Formulation of Phosphorescence Mechanisms in Inorganic Solids Based on a New Model of Defect Conglomeration

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The phosphorescence mechanisms of various phosphors were explored by taking into consideration the presence of interactions between dopant cations and vacancies as well as the effect of co-dopant cations on these interactions. Our study indicates that the distribution of dopant and co-dopant cations around vacancies is not random, and luminescent properties are strongly influenced by this nonrandom distribution. To a first approximation, the ionization potentials of dopants, co-dopants, and host cations can be used to rationalize their tendencies for this nonrandom distribution. On the basis of our analysis, we explained the properties of known phosphorescent materials, examined several factors important for designing new improved phosphors, and discussed how point defects might affect phosphorescence as well as fluorescence.

1. Introduction

The optical properties of certain insulating solid state compounds are primarily governed by their intrinsic and/or extrinsic point defects. Nevertheless, the precise role of these defects remains largely unclear because of the difficulty of identifying and properly characterizing them. It is known that a slight amount of dopants can bring about a drastic color change in solids. For example, pure corundum Al_2O_3 is a white compound. By replacing ~1% of the Al of corundum with Cr, one obtains ruby, whose deep red color arises from the intrasite d → d transition of Cr^{3+}.[1] An even lower defect concentration can induce a color change if the color arises from an intervalence charge transfer. Namely, the replacement of ~0.01% of the Al of corundum with Ti and Fe gives rise to sapphire with blue color. Because only the Ti^{4+} and Fe^{2+} cations located in adjacent face-sharing octahedral sites are responsible for the color, the actual concentration of the defects at work is probably overestimated.[1] In phosphors, the effect of defects is still more pronounced because almost all the luminescence properties originate from a trace amount of dopants in a host lattice.[2]

Dopants in trace amount (i.e., substitutional defects) can act as luminescent centers (i.e., activators). When excited, these activators return to their ground state via a radiative de-excitation. This gives rise to fluorescence or phosphorescence (often referred to as afterglow).[2] The local surrounding of an activator can strongly influence the optical properties of luminophors such as the intensities of the transition and the energy at which the transition occurs. In addition, the environment of an activator may strongly affect the radiative decay time and the nature of the de-excitation mechanism, as will be discussed below.

Commonly, fluorescence and phosphorescence are two well-distinguishable optical phenomena that differ in the persistence time of their luminescence. Typically, a material is classified as phosphorescent if the recombination of photogenerated electrons and holes is significantly delayed. Figure 1 displays the afterglow characteristics of the five well-known phosphorescent materials as a function of time. Explicitly, electrons and/or holes generated in a solid by electronic excitation may be trapped at point defects until they are released by thermal energy at room temperature and recombine via a fluorescence mechanism at a luminescent center.[3] In this context, the term "phosphorescence" does not refer to any spin forbidden transition but refers exclusively to a phenomenon of delayed recombination that requires de-trapping of trapped charge carriers. To enable us to design new phosphors with new targeted properties, it is important to understand how phosphorescence and fluorescence are related to point defects.

It is common to assume that point defects in solids are randomly distributed. However, defect migration can be significant during synthesis at high temperature and cannot be neglected even at room temperature if a material is subjected to a prolonged high-energy excitation (e.g., in plasma displays). To fully understand how phosphorescence and fluorescence are affected by point defects, it is necessary to take into consideration their nonrandom distribution. Most

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(1) Nassau, K. *The Physics and Chemistry of Color, The Fifteen Causes of Color*; Wiley-Interscience: New York, 1983.
(2) Blasse, G.; Grabmaier, B. C. *Luminescence Materials*; Springer-Verlag: Berlin, 1994.
(3) Shionoya, S., Yen, W. M., Eds.; *Phosphor Handbook*; CRC Press: Boca Raton, 1999.

