Prediction and assignment of site occupation and energy levels for Pb^{2+} ions in crystal hosts

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ABSTRACT

The environmental factor h_e of the host was calculated quantitatively in Pb^{2+}-doped 23 compounds based on the dielectric theory of chemical bond for complex crystals. The relationship between the A band energy E_A of Pb^{2+} and the environmental factor h_e was intensively studied. The results indicate that E_A of Pb^{2+} decreases linearly with increasing of h_e. A linear model was proposed which allows us to correctly predict and assign the site occupations and the position of A band for Pb^{2+}-doped compounds if the crystal structure and the refraction index were known. Applied to $SrGa_2O_4:Pb^{2+}$, $CaAl_2B_2O_7:Pb^{2+}$ and $SrAl_2B_2O_7:Pb^{2+}$, the theoretical predictions are in very good agreement with the experimental data. In $SrGa_2O_4:Pb^{2+}$, the excitation spectrum of Pb^{2+} from two different cation sites was identified: the higher energy band of A (265 nm) from the site of Sr2, and the lower ones (280 nm) from the site of Sr1.

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1. Introduction

Spectroscopic properties of Pb^{2+} in different hosts have been extensively investigated because it is an effective activator for luminescence materials widely used in sun-tan lamps, X-ray phosphors or scintillators, etc. [1–7]. Lead(II) ions, belongs to the mercury isoelectronic ions series, such as Ag^-, Hg^0, Tl^+, Sn^{2+}, and Bi^{3+}, whose electronic configuration is $6s^2$ in the fundamental state (level $^1S_0$) and in the first excited state $6s6p$ (level $^1P_1$, $^3P_{0,1,2}$) [8]. Usually, the luminescence of the Pb^{2+} ions is described by the $^1S_0 \rightarrow {}^3P_{1,2} + {}^1P_1$, transitions, which originate from the $6s^2 \rightarrow 6s6p$ interconfigurational transition. In absorption spectrum the transitions from the $^1S_0$ ground state to the $^3P_1$, $^3P_2$ and $^1P_1$ excited states are labeled in the order of increasing energy by A, B and C bands [9]. These transitions are quite diverse and depend strongly on the environmental conditions of Pb^{2+} in a host, since they are involved with transitions between the outer electron shells, and ligand wavefunctions will admix into the sp excited state of Pb^{2+} [10,11]. For example, in the crystal of $KMgF_3:Pb^{2+}$, the A band position at 187 nm ($53,476\,cm^{-1}$, 10 K) [9], but in $PbMoO_4$, the position of A band was 353 nm ($28,310\,cm^{-1}$, 77 K) [12]. In principle the spectroscopy of alkali halide phosphors doped with ns^2 ions is well understood [8]. The influence of the

host lattice on these properties is drastic which fact is considerably less understood [13].

Over the past decades, many attempts have been made to understand how the positions of energy levels are related to the crystalline environment [8,14–26]. According to Jörgensen's investigation, the large variation in absorption spectra of Pb^{2+} was attributed to the nephelauxetic effect [20]. Jörgensen found that the nephelanxetic ratio β can be expressed as: $\beta = 1 - hk$, where h relates to the ligands and k to the central metal. Duffy and Ingram [21] have proposed a quantitative relation between the position of $^1S_0 \rightarrow {}^3P_1$ transition of ns^2 ions and Jörgensen's h functions. Blasse [22] and Bruce and Duffy [23] investigated the relationship between ns^2 ions $^1S_0 \rightarrow {}^3P_1$ transition as well as Eu^{3+} CT transition energy and h, obtained some significant results. However, the detailed factors entering h was not obtained by them. Gao and Zhang [24] studied the mechanism of the nephelauxetic effect for the electronic structure of 3d elements and identified the main factors responsible for the effect. These are: the covalency of chemical bond, polarizabilities of ligand bond volume for the host and the valence and spin state of the center ion. Recently, the environmental factor was revised for the lanthanide ions by our group [25]. We successfully explained the energy difference between the spin-allowed and spin-forbidden states of Tb^{3+} in crystals [25] as well as the barycenter of energy of lanthanide $4f^{N-1}5d$ configuration in inorganic crystals [26]. To our knowledge, there is a quantitative relationship between h_e and the microscopic chemical bond parameters. So, we think that the effective method for studying the quantitative

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relationships between the position of A band of Pb^{2+} and the structure of host lattices is the constituent chemical bonds of crystal materials.

