



A Semiempirical Model to Predict and Assign Site Occupation and sp Level of Pb^{2+} in Fluorides

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Information on the position of A , B , and C bands of Pb^{2+} in 10 different fluoride compounds was collected. Environmental factors h_e of the fluorides were calculated based on the dielectric theory of chemical bond for complex crystals. The relationships between the A , B , and C band energies of Pb^{2+} and h_e were investigated. Three linear formulas were proposed. They allowed us to predict and assign the A , B , and C band energies of Pb^{2+} -doped compounds and were also useful for identifying different Pb^{2+} -occupied lattice sites. The model predicted that the positions of B and C bands for $LiCaAlF_6:Pb^{2+}$ are 162.9 and 150.9 nm, respectively. In $BaY_2F_8:Pb^{2+}$, the excitation spectrum of Pb^{2+} from two different cation sites was identified: the higher energy bands of A , B , and C from the site of Y^{3+} and the lower ones from the site of Ba^{2+} . For $KMgF_3:Pb^{2+}$, the absorption band at 187 nm from the site of K^+ , not Mg^{2+} , was confirmed; moreover, the band at 218 nm was assigned to the A band of Pb^{2+} in the Mg^{2+} site. In addition, the origin of the B and C bands for $BaY_2F_8:Pb^{2+}$ and $LiBaF_3:Pb^{2+}$ is discussed and reassigned.
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Pb^{2+} ($6s^2$) luminescence center belongs to the so-called ns^2 ions, such as Ag^+ , Cd^0 , Tl^+ , Sn^{2+} , and Bi^{2+} , which have been traditional objects of experimental and theoretical investigation for several decades, and attractive luminescence properties have been found.¹⁻¹⁴ The energy level scheme of the free Pb^{2+} ion shows a ground state 1S_0 and triplet and singlet excited states $^3P_{0,1,2}$ and 1P_1 , respectively (see Fig. 1). At sufficiently low activator concentrations, the presence of Pb^{2+} ions induces four absorption bands in the host crystal. They are labeled in the order of increasing energy, the A , B , C , and D bands. The origin of the A , B , and C bands was first qualitatively explained by Seitz.¹⁵ In the basic Seitz model, the A band is assigned to the $^1A_{1g} \rightarrow ^3T_{1u}$ ($^1S_0 \rightarrow ^3P_1$) transition, the C band is assigned to the $^1A_{1g} \rightarrow ^1T_{1u}$ ($^1S_0 \rightarrow ^1P_1$) transition, and the B band is attributed to the transition $^1A_{1g} \rightarrow ^3E_u + ^3T_{2u}$ ($^1S_0 \rightarrow ^3P_2$) levels. The higher energy D absorption band, which does not fit in the Seitz model, was attributed to a charge-transfer-type transition.^{16,17} The luminescence properties of Pb^{2+} ions are strongly dependent on the host lattice and are markedly sensitive to the environment for its s^2 outer electron configuration.¹⁸⁻²¹

Over the past decades, many attempts have been made to understand the A , B , and C bands. In 1951, quantitative approaches to determine them were taken by Williams on the basis of the ionic model.²² Later, Knox and Dexter suggested that a purely ionic description of the luminescence center was erroneous and that modifications would have to be made to obtain more accurate results.^{23,24} Subsequently, Sugano proposed the use of the molecular orbital in the Seitz model to explain the A , B , and C absorption bands. Starting from the framework, the right value for the ratio of the C -band dipole strength to the A -band dipole strength was obtained.²⁵ Bramanti and Mancini noticed that the Sugano formula is independent of the representation and can also be derived using a vacancy-centered model.²⁶ So, a semiempirical molecular orbital calculation was developed for describing the energy levels by them. They described the positions of the A , B , and C bands by three parameters: W_0 , G , and ζ . The quantity W_0 is the energy difference between the first excited state and the ground state, whereas G and ζ are the exchange and spin-orbit energies, respectively. This approach is conceptually more satisfactory than the ionic one. Fujita investigated the polarized absorption bands of $KH_2PO_4:Tl^+$ and $RbH_2PO_4:Tl^+$. The observed A , B , and C bands are qualitatively explained by taking into account the spin-orbit, crystal field, and electronic vibrations.²⁷ The theoretical models we mentioned above could be

used to illustrate the A , B , and C absorption bands of s^2 ions in different hosts when the observed A , B , and C band positions were known. Unfortunately, none of these models could be used to predict the positions of the A , B , and C bands without the experimental data. To the best of our knowledge, the relationships between the band positions and the host lattice are still poorly understood.