10.1021/cm052728q CCC: $33.50

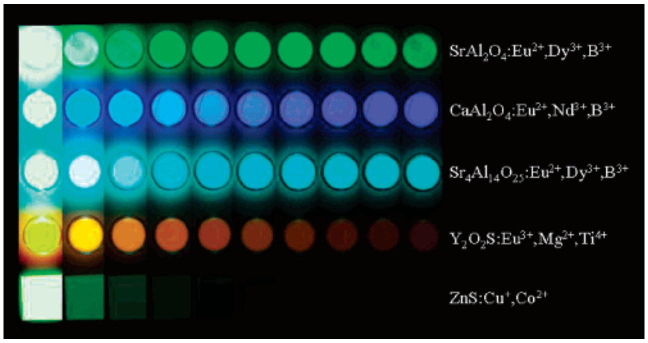

Figure 1. Afterglow characteristics of the five well-known phosphorescent materials $SrAl_2O_4$:Eu^{2+},Dy^{3+},B^{3+}, $CaAl_2O_4$:Eu^{2+},Nd^{3+},B^{3+}, $Sr_4Al_{14}O_{25}$:Eu^{2+},Dy^{3+},B^{3+}, Y_2O_2S:Eu^{3+},Mg^{2+},Ti^{4+}, and ZnS:Cu^{+},Co^{2+}. The first column represents the light emission observed while the samples are under UV irradiation. After stopping the UV irradiation, the afterglows of the samples were recorded at 5 min intervals. The second to the ninth columns represent the results of these consecutive afterglow measurements.

phosphorescence mechanisms proposed in the past are unsatisfactory, in particular, concerning the role of co-dopants. On the basis of analyzing the interactions between point defects and activators as well as the effect of co-dopants on these interactions, we have recently proposed a phosphorescence mechanism for $SrAl_2O_4$:Eu^{2+} and extended it to $SrAl_2O_4$:Eu^{2+},Dy^{3+} and related phosphors.[4] In the present work we review the phosphorescence mechanisms in other types of phosphorescent materials, probe their implications, and discuss their applications.

Our work is organized as follows: In Section 2 we discuss the use of ionization potentials (IPs) of dopant cations as a qualitative measure for their ability to interact with point defects and to conglomerate. In particular, this parameter is shown to be useful in discussing the stabilization of anion vacancy levels by dopant cations and the tendency of anion vacancies to migrate toward dopants and co-dopants. In section 3, this approach is employed to explain the phosphorescence of the most heavily used green phosphor ZnS:Cu^{+}. After describing the phosphorescence mechanisms of three distinctive groups of phosphors in section 4, we examine the three main factors that influence the performance of phosphorescent materials in section 5. In section 6 we account for how point defects affect fluorescence. The essential findings of our work are summarized in section 7.

2. Factors Affecting the Stabilization of Point Defects and Their Agglomeration

At this stage, we recall that the localized levels associated with an anion vacancy (hereafter, the anion vacancy levels) are the empty orbitals of the cations pointing to the anion vacancy, which result from the breaking of the cation−anion bonds. These levels are located just below the conduction band (CB) bottom. Similarly, the localized levels associated with a cation vacancy (hereafter, the cation vacancy levels) are the lone-pair orbitals of the anions surrounding the cation vacancy, which result from the breaking of the cation−anion bonds. These levels lie just above the valence band (VB) top. The trap depths (E_T) associated with these levels (i.e., their energy separation from the CB bottom for an anion vacancy and from the VB top for a cation vacancy) become larger with increasing the strength of the cation−anion bonds of the host lattice.[5] The anion vacancy and the cation vacancy levels can trap photogenerated electrons and holes, respectively. As discussed below, the stability of these levels is affected by their interactions with dopant and co-dopant cations.

Point defects of a solid may move toward the surface where they can be expelled[6] or may condense in shear planes as in Magnéli phases[7] to generate new structural arrangement with a well-established chemical composition. In other words, point defects tend to migrate to provide an overall stabilization of the material. For electrostatic reasons, point defects with a positive net charge (e.g., a Dy^{3+} cation at a Sr^{2+} site or an anion vacancy) tend to get closer to those with a negative net charge (e.g., a Cu^{+} ion at a Zn^{2+} site or a cation vacancy). Substitutional defects that involve no net charge difference (e.g., Eu^{2+} at an Sr^{2+} site in $SrAl_2O_4$:Eu^{2+},Dy^{3+} and co-dopant Co^{2+} at a Zn^{2+} site in ZnS:Cu^{+},Co^{2+}) would not, a priori, migrate in contrast to those involving a net charge difference. However, even if dopant cations do not create a charge deficit or a charge surplus, a nonrandom distribution of defects can be expected because their interactions with the surroundings differ from those of the host cations they replace because of the difference in their electronegativities and IPs.