In this paper, according to the experimental data and dielectric chemical bond theory [24–28], major factors of the environment influencing the position of the A band are given to be the chemical bond volume polarizability, fractional covalence of the chemical bond, and presented charge of the nearest anion in the chemical bonds. The empirical expression between the E_A of Pb^{2+} and these three chemical bond parameters was obtained. A new semiempirical model for predicting the A band position and assigning the site occupations of Pb^{2+} in any inorganic crystal was built. This model can help us better understand the sp energy levels of Pb^{2+} in different host lattices. In addition, it is very helpful and useful in search for new divalent lead doped phosphors.

2. Theoretical methods

The dielectric theory of chemical bond for complex crystals [24–28] is based on the theory developed by Phillips and Van Vechten (PV) [29,30]. According to this theory, a complex crystal $A_aB_bD_dG_g$ (crystal molecular formula) can be written as a linear combination of the subformula of various binary crystals when the crystal structure is known. The subformula of any kind of chemical bond A–B can be written as

$$\frac{N(B-A).a}{N_{CA}}A\frac{N(A-B).b}{N_{CB}}B \tag{1}$$

where A, B, D and G represent the different constituents or different sites of the same element in the crystal formula, and a, b, d and g represent the number of the corresponding elements.

Table 1
Chemical bond parameters relating to the environmental factors and experimental and calculated values of A band of Pb^{2+}.

