_{10}$	33900	–	–	30300	–	[24]
5552300	GdB_3O_6	–	–	–	–	–	[15]
5552440	$YMgB_5O_{10}$	37315	–	–	30675	–	[17,24]
5552460	$YZnB_5O_{10}$	37040	–	–	30120	–	[24]
5552470	$YCdB_5O_{10}$	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	$YAl_3B_4O_{12}$	38500	–	–	34500	–	[1]
5554400	YBO_3	40485	–	54055	34015	31250	[29]

Table 1: Continued

ID		Excitation			Emission		
number	Compound (A)	A	C	D	A	CT	Ref.
5554500	$LuBO_3$	34840	–	–	31850	–	[26]
5554600	$ScBO_3$	34360	–	–	33390	–	[28]
5555430	$CaYBO_4$	35800	–	–	–	–	[30]
5555430	$Ca_4YO(BO_3)_3$	32260	43480	–	26315	–	[31]
5563400	$Y_2Sn_2O_7$	35715	–	–	30300	19610	[32]
5564025	$Li_4SrCa(SiO_4)_2$	32260	–	44445	32260	–	[33]
5564040	$MgGeO_3$	34480	–	46510	27780	–	[34]
5564060	Zn_2GeO_4	33330	–	–	–	19420	[35]
5564300	Gd_2GeO_5	32260	–	42555	22220	–	[36]
5564405	$LiYSiO_4$	35700	–	–	–	–	[30]
5565400	Y_2SiO_5	36295	–	–	29035	16750	[37]
5565500	Lu_2SiO_5	33875	40570	47990	27990	18150	[38]
5570000	$ZnGa_2O_4$	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	$Gd_3Al_5O_{12}$	36100	–	–	26180	–	[42]
5570300	$Gd_3Ga_5O_{12}$	34480	–	–	–	21280	[43]
5570400	$Y_3Al_5O_{12}$	36495	–	49260	32950	21290	[44]
5570400	$Y_4Al_2O_9$	33875	–	–	25810	–	[45]
5570400	$YAlO_3$	35690	–	52500	29600	–	[46]
5570400	$Y_3Ga_5O_{12}$	35200	–	–	31250	23810	[47]
5570500	$Lu_3Al_5O_{12}$	36970	–	49875	33510	20650	[44]

Table 1: Continued

ID		Excitation			Emission		
number	Compound (A)	A	C	D	A	CT	Ref.
5573300	Gd_2GaSbO_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_2WO_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	$CaNb_2O_6$	–	–	31300	19610	–	[5]
5584100	$LaNbO_4$	–	–	32790	24390	–	[54]
5584300	$GdNbO_4$	–	–	32575	22470	–	[55]
5584400	$YNbO_4$	–	–	31850	22520	18520	[56]
5585300	$GdTa_7O_{19}$	32260	–	–	20835	–	[57]
5585400	$YTaO_4$	34480	–	40000	23810	–	[58]
5586030	$CaTiO_3$	–	–	27030	–	17240	[59]
5586400	$Y_2Ti_2O_7$	–	–	31250	–	18180	[22]
5587030	$CaZrO_3$	31250	–	–	25640	–	[40]
5587100	$La_2Zr_2O_7$	34480	–	40820	25975	19420	[60]
5588030	$CaHfO_3$	32500	–	–	26200	–	[47]
5589110	$BaLa_2ZnO_5$	31250	–	37040	24390	–	[61]

Table 1: Continued

ID number	Compound (A)	Excitation A	Excitation C	Excitation D	Emission A	Emission CT	Ref.
5590020	SrO	27260	–	37910	22990	–	[62]
5590030	CaO	28935	–	36455	25445	–	[9]
5590100	La_2O_3	32470	–	40160	21980	20835	[51]
5590104	$NaLaO_2$	28500	–	–	18000	–	[63]
5590300	Gd_2O_3	28820	–	–	23530	18450	[64]
5590304	$NaGdO_2$	29100	–	39500	26000	–	[63]
5590305	$LiGdO_2$	30200	–	38900	21700	–	[63]
5590400	Y_2O_3	30100	–	38000	24400	20800	[1]
5590404	$NaYO_2$	28300	–	39400	26000	–	[63]
5590405	$LiYO_2$	30800	–	–	18000	–	[63]
5590500	Lu_2O_3	26860	–	30380	24800	19520	[51]
5590504	$NaLuO_2$	28400	–	39100	26100	–	[63]
5590505	$LiLuO_2$	30300	–	–	19500	–	[63]
5590600	Sc_2O_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]