A dopant cation that can delocalize its electron density toward its surroundings more (less) readily than the host cation it replaces acts effectively as a cation with a slight surplus (deficit) of electron density. The capability of a cation to delocalize its electron density may be measured by its polarizability, electronegativity, or redox potential in the host lattice. Unfortunately, such data are not available. However, IPs of ions in the gaseous state are available for various oxidation states and may be used to approximate the trends in the redox potentials of the ions present in a given host lattice. In general, the ability of a dopant cation to delocalize its electron density to an empty anion vacancy level should increase with decreasing its IP. Thus, a dopant cation with a lower IP with respect to that of the host cation it replaces should have a stronger tendency to attract an anion vacancy and, hence, stabilize the energy of the associated trapped electron. The above discussion suggests that (a) the distribution of anion vacancies around dopant cations may not be random and (b) such a nonrandom distribution of point defects and a change in the trap depths of some traps (associated with anion and cation vacancies) by dopant cations may be explained by comparing the IPs of the cations. In our recent study[4] these two key ideas were employed to formulate the phosphorescence mechanism for the longest-lasting phosphor $SrAl_2O_4$:Eu^{2+},Dy^{3+},B^{3+}, which is depicted in Figure 2.

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(4) Clabau, F.; Rocquefelte, X.; Jobic, S.; Deniard, P.; Whangbo, M.-H.; Garcia, A.; Le Mercier, T. *Chem. Mater.* **2005**, *17*, 3904.

(5) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

(6) Agullo-Lopez, F.; Catlow, C. A.; Towsend, P. D. *Point Defects in Materials*; Academic Press: London, 1988.

(7) Anderson, J. S.; Collen, B.; Knylenstiren, U.; Magnéli, A. *Acta Chem. Scand.* **1957**, *11*, 1641.

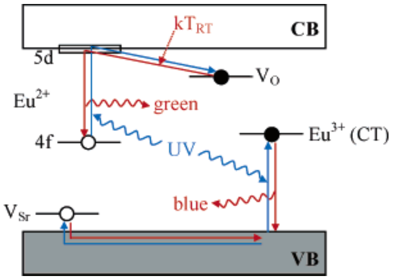

Figure 2. Phosphorescence mechanism by Clabau et al. for $SrAl_2O_4:Eu^{2+}$ and its derivatives.[4] Under UV excitation, Eu^{2+} luminescent centers are excited according to the $4f^7$ ($^8S_{7/2}$) → $4f^65d^1$ transition. The promoted electrons can be trapped in the vicinity of the photogenerated Eu^{3+} cations at an oxygen vacancy (V_O) level. The thermal energy at ambient temperature induces the detrapping of the trapped electrons to the 5d levels of Eu^{3+}, which leads to the $4f^65d^1$ → $4f^7$ ($^8S_{7/2}$) green phosphorescence. The blue emission observed below 150 K is attributed to the systematic presence of Eu^{3+} cations in trace amounts after synthesis. These Eu^{3+} ions are reduced under UV into Eu^{2+} while holes generated in the VB can be trapped at the cation vacancy level (e.g., a Sr vacancy level V_{Sr}). The return to the ground state occurs with hole detrapping according to the charge-transfer $Eu^{2+} + O^- \rightarrow Eu^{3+} + O^{2-}$.

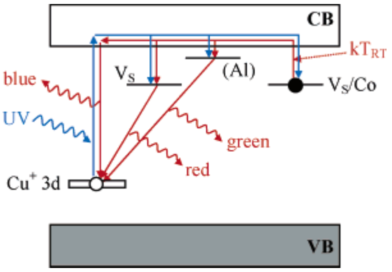

Figure 3. Origin of the red, green, and blue luminescent lines according to the phosphorescence mechanism of the copper doped zinc sulfide series proposed in ref 3. The shallow acceptor level (Al) is formed by Al^{3+} when the latter is used as a co-dopant, and the acceptor level V_S/Co represents either the V_S level or the Co^{2+} level.