Crystals	n	Bond	$f_c{}^\mu$	$\alpha_b{}^\mu$ (Å³)	$Q_B\mu$	C.N.	h_e	$E_{A,exp}$ (cm⁻¹)	$E_{A,cal}$ (cm⁻¹)	$\Delta_{error}\%$
CaF₂	1.425	Ca–F	0.0523	0.3110	1	8	0.361	48,780[a]	48,797	−0.034
SrF₂	1.432	Sr–F	0.0466	0.3775	1	8	0.375	50,544[a]	48,428	4.187
BaF₂	1.466	Ba–F	0.0433	0.4925	1	8	0.413	49,020[a]	47,426	3.251
YF₃		Y–F1	0.056	0.4474	1	3	0.455	47,619[a]	46,320	2.728
		Y–F2	0.0562	0.3914	1	6				
LaF₃	1.590	La–F1	0.0288	0.344	1.091	8	0.393	50,000[a]	47,953	4.093
		La–F2	0.0660	0.4493	0.818	2				
		La–F3	0.0660	0.4613	0.818	1				
LiBaF₃	1.544	Ba–F	0.0147	0.1503	1	12	0.163	52,356[a]	54,014	−3.167
KMgF₃	1.428	K–F	0.0218	0.0997	0.5	12	0.081	53,476[a]	56,175	−5.046
		Mg–F	0.0642	0.1712	2	6	0.514	45,900[b]	44,732	2.544
BaY₂F₈	1.498	Ba–F1	0.0044	0.0338	0.667	8	0.159	53,476[a]	54,119	−1.203
		Ba–F2	0.0108	0.0898	0.5	2				
		Ba–F3	0.0607	0.8015	0.5	2				
		Y–F1	0.0070	0.0468	1.5	4	0.376	50,000[a]	48,401	3.197
		Y–F2	0.0155	0.1213	1.125	2				
		Y–F3	0.0872	0.6066	1.125	2				
BaGa₂O₄	1.750*	Ba–O1	0.0681	0.4022	0.667	6	0.986	32,787[c]	32,328	1.400
		Ba–O2	0.0523	0.7157	2	6				
BaAl₂O₄	1.657	Ba–O1	0.0402	0.5260	2	6	0.743	38,462[c]	38,731	−0.699
		Ba–O2	0.0523	0.3191	0.667	6				
SrClF	1.600*	Sr–F	0.0589	0.3810	0.889	4	0.453	45,455[d]	46,372	−2.018
		Sr–Cl	0.0343	0.6357	1.111	5				
BaClF	1.620*	Ba–F	0.0529	0.6077	0.889	4	0.472	45,455[d]	45,872	−0.917
		Ba–Cl	0.0307	0.6380	1.111	5				
SrBrF	1.580*	Sr–F	0.0512	0.3570	0.889	4	0.443	46,512[d]	46,636	−0.266
		Sr–Br	0.0303	0.7427	1.111	5				
BaBrF	1.600*	Ba–F	0.0466	0.4504	0.889	4	0.463	46,512[d]	46,109	0.867
		Ba–Br	0.0279	0.8588	1.111	5				
PbMoO₄	2.320	Pb–O	0.2264	1.0504	0.75	8	1.034	29,310[e]	31,063	−5.981
PbWO₄	2.220	Pb–O	0.2092	0.9778	0.75	8	0.959	32,988[e]	33,039	−0.156
BaWO₄	1.842	Ba–O	0.1191	0.8201	0.75	8	0.663	40,462[f]	40,839	−0.932
CaMoO₄	1.980	Ca–O	0.1764	0.6173	0.75	8	0.700	39,037[g]	39,864	−2.119
Y₃Ga₅O₁₂	1.940	Y–O	0.0860	0.4260	1.5	8	0.812	36,891[h]	36,913	−0.059
Lu₃Al₅O₁₂	1.840	Lu–O	0.0800	0.3822	1.5	8	0.742	39,311[h]	38,757	1.409
SrZnO₂	2.30	Sr–O1	0.0667	0.3479	3	3	0.997	31,546[i]	32,012	−1.476
		Sr–O2	0.3890	0.4231	1.5	1				
CdCl₂	1.700	Cd–Cl	0.0956	1.1485	1	6	0.812	37,088[j]	36,913	0.472
BaZrO₃	2.2	Ba–O	0.0728	0.4613	1	12	0.635	39,461[k]	41,530	−5.243

$\Delta_{error}=(E_{exp}-E_{cal})/E_{exp}$.
The refractive index n of crystals from Refs. 41, some compounds for which n values are unknown and estimated from the isostructural compounds are marked with an asterisk; the experimental values of A band energy from references

[a] Ref. [9].
[b] Ref. [33].
[c] Ref. [34].
[d] Ref. [10].
[e] Ref. [12].
[f] Ref. [3].
[g] Ref. [35].
[h] Ref. [36].
[i] Ref. [6].
[j] Ref. [37].
[k] Ref. [38].

$N(I–J)$ is the number of I ions in the coordination group of a J ion. N_{CA} and N_{CB} are the nearest-coordination numbers for each element in the crystal. Therefore, in a subformula equation of a complex crystal, the charge Q presented by each coordination anion can be obtained from the valence conservation and electric neutrality of the subformula. For any binary crystal A_mB_n, Q_A is the normal valence of the cation A, and Q_B is obtained from $Q_B = mQ_A/n$. For example, given a complex example like YPO_4, we can obtain $YPO_4 = YO_{8/3} + PO_{4/3}$ in terms of Eq. (1). For $YO_{8/3}$, let $Q_Y = 3.0$; then the presented charge of the O ion is $Q_O = 3/8 \times 3 = 1.125$ in the Y–O chemical bond. For $PO_{4/3}$, let $Q_P = 5.0$; the presented charge of the O ion is $Q_O = 3/4 \times 5.0 = 3.75$ in the P–O chemical bond. From that, we can find that the presented charges in various chemical bonds are different.