The aim of this work is to study how the positions of the A , B , and C bands are related to the crystalline environment. Once the trends are firmly established, not only qualitatively but also quantitatively, they can help us to better understand the energy levels of Pb^{2+} in different host lattices, and the positions of the A , B , and C bands for a divalent lead in the uninvestigated materials can be predicted. Moreover, a better understanding of the energy levels of Pb^{2+} in different host lattices is helpful and useful in the search for new phosphors. Considering the fact that the energies of these bands depend on the sites occupied by Pb^{2+} , the ligands, and the crystal structures of the host lattices,¹ it is thought that the most effective method for the study of the quantitative relationships between the A , B , and C bands and the structure of the host lattices is the constituent chemical bonds of crystal materials. In the present paper, fluoride crystals doped with lead(II) were chosen to investigate relationships between the three bands and the crystalline environment because fluorides are well suited for the study of spectroscopic properties.²⁸ The experimental data of the A , B , and C bands for lead(II)-doped fluoride compounds were collected.

In this paper, according to the experimental data^{6,7,10} and dielectric chemical bond theory,²⁹⁻³¹ major factors of the environment influencing the positions of the A , B , and C bands 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 band energies of Pb^{2+} and these three chemical bond parameters was obtained.

Theoretical Methods

The dielectric theory of the chemical bond for complex crystals is based on the theory developed by Phillips and Van Vechten.^{32,33} The detailed theoretical method can be found elsewhere.²⁹⁻³¹ In this paper, only a brief description is given. According to this theory, a complex crystal $E_e F_f G_g H_h$ (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 $E-F$ can be written as

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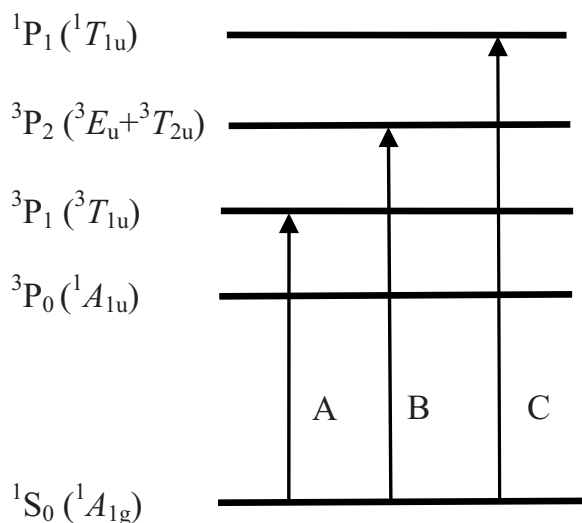


Figure 1. Energy level scheme of a free s^2 ion.

$$\frac{N(F-E)e}{N_{CE}} E \frac{N(E-F)f}{N_{CF}} F \quad [1]$$

where E, F, G, and H represent the different constituents or different sites of the same element in the crystal formula, and e , f , g , and h represent the number of the corresponding elements. $N(I-J)$ is the number of I ions in the coordination group of a J ion. N_{CE} and N_{CF} are the nearest-neighbor 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.

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

$$(Z_E^\mu)^* = Z_E^\mu q_E^\mu \quad [2]$$

where Z_E^μ is the number of valence electrons of the E ion and q_E^μ is the effective charge of each valence electron of each E ion. The effective valence electron density associated with the bond μ is

$$(N_e^\mu)^* = (n_e^\mu)^* / v_b^\mu \quad [3]$$

$$(n_e^\mu)^* = (Z_E^\mu)^* / N_{CE}^\mu + (Z_F^\mu)^* / N_{CF}^\mu \quad [4]$$

$$v_b^\mu = (d^\mu)^3 / \sum_v (d^\mu)^3 N_b^v \quad [5]$$

where $(n_e^\mu)^*$ is the effective number of valence electrons per μ bond, v_b^μ is the bond volume, d^μ is the nearest-neighbor distance (in angstroms) 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. The average energy gap E_g^μ for every μ bond can be separated into homopolar gaps E_h^μ and heteropolar C^μ parts

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2 \quad [6]$$

$$E_h^\mu = 39.74 / (d^\mu)^{2.48} \quad [7]$$

$$C^\mu = 14.4b^\mu \exp(-k_s^\mu r_o^\mu) [(Z_A^\mu)^* / r_o^\mu - w(Z_B^\mu) / r_o^\mu] \quad [8]$$

with

$$r_o^\mu = d^\mu / 2 \quad [9]$$

$$k_s^\mu = (4k_F^\mu / \pi a_B)^{1/2} \quad k_F^\mu = [3\pi^2 (N_e^\mu)^*]^{1/3} \quad [10]$$

Here, w is the number ratio of two elements F and E in the subformula, k_s^μ is the Thomas–Fermi screening factor, a_B is the Bohr radius, and b^μ is a correction factor depending on the crystal structure. The fractional ionicity f_i^μ and covalence f_c^μ of the individual bond can be determined as

$$f_i^\mu = (C^\mu)^2 / (E_g^\mu)^2 \quad f_c^\mu = (E_h^\mu)^2 / (E_g^\mu)^2 \quad [11]$$