3. Phosphorescence of $ZnS:Cu^+$ and $ZnS:Cu^+,Co^{2+}$

The oldest phosphorescent material, which is also one of the most heavily used green fluorescent phosphors, is $ZnS:Cu^+$. Under UV irradiation an electron of $ZnS:Cu^+$ is excited from the 3d levels of Cu^+ to the CBs (i.e., $Cu^+ + h\nu \rightarrow Cu^{2+} + e^-$), which gives rise to blue, green, and red emissions as the electron returns to its ground state (i.e., $Cu^{2+} + e^- \rightarrow Cu^+ + h\nu'$).[3] As depicted in Figure 3, it has been suggested[3] that the blue emission is caused by the de-excitation from the CB bottom to the 3d levels of Cu^{2+}, the red emission is caused by the de-excitation of an electron from an anion vacancy level (V_S) to a nearby Cu^{2+} ion, and the green emission is caused by the de-excitation from a shallower acceptor level to a nearby Cu^{2+} ion. Here a shallow acceptor level is supposed to form, for example, by Al^{3+} when the latter is used as a co-dopant.[3] The phosphorescence of ZnS:Cu, even if known since the 10th century, remains not fully understood. In this section, we analyze the phosphorescence of $ZnS:Cu^+$ and show that the optical properties of this phosphor may readily be explained by considering the stabilization of anion vacancy levels by dopant cations and by using the IPs of cations as a qualitative measure for their tendency to attract anion vacancies.

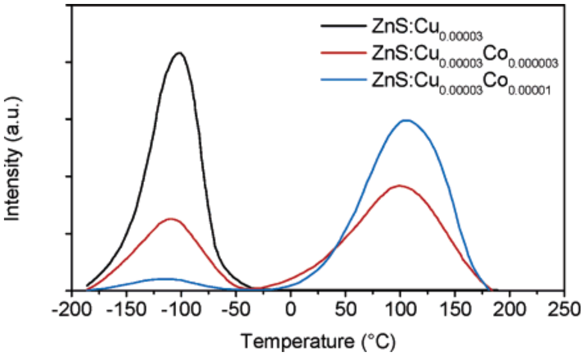

Figure 4. TL curves measured for $ZnS:Cu_{0.00003}Co_x$ ($x = 0$ in black, $x = 3 \times 10^{-5}$ in red, and $x = 10^{-4}$ in blue) after irradiation at 365 nm with a heating rate of 120 °C/min (adapted from ref 8).

The phosphorescence of $ZnS:Cu^+$ is diminished when it is co-doped with Al^{3+} or Cl^-.[3] This co-doping implies a decrease in the concentration of the anion vacancies V_S, so the anion vacancies should be the electron traps of $ZnS:Cu^+$. More precisely speaking, the electron traps should be the sulfur vacancies located far away from the Cu^+ activator, because the anion vacancies close to Cu^+ would induce a direct, instantaneous, radiative recombination due to the extended 3d/4s orbitals of copper, which partially overlap with the orbitals associated with the traps. The co-doping of $ZnS:Cu^+$ with Co^{2+} significantly improves the phosphorescence of $ZnS:Cu^+$. The thermoluminescence (TL) curves of $ZnS:Cu^+$ and $ZnS:Cu^+,Co^{2+}$ show[8] that the Co^{2+} co-doping reduces the peak intensity at −100 °C while increasing that at +100 °C without significantly changing the trap concentration (Figure 4). Namely, the Co^{2+} co-doping increases the depth of the already existing electron traps. Given the same oxidation states of Zn^{2+} and Co^{2+}, one may not have anticipated an agglomeration of Co^{2+} with sulfur vacancies with concomitant trap depth modification.

The IPs of Cu^+, Co^{2+}, and Zn^{2+} are 20.3, 33.6, and 39.8 eV, respectively.[9] Thus, the ability of these cations to attract and stabilize an anion vacancy would decrease in the order $Cu^+ \gg Co^{2+} > Zn^{2+}$. When a Cu^+ center lies close to a V_S vacancy, their strong interaction prevents the V_S level from acting as an electron trap as already mentioned. The great attraction between Cu^+ and V_S would, therefore, explain in part the weak phosphorescence of $ZnS:Cu^+$ in the absence of Co^{2+} co-doping. Because the IP of Co^{2+} is higher than that of Cu^+ and lower than that of Zn^{2+}, the co-dopant Co^{2+} ions attract the anion vacancies that are not proximate to Cu^+ ions, that is, only those anion vacancies distant enough from Cu^+ to act as electron traps. Consequently, the number of electron traps does not necessarily increase upon co-doping with Co^{2+}, but Co^{2+} can stabilize an anion vacancy level better than Zn^{2+}, thereby increasing the trap depth E_T. To enhance the phosphorescence, therefore, it is necessary to place as many anion vacancies as possible close to Co^{2+} and minimize the number of anion vacancies close to Cu^+. Experimentally, this might be achieved by adopting appropriate synthetic procedures. One might carry out a preliminary synthesis of $ZnS:Co^{2+}$ by a ceramic route at high temperature and then incorporate Cu^+ by mixing and annealing $ZnS:Co^{2+}$ at low temperature with copper sulfide (e.g., Cu_2S). In this way, sulfur vacancies would be arranged