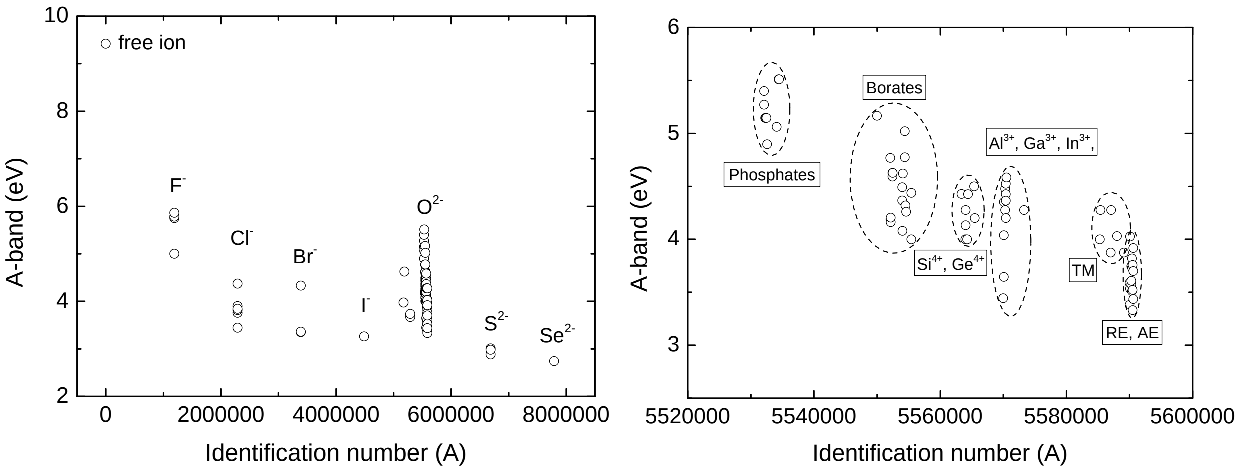

Figure 3: The A-band energies of Bi^{3+} in compounds.

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 sequence[67]

$$\mathrm{F^{-} < O^{2-} < Cl^{-} < Br^{-} < I^{-} < S^{2-} < Se^{-}} \tag{1}$$

$$\mathrm{P^{5+} < B^{3+} < Si^{4+} < Al^{3+} < RE^{3+} < AE^{2+}} \tag{2}$$

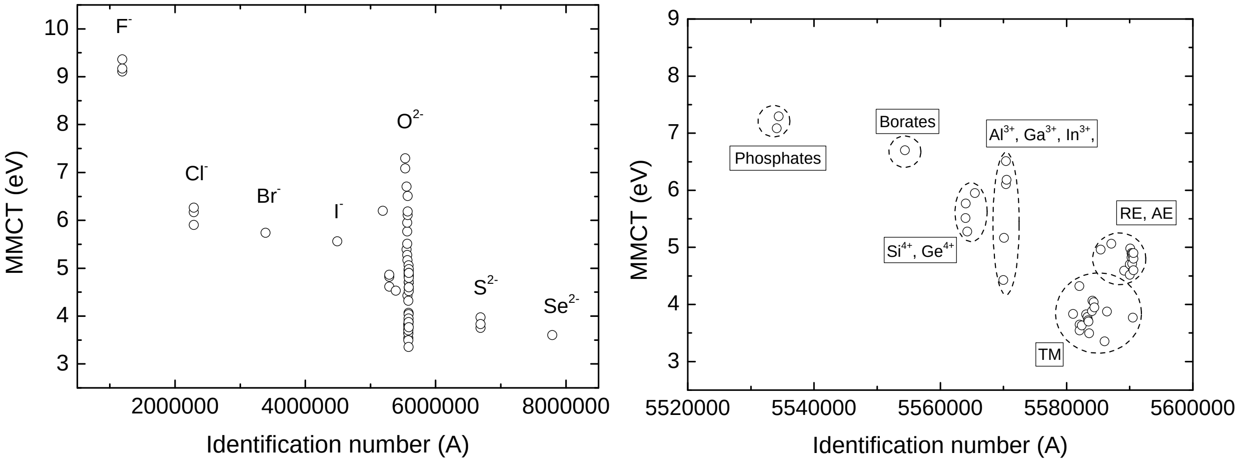

Figure 4: The MMCT energies of Bi^{3+} in compounds.

Eu^{3+} charge transfer energies in compounds[68]

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 $^3P_1$ state is located inside or close to the conduction band bottom.

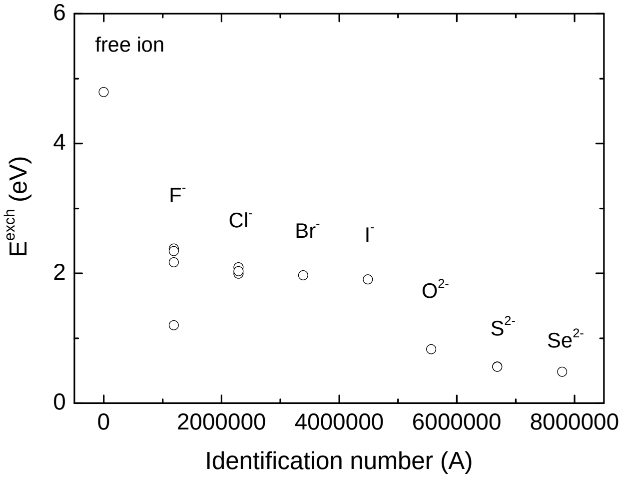

Figure 5: The exchange energies (E^{exch} of Bi^{3+} in compounds.