According to the Lorentz formula

$$(\epsilon^\mu - 1) / (\epsilon^\mu + 2) = 4\pi\alpha_o^\mu / 3 \quad [12]$$

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

$$\alpha_b^\mu = v_b^\mu \alpha_o^\mu \quad [13]$$

If the crystal structure and the refractive index (n) are known, the bond volume polarizability $\alpha(i)$, the fractional covalence $f_c(i)$ of the chemical bond between the central ion and the nearest anion numbered i , and the presented charge $Q(i)$ of the nearest anions can be calculated by the method mentioned above. The environmental factor designated by the symbol h_e ³⁴ can be expressed as

$$h_e = \left[\sum f_c(i) \alpha(i) Q(i)^2 \right]^{1/2} \quad [14]$$

Results and Discussion

Due to the high optical quality of crystals and their wide transmission range, fluorides are well suited for the study of spectroscopic properties. They have brought a major contribution to the knowledge of luminescence processes.²⁸ In addition, the experimental data of the A, B, and C bands for Pb^{2+} -doped fluoride compounds are very complete compared with other hosts.^{6,7,10} First, we summarize the experimental data of the Pb^{2+} -doped fluoride compounds (see Table I). Next, using the dielectric theory of the chemical bond for complex crystals, we calculate the chemical bond parameters and environmental factors for the corresponding compounds. The calculated values of the environmental factors h_e are compiled in Table I (column 4). Column 2 shows the refractive index n of the crystals.

Figure 2 plots the peak positions of the A, B, and C bands of Pb^{2+} against the environmental factor of fluoride crystals. All of the E_A , E_B , and E_C decrease with the increase in h_e . Three empirical formulas were obtained by fitting the curves and can be written as

$$Pb^{2+} \text{ A band: } E_A = 54,918 - 14,225 \times h_e \quad [15]$$

$$Pb^{2+} \text{ B band: } E_B = 66,567 - 16,730 \times h_e \quad [16]$$

$$Pb^{2+} \text{ C band: } E_C = 73,789 - 24,331 \times h_e \quad [17]$$

By using expressions 15–17, E_A , E_B , and E_C of Pb^{2+} ions were calculated and are listed in Table I (columns 6, 9, and 12). Columns 7, 10, and 13 provide the error ratio (Δ_{error}), which was calculated from the experimental and calculated results, $\Delta_{\text{error}} = (E_{\text{exp}} - E_{\text{cal}}) / E_{\text{exp}}$. The results indicated that the calculated values excellently agree with the experimental data. In most cases, the error ratio is less than 1%. Compared with the experimental data, the maximum error of the calculated results was 2473 cm^{-1} of the C band for $BaY_2F_8:Pb^{2+}$; the error ratio was only 3.68%. In addition, the A and B bands are almost two parallel lines (see Fig. 2), their slopes are $-14,225$ and $-16,730$, respectively, but the C band shows a closing tendency to the B band; its slope is $-24,331$. This means that the sensitivity of the A and B bands to the environment of the host is very similar; the C band is the most sensitive energy level compared with the A and B bands. For example, in $KMgF_3$ crystal, which has a minimum environmental factor $h_e = 0.081$ (K^+ site), the positions of the A, B, and C bands are 187 nm ($53,476 \text{ cm}^{-1}$), 157 nm ($64,935 \text{ cm}^{-1}$), and 138 nm ($72,464 \text{ cm}^{-1}$), respectively. In YF_3 ,

Table I. Experimental and calculated sp-level energies of Pb²⁺ in fluorides and environmental factors h_e .

Crystals	n	Bond	h_e	$E_{A,exp}^a$	$E_{A,cal}$	$\Delta_{A,error}^a$ (%)	$E_{B,exp}^a$	$E_{B,cal}$	$\Delta_{B,error}^a$ (%)	$E_{C,exp}^a$	$E_{C,cal}$	$\Delta_{C,error}^a$ (%)
α -PbF ₂	2.000 ^b	Pb–F	0.640	45,973	45,814	0.35						
β -PbF ₂	1.761	Pb–F	0.642	45,893	45,786	0.23						
CaF ₂	1.425	Ca–F	0.361	49,038	49,783	–1.52	60,606	60,527	0.13	64,927	65,006	–0.12
SrF ₂	1.432	Sr–F	0.374	49,199	49,598	–0.81	60,606	60,310	0.49	64,846	64,689	0.24
BaF ₂	1.466	Ba–F	0.413	49,361	49,043	0.64	60,491	59,658	1.38	64,121	63,740	0.59
YF ₃	1.559	Y–F	0.455	47,619	48,446	–1.74	58,824	58,955	–0.22	61,728	62,718	–1.60
LaF ₃	1.590	La–F	0.393	50,000	49,328	1.34				62,893	64,227	–2.12
LiBaF ₃	1.544	Ba–F	0.163	52,356	52,599	–0.46	64,113	63,840	0.43	70,922	69,823	1.55
KMgF ₃	1.428	K–F	0.081	53,476	53,766	–0.54	64,935	65,212	–0.43	72,464	71,818	0.89
		Mg–F	0.514		47,606							
BaY ₂ F ₈	1.498	Ba–F	0.376	50,000	49,569	0.86	59,010	60,277	–2.15	67,114	64,641	3.68
		Y–F	0.159	53,476	52,656	1.53	64,103	63,907	0.31	67,568	69,920	–3.48

^a References 6, 7, and 10; n : index of refraction; E_{exp} : experimental data of A, B, and C bands (cm^{–1}); E_{cal} : calculated values of A, B, and C bands (cm^{–1}); and Δ_{error} : error ratio, $\Delta_{error} = (E_{exp} - E_{cal})/E_{exp}$.