Having listed the subformula equation of a complex crystal and given the charge presented by each ion, we can obtain the number of effective valence electrons of each ion

$$(Z_A^\mu)^* = Z_A^\mu q_A^\mu \tag{2}$$

where Z_A^μ is the number of valence electrons of the A ion and q_A^μ the effective charge of each valence electron of each A ion.

The effective valence election density associated with the bond μ is

$$(N_e^\mu)^* = (n_e^\mu)^*/v_b^\mu \tag{3}$$

The number of effective valence electrons (n_e^μ) per μ bond is

$$(n_e^\mu)^* = (Z_A^\mu)^*/N_{CA}^\mu + (Z_B^\mu)^*/N_{CB}^\mu \tag{4}$$

The chemical bond volume of type-μ bond v_b^μ (in Å³) is

$$v_b^\mu = (d^\mu)^3 / \sum_v (d^\mu)^3 N_b^v \tag{5}$$

where d^μ is the nearest-neighboring distance (in Å) and the denominator is merely the required normalization factor, and the sum over v runs over all of the different types of bonds. N_b^v is the number of bonds of type v in per cubic centimeters, which can be obtained from the crystal structural data.

According to PV theory [29,30], the susceptibility χ^μ of any bond is described as

$$\chi^\mu = (\hbar\Omega_p^\mu)^2 / 4\pi(E_g^\mu)^2 \tag{6}$$

where Ω_p^μ is the plasma frequency,

$$(\Omega_p^\mu)^2 = [4\pi(N_e^\mu)^* e^2/m]D_\mu A_\mu \tag{7}$$

where D_μ and A_μ are the correction factors defined in [30,31], e and m are the electronic charge and mass, respectively.

In Eq. (6), E_g^μ (in eV) is the average energy band gap, and can be separated into homopolar energy E_h^μ (in eV) and heteropolar energy C^μ (in eV) as shown in the equation below:

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2 \tag{8}$$

where

$$E_h^\mu = 39.74/(d^\mu)^{2.48} \tag{9}$$

$$C^\mu = 14.4b^\mu \exp(-k_s^\mu r_o^\mu)[(Z_A^\mu)^*/(Z_A^\mu)^* - n(Z_B^\mu)^*/r_o^\mu] \tag{10}$$

with

$$r_o^\mu = d^\mu/2 \tag{11}$$

$$k_s^\mu = (4k_F^\mu/\pi a_B)^{1/2} \tag{12}$$

$$k_F^\mu = [3\pi^2(N_e^\mu)^*]^{1/3} \tag{13}$$

Here b^μ is a correction factor depending on the crystal structure, k_s^μ the Thomas–Fermi screening factor, n the number ratio of two elements B and A in the subformula, r_o^μ the average radius between A and B atoms, and a_B the Bohr radius. Once the

refractive index of a crystal is known, the value of b^μ and C^μ can be obtained by using Eqs. (6), (8), (10) and the following equation:

$$\chi = (\varepsilon-1)/4\pi = \sum_\mu F^\mu \chi^\mu = \sum_\mu N_b^\mu \chi_b^\mu \tag{14}$$

where χ is the total linear susceptibility of a crystal, ε the dielectric constant, which can be obtained from the index of refraction, n ($\varepsilon = n^2$). F^μ the fraction of bands of type μ composing the crystal. χ_b^μ the susceptibility of a single bond of type μ.