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(8) Hoogenstraaten, W.; Klasens, H. *J. Electrochem. Soc.* **1953**, *100*, 366.
(9) Emsley, J. *The Elements*; Clarendon Press: Oxford, 1991.

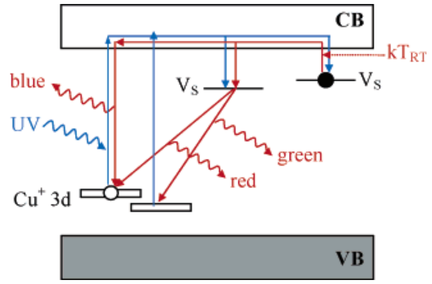

Figure 5. Fluorescence and phosphorescence mechanisms proposed for the ZnS:Cu series in this work. The V_S levels capable of trapping an electron are far away from a sulfur vacancy.

preferentially around Co^{2+} but not around Cu^+, because the vacancy migration toward Cu^+ is not favored at a low annealing temperature.

It is of interest to consider the origin of the blue, green, and red emissions of the ZnS:Cu^+ phosphor. The luminescence properties of ZnS:Cu^+ determined after synthesis by a soft route without heating and also after heating at 1000 °C for 10 h have been reported.[10] The blue emission is always present, so it is reasonable to assign it to the de-excitation from the CB to Cu^{2+}. The green and red emissions appear only after the heating at a high temperature that can induce defect migration. The migration of point defects in ZnS:Cu^+ would lead to an agglomeration of Cu^+ and V_S for the reasons discussed above. Then, the green and red emissions could be assigned to transitions from a localized anion vacancy level to the d levels of copper cations. The difference in the green and red emissions is naturally explained by considering the existence of two kinds of Cu^+ ions (i.e., at trigonal planar and tetrahedral sites) in the vicinity of V_S, because the spatial extension of the 3d orbitals of Cu^+ is sufficiently large so that a direct radiative recombination can take place even when the vacancy is located in the second coordination sphere of Cu^{2+}. These two radiative returns would be characterized by two different fluorescent decay times. In fact, the geometry optimization study carried out with the VASP program package[11,12] shows that a copper cation in a tetrahedral site surrounded by three sulfur anions and a sulfur vacancy, $[CuS_3\square]$, is unstable and relaxes to become a $[CuS_3]$ trigonal planar unit, and that the highest-occupied d-block level of this $[CuS_3]$ trigonal planar unit is lower in energy by some tenths of an electronvolt from that of the $[CuS_4]$ tetrahedral unit. Our phosphorescence and fluorescence mechanisms for ZnS:Cu^+ are presented in Figure 5.

4. Three Classes of Phosphors

On the basis of the phosphorescence mechanisms discussed for the oldest phosphorescent compound ZnS:Cu^+,Co^{2+} (see above) and the most outstanding phosphorescent compound $SrAl_2O_4$:Eu^{2+},Dy^{3+} and its un-co-doped analogue,[4] we are able to make general comments on phosphorescent materials. First, the existence of phosphorescent compounds derived from luminescent materials that are widely used for their fluorescent properties (e.g., ZnS:Cu^+,Co^{2+} [8] from ZnS:Cu^+, Y_2O_2S:Eu^{3+},Mg^{2+},Ti^{4+} [13−15] from Y_2O_2S:Eu^{3+}, and $BaMgAl_{10}O_{17}$:Eu^{2+},Co^{2+} [16] from $BaMgAl_{10}O_{17}$:Eu^{2+}) suggests that a large number of materials known as fluorescent can be made phosphorescent by a proper doping and by using a proper synthetic procedure. Second, a phosphorescence mechanism must not invoke chemical elements to adopt unstable oxidation states. Namely, phosphorescence mechanisms should not be based on highly unstable chemical species such as Dy^{4+}, Eu^+,[17] and Co^+.[18] The latter has three important consequences: (1) The occurrence of phosphorescence is governed by the ability of the activator to be oxidized or reduced after excitation takes place. (2) The phosphorescence mechanisms will depend on the propensity of the luminescent centers to be oxidized or reduced in the host lattice. (3) The traps present in the absence of co-dopants are necessarily intrinsic defects (i.e., vacancies). Thus co-doping is expected to change the number and the trap depth of the vacancies responsible for the carrier trapping because co-doping affects the afterglow duration.