^b The refractive index data n of α -PbF₂ are not available in literature and are estimated from the isostructural compounds: PbX₂ (X = Cl, Br, I).

$h_e = 0.455$; the positions of the A, B, and C bands of Pb²⁺ are 210 nm (47,619 cm^{–1}), 170 nm (58,824 cm^{–1}), and 167 nm (61,728 cm^{–1}), respectively. The energy level decrease (ΔE_A , ΔE_B , and ΔE_C) of these bands from KMgF₃ (K⁺ site) to YF₃ are 5857, 6111, and 10,736 cm^{–1}, respectively. Moreover, for KMgF₃:Pb²⁺, the distance of the A and B bands E_{B-A} is 11,459 cm^{–1} and the B and C bands E_{C-B} is 7529 cm^{–1}; in YF₃:Pb²⁺, the E_{B-A} is 11,204 cm^{–1} and the E_{C-B} is 2905 cm^{–1}. The distance of the B and C bands obviously become smaller with an increase in h_e . This means that the position of the C band would be very close to the B band of Pb²⁺ if they could be observed in some Pb²⁺-doped oxide and silicate crystals because the h_e of these crystals are larger than fluoride compounds according to the previous work of our group.^{31,35} Furthermore, according to our model, when the h_e is larger than 0.96, the predicted position of the B band would exceed that of the C bands. So, it is assumed that in the host where h_e is larger than 0.96, there may be only one band that could be observed in the B and C band regions of Pb²⁺. BaSi₂O₅:Pb²⁺ was chosen to confirm our assumption in the Applications section.

Applications

The applications of our model in the prediction, assignment, and reassignment of A, B, C, and D band positions of Pb²⁺ in complex crystals are discussed in this section.

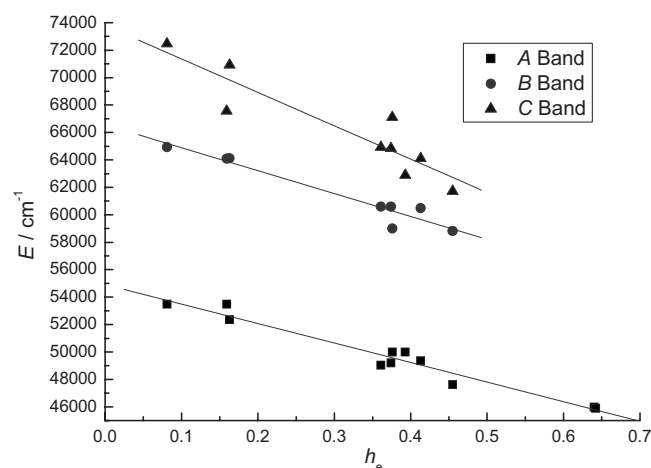
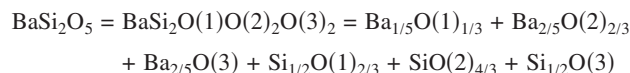


Figure 2. The relations between the sp-level energies of Pb²⁺ and the environmental factors h_e .

Prediction, assignment, and reassignment of A, B, and C band positions.—One of the important applications of our model is to predict and assign the energy E_A , E_B , and E_C of Pb²⁺ in different crystals. Hereafter, we take the fluoride crystal LiCaAlF₆:Pb²⁺ and silicate BaSi₂O₅:Pb²⁺ as examples to demonstrate our model. The crystal structures of LiCaAlF₆ and BaSi₂O₅ were reported in detail.^{36,37} LiCaAlF₆ is trigonal space group $P\bar{3}1$, and all metal ions are octahedrally coordinated by six fluoride ions.³⁶ Due to the similar size of Ca²⁺ (1.0 Å) and Pb²⁺ (1.19 Å) ions, compared to Li⁺ (0.76 Å) and Al³⁺ (0.535 Å) ones,³⁸ the Pb²⁺ occupies the Ca²⁺ sites of the host lattice. The structure of BaSi₂O₅ is orthorhombic space group $Pcmm$; it is characterized by having SiO₄ tetrahedral, and each Ba ion is surrounded by seven oxygen ions.³⁷

According to the previous model mentioned, we can decompose LiCaAlF₆ and BaSi₂O₅ into their subformula equations as



Using the known refractive indexes n of LiCaAlF₆ ($n = 1.387$) and BaSi₂O₅ ($n = 1.613$),³⁹ the detailed bond parameters and h_e of each type of bond were calculated. The results of h_e are presented in Table II. Based on Eq. 15–17, E_A , E_B , and E_C of LiCaAlF₆:Pb²⁺ and BaSi₂O₅:Pb²⁺ were calculated and are listed in Table II (columns 8, 9, and 10).