The fractional ionicity f_i^μ and covalence f_c^μ of the individual bond can be determined as

$$f_i^\mu = (C^\mu)^2/(E_g^\mu)^2 \quad f_c^\mu = (E_h^\mu)^2/(E_g^\mu)^2 \tag{15}$$

According to the Lorentz formula,

$$(\varepsilon^\mu-1)/(\varepsilon^\mu+2) = 4\pi\alpha_o^\mu/3 \tag{16}$$

The polarizability coefficient of the μ-bond, α_o^μ, can be obtained; this denotes the polarizability of the μ bond per cubic ångström. The polarizability of the type-μ bond volume can be written as

$$\alpha_b^\mu = v_b^\mu \alpha_o^\mu \tag{17}$$

If the crystal structure and the refractive index (n) are known, the chemical bond parameters: the bond distance (d^μ); the fractional covalence (f_c^μ); the polarizability of chemical bond volume (α_b^μ) and the charge presented by the nearest anion (Q_B^μ), can be calculated by using the above dielectric theory of chemical bond for complex crystals. It has been successfully found that these three chemical bond parameters relate to the environmental factor (h_e) [25], which can be expressed as

$$h_e = \left[\sum_\mu f_c^\mu \alpha_b^\mu (Q_B^\mu)^2\right]^{1/2} \tag{18}$$

Here, we considered $KMgF_3$ as example. On the basis of the detailed cell parameters of $KMgF_3$ [32], we can calculate the bond distance d^μ of the K–F and Mg–F, which are 2.8143 and 1.9900 Å, respectively; the coordination numbers (C.N.) of K and Mg ions, which are 12 and 6, respectively. According to the mentioned method, $KMgF_3$ can be decomposed into its subformula equations as
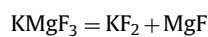
$$KMgF_3 = KF_2 + MgF$$

Then the charge Q_B^μ presented by each coordination anion can be obtained from the valence conservation and electric neutrality
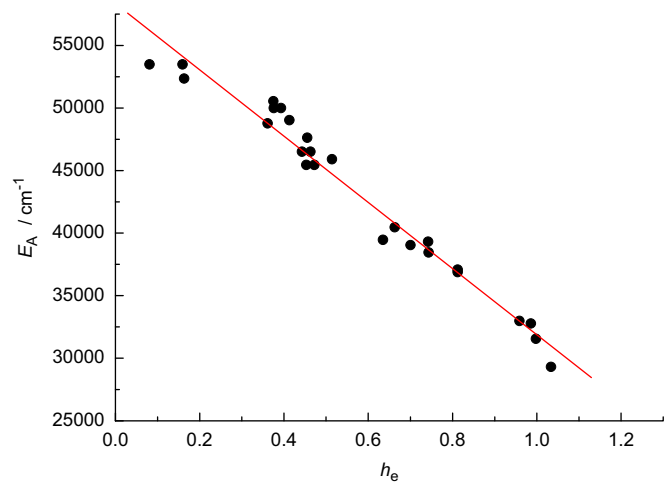

Fig. 1. The relation between the energy of A band E_A and the environmental factors h_e.

of subformula. In this equation, the charge presented by K and Mg equate to their valence charges: 1+ and 2+, respectively. So the charges presented by F ions in the K–F and Mg–F bonds are: $Q_{F-K}=1/2=0.5$ and $Q_{F-Mg}=2/1=2$, respectively. Using the refractive index of $KMgF_3$ $n=1.428$ in Eq. (14); then, E_h^μ and C^μ of K and Mg can be calculated from (6), (8)–(10) and (14): for K, E_h^μ and C^μ are 3.0534 and 20.4364, respectively; for Mg, E_h^μ and C^μ are 7.2122 and 27.5369, respectively. Then, f_c^μ and α_b^μ for K–F and Mg–F bonds can be obtained from (6), (15)–(17): for K–F bond, f_c^μ and α_b^μ are 0.0218 and 0.0997, respectively; for Mg–F bond, f_c^μ and α_b^μ are 0.0642 and 0.1712, respectively. So the environmental factor h_e of $KMgF_3$ can be obtained

The site of K: $h_e=[12\times0.0218\times0.0997\times(0.5)2]^{1/2}=0.081$
The site of Mg: $h_e=[6\times0.0642\times0.1712\times(2)2]^{1/2}=0.514$