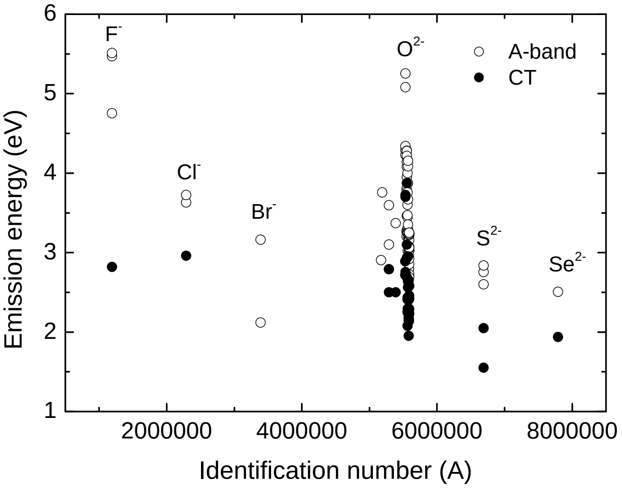

Figure 6: The A-band and CT emission energies in compounds.

The fact that the MMCT/pair emission is rather constant could indicate that the emission is not from cation-Bi^{3+} luminescence transition but from bismuth pairs (IVCT).

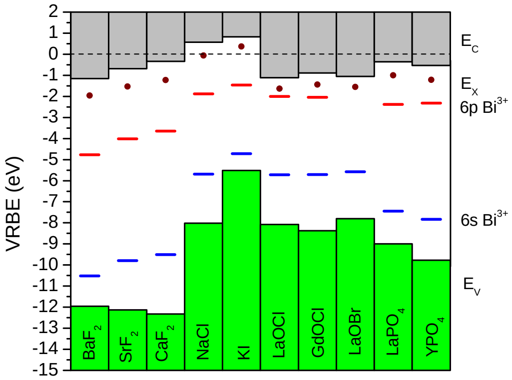

Figure 7: The vacuum referred binding energies of Bi^{3+} in compounds.

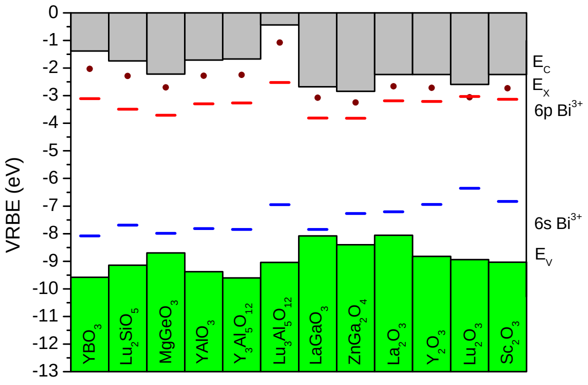

Figure 8: The vacuum referred binding energies of Bi^{3+} in compounds.

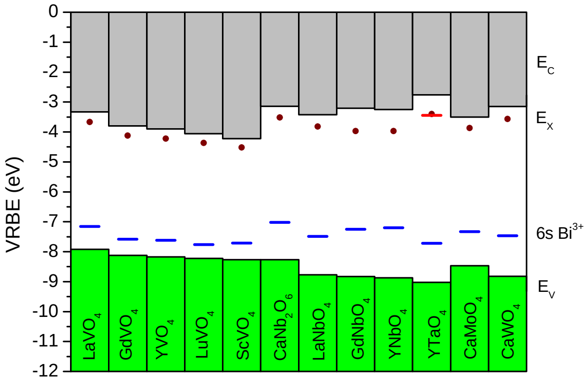

Figure 9: The vacuum referred binding energies of Bi^{3+} in compounds.

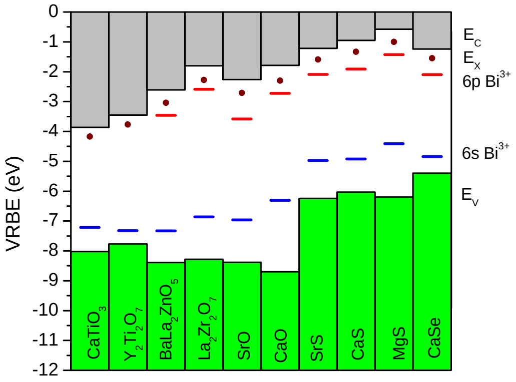

Figure 10: The vacuum referred binding energies of Bi^{3+} in compounds.

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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