In LiCaAlF₆:Pb²⁺, the calculated values of the A, B, and C bands are 50,522 cm^{–1} (197.9 nm), 61,397 cm^{–1} (162.9 nm), and 66,271 cm^{–1} (150.9 nm), respectively. The experimental data are 192 nm (52,083 cm^{–1}, A1) with the shoulder at 200 nm (50,000 cm^{–1}, A2) at room temperature,² and the corresponding average value (51,042 cm^{–1}) is listed in column 5 of Table II. It can be seen that the theoretical value (50,522 cm^{–1}) agrees well with the experimental data (51,042 cm^{–1}). The error ratio is only 1.02%. But, the absorption spectrum below 180 nm has not been studied; according to our model, the predicted positions of the B and C bands are 162.9 nm (61,397 cm^{–1}) and 150.9 nm (66,271 cm^{–1}), respectively.

As for BaSi₂O₅:Pb²⁺, the calculated values of the A, B, and C bands are 35,956 cm^{–1} (278.1 nm), 44,266 cm^{–1} (225.9 nm), and 41,356 cm^{–1} (241.8 nm), respectively. It is shown that the calculated and experimental spectra or the sp energy levels of Pb²⁺ have similar regions, which are 225–280 and 220–280 nm,^{4,40} respectively. The calculated value of the C band is lower than the B band. According to the Results and Discussion section, we suggested that

Table II. Experimental and calculated sp-level energies of $\text{LiCaAlF}_6\text{:Pb}^{2+}$ and $\text{BaSi}_2\text{O}_5\text{:Pb}^{2+}$.

Crystals	n	Bond	h_c	$E_{A,\text{exp}}$	$E_{B,\text{exp}}$	$E_{C,\text{exp}}$	$E_{A,\text{cal}}$	$E_{B,\text{cal}}$	$E_{C,\text{cal}}$	Δ_{error} (%)
LiCaAlF_6	1.387 ^a	Ca–F	0.309	51,042 ^b			50,522	61,397	66,271	1.02
BaSi_2O_5	1.613 ^a	Ba–O	1.333			40,816 ^c	35,956	44,266	41,356	–1.32

^a The refractive index n of crystals from Ref. 39.^b The experimental values from Ref. 2 (cm^{-1}).^c The experimental values from Ref. 4 and 41 (cm^{-1}); $\Delta_{\text{error}} = (E_{\text{exp}} - E_{\text{cal}})/E_{\text{exp}}$; for $\text{LiCaAlF}_6\text{:Pb}^{2+}$, $\Delta_{\text{error}} = (E_{A,\text{exp}} - E_{A,\text{cal}})/E_{A,\text{exp}}$; for $\text{BaSi}_2\text{O}_5\text{:Pb}^{2+}$, $\Delta_{\text{error}} = (E_{C,\text{exp}} - E_{C,\text{cal}})/E_{C,\text{exp}}$.

only the C band could be observed for $\text{BaSi}_2\text{O}_5\text{:Pb}^{2+}$ in the 220–280 nm region. In Ref. 4 and 40, the excitation spectrum in the region of 220–280 nm exhibits only one broad band with a peak near 245 nm. The observed data (245 nm) are very close to the calculated value of the C band (243.2 nm). This band was assigned to the $^1\text{S}_0 \rightarrow ^1\text{P}_1$ transition (C band) according to our model, which is consistent with literature assignment.^{4,40} Equations 15–17 demonstrate an excellent predictive power.

For $\text{LiBaF}_3\text{:Pb}^{2+}$, the predicted values of the B and C bands are 63,840 cm^{-1} (156.6 nm) and 69,823 cm^{-1} (143.2 nm), respectively. (see Table I). However, the observed bands at 158, 154, and 141 nm were assigned to the B , C , and D bands, respectively.⁶ The distances of 154 and 158 nm as well as 141 and 154 nm are 1644 and 5987 cm^{-1} , respectively. According to Ref. 12 and 41, the peak separations of the B band ($E_{B1} - E_{B2}$) for KCl:Sn^{2+} and KCl:In^{2+} are 1129 and 565 cm^{-1} , respectively; the distances of the B and C bands of KCl:Sn^{2+} , KCl:In^{2+} , and KCl:Tl^{2+} are 3726, 6130, and 3388 cm^{-1} , respectively. Thus, from the above fact, the 158, 154, and 141 nm bands are reassigned to the $B1$, $B2$, and C bands of Pb^{2+} , respectively. The calculated values excellently agree with the reassigned bands.