3. Results and discussion

The A band energy E_A of Pb^{2+} depends strongly on the nature of the surrounding ions. To investigate the relationship between A band energy and host, the experimental values of E_A in 23 crystals were collected and listed in Table 1 (column 9). It should be noticed that most of these data were measured at temperatures around 10 K, except $BaWO_4:Pb^{2+}$ (RT) [3], $PbMoO_4$ (77 K) [12], $CaMoO_4:Pb^{2+}$ (RT) [35], $Y_3Ga_5O_{12}:Pb^{2+}$ (77 K) [36], $Lu_3Al_5O_{12}:Pb^{2+}$ (77 K) [36], $CdCl_2:Pb^{2+}$ (RT) [37], and $BaZrO_3:Pb^{2+}$ (77 K) [38]. Usually, the position of A band shifts to low energy with increasing temperature due to a shift of the optical absorption edge [10,11]. Therefore, the values for $E_{A,exp}$ which were not measured at 10 K are compiled by adding 1000 cm^{-1} at 77 K or by adding 2000 cm^{-1} at RT. Additionally, the chemical bond parameters and environmental factors for the 23 corresponding compounds were calculated using the theory mentioned above. The results are compiled in Table 1.

The second column shows values of the refractive index n. Columns 4–8 give the parameters: the covalency of the chemical bond (f_c^μ), the polarizability of the chemical bond volume (α_b^μ), the presented charge of the nearest anion (Q_B^μ), the coordination number of the central ion (C.N.), and the environmental factor (h_e), respectively. The relationship between the A band energy E_A and the environmental factor h_e is shown in Fig. 1. It is certainly found that E_A decreases with the increase of h_e. A linear relation between E_A and h_e can be simulated and expressed as

$$E_A = 58336 - 26466 h_e \qquad (19)$$

By using expression (19), E_A of Pb^{2+} ion was calculated for the 23 crystals and listed in column 10 of Table 1. It shows that the calculated values of E_A agree satisfactorily with the experimental data. The maximum error between the experimental and calculated values is 1660 cm^{-1} for $PbMoO_4$, the error ratio is only -5.664%. The last column represents the error ratio, which is almost within 3%. The error may be due to uncertainties in experimental measurements, for instance, different measuring temperature and monitoring wavelength. Moreover, according to literature [7], the different concentrations of Pb^{2+} can lead to changes in crystal lattice parameters and spectrum peak position, which may also contribute the error.

4. Applications

From the above discussion, it can be concluded that the A band energy of Pb^{2+} has a direct relationship with the environmental factor, and a good empirical formula between h_e and E_A is obtained. Therefore, we consider that the current computational method can serve as a prediction tool and can be applied to the predictions of A band position and clarifies the site occupation for Pb^{2+}. The applications of our model in these fields are presented in this section.

Table 2
Chemical bond parameters relating to the environmental factors and comparison between theoretical calculated $E_{A,cal}$ and experimental $E_{A,exp}$.

crystals	n	Bond	f_c^μ	α_b^μ (Å^3)	$Q_B\mu$	C.N.	h_e	$E_{A,exp}$ (cm^{-1})	$E_{A,ca\,1}$(cm^{-1})	$\Delta_{error}\%$
$CaAl_2B_2O_7$	1.563[a]	Ca–O1	0.1373	0.5593	1	6	0.679	40,168[b]	40,366	−0.492
$SrAl_2B_2O_7$	1.570[a]	Sr–O1	0.1199	0.7213	1	6	0.720	38,101[b]	39,280	−3.096

$\Delta_{error}=(E_{exp}-E_{cal})/E_{exp}$.
[a] The refractive index n of crystals from Ref. [41].
[b] The experimental values from Ref. [42].

Table 3
Chemical bond parameters relating to the environmental factors and comparison between theoretical calculated $E_{A,cal}$ and experimental $E_{A,exp}$.