Clarify the site occupation.— Another important application of our model is to clarify the site occupation of Pb^{2+} when Pb^{2+} occupies more than one different site in the lead(II)-doped complex. For the past decades, much work has been focused on the host lattice dependence of the luminescence of s^2 ions.^{6,42–44} Compared to the experimental effort, theoretical studies of the site selective spectrum were very limited, and the spectrum assignments were rather tentative. Here, we chose $\text{BaY}_2\text{F}_8\text{:Pb}^{2+}$ and $\text{KMgF}_3\text{:Pb}^{2+}$ as examples to demonstrate the application of our model. BaY_2F_8 has a monoclinic crystalline structure with C_{2h}^3 ($C2/m$), $Z = 2$ space group.⁴⁵ The reticular constants are $a = 6.935$ Å, $b = 10.457$ Å, and $c = 4.243$ Å, with angle $\gamma = 99.7^\circ$ between the a -axis and the c -axis. The primitive cell contains two BaY_2F_8 molecules. The Ba^{2+} and Y^{3+} ions lattice sites are surrounded by 12 and 8 F^- anions, respectively. Spectroscopic analysis shows that there are two sites (sites I and II) for Pb^{2+} in $\text{BaY}_2\text{F}_8\text{:Pb}^{2+}$.⁶ The positions of the excitation bands are at a high energy in site I compared to those in site II. The experimental data of the excitation bands are listed in Table I (columns 5, 8, and 11). The spectral behavior of the bands does not depend on the Pb^{2+} concentration. However, these two sites have not yet been identified. The ionic radii of Ba^{2+} , Y^{3+} , and Pb^{2+} ions are listed in Table III. The ionic radius difference of Pb^{2+} and Ba^{2+} is $\Delta r_{\text{Pb-Ba}} = 0.12$; that of Pb^{2+} and Y^{3+} is $\Delta r_{\text{Pb-Y}} = 0.271$. It can be seen that both the $\Delta r_{\text{Pb-Ba}}$ and $\Delta r_{\text{Pb-Y}}$ are very small, so it is natural to consider that Pb^{2+} enters substitutionally into the Ba^{2+} and Y^{3+} sites. Obviously that the two different sites (sites I and II) could be assigned to Ba^{2+} and Y^{3+} sites. Unfortunately, research on $\text{BaY}_2\text{F}_8\text{:Pb}^{2+}$ was not developed in depth; their definite assignments are still unknown. However, on the basis of the crystal structure data,⁴⁵ BaY_2F_8 can be decomposed into a linear combination of the subformula of various binaries. The calculated values of the environmental factors of Ba^{2+} and Y^{3+} sites are 0.376 and 0.159, respectively, according to the dielectric theory of the chemical bond for

complex crystals methods. Then, using Eq. 15–17, we predict that the positions of the A , B , and C bands of Pb^{2+} in the Ba^{2+} site are 201.7 nm (49,569 cm^{-1}), 165.9 nm (60,277 cm^{-1}), and 154.7 nm (64,641 cm^{-1}), respectively; the positions of the A , B , and C bands of Pb^{2+} in the Y^{3+} site are 189.9 nm (5265 cm^{-1}), 156.5 nm (63,907 cm^{-1}), and 143.0 nm (69,920 cm^{-1}), respectively. Therefore, we concluded that the excitation band (A) at 200 nm of Pb^{2+} in site II is from the Ba^{2+} site, and the bands (A , B , and C) at 187, 156, and 148 nm in site I are from the Y^{3+} site. It can be seen that the calculated values excellently agree with the experimental data. The observed bands at 172, 167, and 149 nm in site II were assigned to the B , C , and D bands, respectively.⁶ The predicted position for the B band (165.9 nm) in the Ba^{2+} site is very close to that of the B and C bands reported in Ref. 6; however, the predicted position for the C band (154.7 nm) is close to that of the D band. Compared with the same situation of $\text{LiBaF}_3\text{:Pb}^{2+}$, which was mentioned above, the 172, 167, and 149 nm in site II are reassigned to the $B1$, $B2$, and C bands of Pb^{2+} in the Ba^{2+} site, respectively.

The luminescence characteristics of $\text{KMgF}_3\text{:Pb}^{2+}$ were extensively investigated in the last three decades.^{8,9,46} In the absorption spectrum, a band peak at 187 nm was observed by different authors.^{6,8} But, the assignment of this band by different groups is very contradictory. It was attributed to the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ (A band) transition in the K^+ site by Babin et al.⁶ and to the $^1\text{S}_0 \rightarrow ^3\text{P}_2$ (B band) transition in the Mg^{2+} site by Missori and Scacco.⁸ KMgF_3 has the cubic perovskite structure.⁴⁷ In this perovskite, the K^+ ion is in the cubic 12 coordination of F^- , whereas Mg^{2+} is octahedrally coordinated by F^- . The ion radii of K^+ , Mg^{2+} , and Pb^{2+} are listed in Table III. As the ion radii of Mg^{2+} (0.72 Å, VI) and Pb^{2+} (1.19 Å, VI) are dramatically different, it is difficult for the Pb^{2+} to substitute for the Mg^{2+} ion. So, it is natural to think that the one possible site available for incorporating Pb^{2+} (1.49 Å, XII) in the KMgF_3 lattices is the K^+ sites (1.64 Å, XII). To clarify the site occupation of Pb^{2+} in the KMgF_3 crystal, the environmental factors of the K^+ and Mg^{2+} sites were calculated (see Table I). Using Eq. 15 and 16, the predicted positions of Pb^{2+} in the K^+ and Mg^{2+} sites are $E_{A,K} = 53,766$ cm^{-1} (186.0 nm), $E_{A,Mg} = 47,606$ cm^{-1} (210.1 nm), $E_{B,K} = 65,212$ cm^{-1} (153.3 nm), and $E_{B,Mg} = 57,968$ cm^{-1} (172.5 nm). The calculated value $E_{A,K} = 53,766$ cm^{-1} (186.0 nm) agrees well with the experimental data, 187 nm (53,476 cm^{-1}). The results

Table III. Ionic radius (Å)^a for some cations.

Ion	VI ^b	VIII ^b	XII ^b
Pb^{2+}	1.19	1.29	1.49
Ba^{2+}			1.61
Y^{3+}		1.019	
K^+			1.64
Mg^{2+}	0.72	0.89	

^a Reference 38.^b These numbers represent the coordination numbers of the cations.

confirm that the Pb^{2+} impurity substitutionally replaces the K^+ ion and not Mg^{2+} in the KMgF_3 lattice. If Pb^{2+} ions occupy the Mg^{2+} sites, the position of the *A* band should be at 210.1 nm according to our model. This hypothesis is confirmed from the absorption spectrum where a weak absorption band at 218 nm was observed by Horsch et al.,⁹ which can be ascribed to the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ (*A* band) transition of Pb^{2+} in the Mg^{2+} site according to our model.

Conclusions

We investigated the relationships between the positions of the *A*, *B*, and *C* bands for Pb^{2+} and the crystalline environment based on the dielectric theory of the chemical bond for complex crystals to obtain a useful tool to correctly predict and assign the site occupations and the energy levels of Pb^{2+} -doped compounds. The calculated results indicate that 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 are the three microcosmic factors that determine the energies of the *A*, *B*, and *C* bands. An additional factor that contains these three factors was defined as the environmental factor (h_e). Our method has successfully built links between the E_A , E_B , and E_C of Pb^{2+} and the environmental factor h_e . It is shown that the E_A , E_B , and E_C of Pb^{2+} all decrease with an increase in h_e . The theoretical results are in excellent agreement with the experimental values. A semiempirical model to predict and assign the site occupation and sp-level energies of Pb^{2+} in fluoride crystals was obtained. Applied to fluoride crystal $\text{LiCaAlF}_6\text{:Pb}^{2+}$ and silicate $\text{BaSi}_2\text{O}_5\text{:Pb}^{2+}$, the predictions are compared with the experimental data. The agreement is satisfactory, and it is shown that our semiempirical model can also be applied to complex fluorides and silicates. Most importantly, the site occupations of Pb^{2+} in the BaY_2F_8 and KMgF_3 crystals were clarified by our model. In $\text{BaY}_2\text{F}_8\text{:Pb}^{2+}$, the higher E_A , E_B , and E_C originate from the site of Y^{3+} , and the lower ones originate from the site of Ba^{2+} . In addition, the bands at 172, 167, and 149 nm in site II are reassigned to the *B*1, *B*2, and *C* bands of Pb^{2+} in the Ba^{2+} site, respectively. For $\text{LiBaF}_3\text{:Pb}^{2+}$, the 158, 154, and 141 nm bands are reassigned to the *B*1, *B*2, and *C* bands of Pb^{2+} , respectively. As for $\text{KMgF}_3\text{:Pb}^{2+}$, we concluded that the absorption bands at 187 and 218 nm were attributed to the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ (*A* band) transition of Pb^{2+} in the K^+ and Mg^{2+} sites, respectively. The positions of the sp energy levels of Pb^{2+} in fluoride crystals are usually in the vacuum ultraviolet (VUV) region; therefore, our work is significant for the theoretical study of VUV phosphors, which has become a research hotspot.