Crystals	n	Bond	f_c^μ	α_b^μ (Å^3)	Q_B^μ	C.N.	h_e	$E_{A,exp}$ (cm^{-1})	$E_{A,cal}$ (cm^{-1})	$\Delta_{error}\%$
$SrGa_2O_4$	1.752[a]	Sr1–O1	0.1714	0.823	1	1	0.874	35,714	35,205	1.426
		Sr1–O2	0.1681	0.9861	1	1				
		Sr1–O4	0.1706	0.8555	1	1				
		Sr1–O5	0.0859	0.8245	1.333	1				
		Sr1–O6	0.0887	0.5784	1.333	1				
		Sr1–O7	0.0885	0.592	1.333	1				
		Sr2–O3	0.1705	0.8587	1	1	0.812	37,736	36,846	2.360
		Sr2–O5	0.0896	0.5274	1.333	1				
		Sr2–O6	0.0858	0.829	1.333	1				
		Sr2–O7	0.0897	0.5187	1.333	1				
		Sr2–O8	0.0869	0.7112	1.333	2				

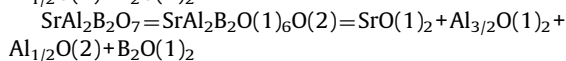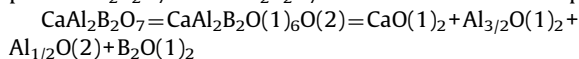$\Delta_{error}=(E_{exp}-E_{cal})/E_{exp}$.
[b] The experimental values from Ref. [34].
[a] The refractive index n of the crystal from Ref. [41].

4.1. Prediction A band position

One of the important applications of our model is to predict and assign the energy E_A of Pb^{2+} in different crystals. Hereafter, we will take the aluminum borates $CaAl_2B_2O_7:Pb^{2+}$ and $SrAl_2B_2O_7:Pb^{2+}$ as examples to demonstrate our model. They are characterized by having an association of BO_3 triangles, MO_6 octahedra and AlO_4 tetrahedra. The crystal structure of $SrAl_2B_2O_7$ and $CaAl_2B_2O_7$ were reported in detail [39,40].

According to the previous model mentioned, we can decompose $CaAl_2B_2O_7$ and $SrAl_2B_2O_7$ into their subformula equations as

$CaAl_2B_2O_7 = CaAl_2B_2O(1)_6O(2) = CaO(1)_2 + Al_{3/2}O(1)_2 + Al_{1/2}O(2) + B_2O(1)_2$

$SrAl_2B_2O_7 = SrAl_2B_2O(1)_6O(2) = SrO(1)_2 + Al_{3/2}O(1)_2 + Al_{1/2}O(2) + B_2O(1)_2$

Using the known refractive index of $CaAl_2B_2O_7$ $n=1.563$, $SrAl_2B_2O_7$ $n=1.57$ [41], the detailed bond parameters and h_e of each type of bond were calculated and their values are listed in Table 2. On the basis of Eq. (19), the E_A of $CaAl_2B_2O_7:Pb^{2+}$ and $SrAl_2B_2O_7:Pb^{2+}$ are predicted to be 40,366 and 39,280 cm^{-1}. The experimental data of $CaAl_2B_2O_7:Pb^{2+}$ and $SrAl_2B_2O_7:Pb^{2+}$ were recorded at RT [42], so these data were estimated by adding 2000 cm^{-1} according to the treatment of experimental values at RT in Table 1. The corresponding data are displayed in column 9 of Table 2. It can be seen that the theoretical values (40,366 and 39,280 cm^{-1}) are almost close to the experimental values (40,168 and 38,101 cm^{-1}). The error ratios were -0.492% and -3.096%, respectively. And the experimental values E_A also decrease with the increase of h_e, which show the same tendency as shown in Fig. 1. That is to say, Eq. (19) demonstrates an excellent predictive power. For any compound, if the structure and the refractive index n are known, by using the dielectric theory of chemical bond for complex crystals theory, the environmental factor h_e of the crystal can be calculated, then the A band energy of Pb^{2+} can be predicted by the empirical formula (19).