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References

1. S. Taşcıoğlu, İ. Pekgözlü, and A. Mergen, *Mater. Chem. Phys.*, **112**, 78 (2008).
2. A. Novoselov, J. Pejchal, M. Nikl, and A. Yoshikawa, in *Nuclear Science Symposium and Medical Imaging Conference 2007*, Vol. 3, Honolulu, HI, IEEE, p. 2184 (2007).
3. M. A. Kale, C. P. Joshi, S. V. Moharil, P. L. Muthal, and S. M. Dhopte, *J. Lumin.*, **128**, 1225 (2008).
4. V. B. Bhatkar, S. K. Omanwar, and S. V. Moharil, *Opt. Mater. (Amsterdam, Neth.)*, **29**, 1066 (2007).
5. L. K. Aminov, S. I. Nikitin, N. I. Silkin, A. A. Shakhov, R. V. Yusupov, R. Yu. Abdulsabirov, and S. L. Korableva, *J. Phys.: Condens. Matter*, **18**, 4985 (2006).
6. V. Babin, K. D. Oskam, P. Vergeer, and A. Meijerink, *Radiat. Meas.*, **38**, 767 (2004).
7. M. Itoh, H. Nakagawa, M. Kitaura, M. Fujitak, and D. L. Alov, *J. Phys.: Condens. Matter*, **11**, 3003 (1999).
8. M. Missori and A. Scacco, *Solid State Commun.*, **76**, 5 (1990).
9. G. Horsch and H. J. Paus, *Opt. Commun.*, **60**, 69 (1986).
10. K. P. Oboth, F. J. Lohmeier, and F. Fischer, *Phys. Status Solidi B*, **154**, 789 (1989).
11. P. W. M. Jacobs, *J. Phys. Chem. Solids*, **52**, 35 (1991).
12. A. Ranfagni, D. Mugnai, M. Bacci, G. Viliani, and M. P. Fontana, *Adv. Phys.*, **32**, 823 (1983).
13. A. Manavbasi and J. C. LaCombe, *J. Lumin.*, **128**, 129 (2008).
14. H. F. Folkerts, J. Zuidema, and G. Blasse, *Solid State Commun.*, **99**, 655 (1996).
15. F. Seitz, *J. Chem. Phys.*, **6**, 150 (1938).
16. T. Tsuboi, *Phys. Status Solidi B*, **96**, 321 (1979).
17. T. Tsuboi and S. Sakoda, *Phys. Rev. B*, **22**, 4972 (1980).
18. C. P. Joshi and S. V. Moharil, *Phys. Status Solidi B*, **220**, 985 (2000).
19. F. Agulló-López, J. M. Calleja, F. Cussó, F. Jaque, and F. J. López, *Prog. Mater. Sci.*, **30**, 187 (1986).
20. H. F. Folkerts, A. van Dijken, and G. Blasse, *J. Phys.: Condens. Matter*, **7**, 10049 (1995).
21. H. F. Folkerts, M. A. Hamstra, and G. Blasse, *Chem. Phys. Lett.*, **246**, 135 (1995).
22. F. E. Williams and M. H. Hebb, *Phys. Rev.*, **84**, 1181 (1951).
23. R. S. Knox and D. L. Dexter, *Phys. Rev.*, **104**, 1245 (1956).
24. R. S. Knox, *Phys. Rev.*, **115**, 1095 (1959).
25. S. Sugano, *J. Chem. Phys.*, **36**, 122 (1962).
26. D. Bramanti and M. Mancini, *Phys. Rev. B*, **3**, 3670 (1971).
27. I. Fujita, *Phys. Rev. B*, **49**, 6462 (1994).
28. T. Nakajima, B. Zemva, and A. Tressaud, *Advanced Inorganic Fluorides: Synthesis, Characterization, and Applications*, p. 315, Elsevier, New York (2000).
29. S. Y. Zhang, *Chin. J. Chem. Phys.*, **4**, 109 (1991).
30. D. F. Xue and S. Y. Zhang, *J. Phys. Chem. A*, **101**, 5547 (1997).
31. J. S. Shi and S. Y. Zhang, *J. Phys. Chem. B*, **108**, 18845 (2004).
32. J. C. Phillips, *Rev. Mod. Phys.*, **42**, 317 (1970).
33. J. A. Van Vechten, *Phys. Rev.*, **182**, 891 (1969).
34. F. M. Gao and S. Y. Zhang, *J. Phys. Chem. Solids*, **58**, 1991 (1997).
35. L. Li, S. H. Zhou, and S. Y. Zhang, *J. Lumin.*, **129**, 187 (2009).
36. W. Viebahn, *Z. Anorg. Allg. Chem.*, **386**, 335 (1971).
37. R. M. Douglass, *Am. Mineral.*, **43**, 517 (1958).
38. R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr.*, **32**, 751 (1976).
39. M. J. Weber, *Handbook of Optical Materials*, pp. 82 and 84, CRC Press, Boca Raton, FL (2002).
40. Y. B. Tang, Q. H. Yang, R. X. Huang, X. Z. Zhu, and H. B. Wang, *Chin. J. Lumin.*, **27**, 745 (2006).
41. T. Tsuboi and Y. Nakai, *Phys. Rev. B*, **8**, 1698 (1973).
42. H. F. Folkerts and G. Blasse, *J. Mater. Chem.*, **5**, 273 (1995).
43. H. F. Folkerts, F. Ghianni, and G. Blasse, *J. Phys. Chem. Solids*, **57**, 1659 (1996).
44. M. Mehnaoui, G. Panczer, R. Ternane, M. Trabelsi-Ayedi, and G. Boulon, *Opt. Mater. (Amsterdam, Neth.)*, **30**, 1672 (2008).
45. L. H. Guilbert, J. Y. Gesland, A. Bulou, and R. Retoux, *Mater. Res. Bull.*, **28**, 923 (1993).
46. M. Missori, C. Sanipoli, and A. Scacco, *Radiat. Eff. Defects Solids*, **119**, 349 (1991).
47. R. C. DeVries and R. Roy, *J. Am. Chem. Soc.*, **75**, 2479 (1953).