4.2. Clarify the site occupation

Another most important application of our model is to clarify the site occupation of Pb^{2+} when Pb^{2+} occupies more than one different site in lead (II)-doped complex. For the past decades, a lot of studies had been focused on the host lattice dependence of the luminescence of s^2 ions [3–5,9,34,38]. Compared to the effort devoted to experimental work, theoretical studies of the site selective spectrum have been very limited, and the spectrum assignments were rather tentative. Here we chose $SrGa_2O_4:Pb^{2+}$ as an example to demonstrate the application of our model. The structure of $SrGa_2O_4$ is monoclinic (space group $P\,1\,2_1/c\,1$, $Z=8$) with $a=8.392$ Å, $b=9.018$ Å, $c=10.697$ Å, $\beta=93.9°$ [43], and there are two Sr sites available for Pb^{2+}, which occur in equal amounts [34]. Both distinct Sr atoms are coordinated with six oxygen atoms. In experiment, two values for E_A of Pb^{2+} were reported and they are 265 nm (37,736 cm^{-1}, 4.2 K) and 280 nm (35,714 cm^{-1}, 4.2 K), respectively [34], it is very difficult to clarify which sites they come from through the experiments. However, on the basis of the crystal structure data [43], $SrGa_2O_4$ can be decomposed into a linear combination of the subformula of various binaries. The useful chemical parameters and environmental factor h_e is listed in Table 3.

Using Eq. (19), the calculated values for E_A of Pb^{2+} occupying Sr1 and Sr2 sites were 35,205 and 36,846 cm^{-1}, respectively. They are in very good agreement with the experiment (35,714 and 37,736 cm^{-1}). Therefore, on the basis of our model, it can be concluded that the experimental results of 265 nm (37,736 cm^{-1}, 4.2 K) and 280 nm (35,714 cm^{-1}, 4.2 K) were from Sr2 and Sr1 sites, respectively.

5. Conclusions

In conclusion, we have used dielectric theory of the chemical bond for complex crystals to study the relationship between the position of the A band for Pb^{2+} and the crystalline environment to obtain a useful tool to correctly predict and assign the site occupations and the energy level of Pb^{2+}-doped compounds. It is found that three microcosmic factors should be met to confirm the A band energy of Pb^{2+}: the chemical bond volume polarizability, the fractional covalency of the chemical bond between the central ion and the nearest anion, and the charge presented by the nearest anion. A new factor which contains these three factors was defined as environmental factor (h_e). A good empirical formula between h_e and E_A is obtained. The calculated results are in good agreement with the experimental values, the maximal error is 1660 cm^{-1} for $PbMoO_4$, and the error ratio is only -5.664%. For any crystal, if the structure and refractive index n are known, E_A of Pb^{2+} can be calculated by our method. Applied to the $CaAl_2B_2O_7:Pb^{2+}$, $SrAl_2B_2O_7:Pb^{2+}$ and $SrGa_2O_4:Pb^{2+}$, the results indicated that the calculated values excellently agree with the experimental data. More importantly, using our model, the site occupation of Pb^{2+} in lead(II)-doped complex compounds can be assigned accurately. For instance, two excitation bands, peaking at 265 and 280 nm of $SrGa_2O_4:Pb^{2+}$, are concluded to arise from the Sr2 and Sr1 sites, respectively. This is especially important for an interpretation of the luminescence properties of Pb^{2+} in complex crystals. In addition, this model can help us better understand the relationship between sp energy level of any other ns^2 ions (e.g., Tl^+, Sn^{2+} and Bi^{3+}) and the structure of the crystals. Further systematic studies are underway.

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