In all reported phosphorescent materials,[4] luminescence requires one of the three prior excitations, that is, 4f → 5d, 3d → CB, and 4f → 4f. In this section we show that each excitation type gives rise to a unique phosphorescence mechanism. As in section 3, these mechanisms rely naturally on the interactions of anion or cation vacancies with dopant (and co-dopant) cations.

4.1. Phosphorescence Associated with 4f → 5d Excitations. The phosphorescence of the Eu^{2+} ($4f^7$), Ce^{3+} ($4f^1$), Tb^{3+} ($4f^8$), and Pr^{3+} ($4f^2$) rare-earth cation luminescence centers is associated with the $(4f)^{n-1}(5d)^1 \rightarrow (4f)^n(5d)$ or $(4f)^{n*} \rightarrow (4f)^n$ transitions, which are systematically induced by a $(4f)^n(5d)^0 \rightarrow (4f)^{n-1}(5d)^1$ excitation.[19] (Neither the direct electron excitation from Eu^{2+} and Ce^{3+} cations to the CB nor that from Tb^{3+} and Pr^{3+} cations to a $(4f)^{n*}$ excited-state triggers phosphorescence as shown by excitation measurements.) These ions can exist in their oxidized states Eu^{3+}, Ce^{4+}, Tb^{4+}, and Pr^{4+} so that the electron promoted to a 5d orbital under excitation may potentially be trapped by anion vacancies. Because a direct excitation into the CB does not induce phosphorescence and because the diffuse 5d orbitals of a rare-earth cation present as a dopant in an oxide or a sulfide of a main-group element (e.g., aluminates, silicates, and aluminosilicates) do not mix sufficiently with the orbitals forming the CB bottom of the host lattice to give rise to extended crystal orbitals, the occurrence of phosphorescence requires the existence of anion vacancies close to the activators as in the case of $SrAl_2O_4$:Eu^{2+} and $SrAl_2O_4$:Eu^{2+},

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(10) Bol, A.; Ferwerda, J.; Bergwerff, J.; Meijerink, A. *J. Lumin.* **2002**, *99*, 325.

(11) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, *558*.

(12) Kresse, G.; Hafner, J. *VASP program*, version 4.6; Institut für Materialphysik, Universität Wien: Wien, Austria, 2000.

(13) Murazaki, Y.; Arai, K.; Ichinomiya, K. Technical Report; Technical Division of Japan Chem., Ltd., 1996.

(14) Wang, X.; Zhang, Z.; Tang, Z.; Lin, Y. *Mater. Chem. Phys.* **2003**, *80*, 1.

(15) Zhang, J.; Zhang, Z.; Tang, Z.; Wang, T. *Ceram. Int.* **2004**, *30*, 225.

(16) Jüstel, T.; Bechtel, H.; Mayr, W.; Wiechert, D. *J. Lumin.* **2003**, *104*, 137.

(17) Matsuzawa, T.; Aoki, Y.; Takeuchi, N.; Maruyama, Y. *J. Electrochem. Soc.* **1996**, *143*, 2670.

(18) Klasens, H. A. *J. Electrochem. Soc.* **1953**, *100*, 72.

(19) Nakagawa, H.; Ebisu, K.; Zhang, M.; Kitaura, M. *J. Lumin.* **2003**, *102*−*103*, 590.

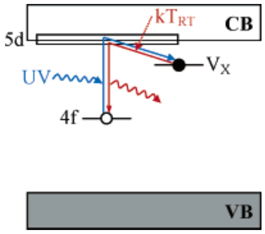

Figure 6. Phosphorescence mechanism based on the oxidation of rare-earth ions Eu^{2+}, Ce^{3+}, Tb^{3+}, and Pr^{3+}, where V_X represents an anion vacancy level. A direct electron−hole recombination is not expected from the trapped electron because the f orbitals of a rare-earth ion are very contracted.

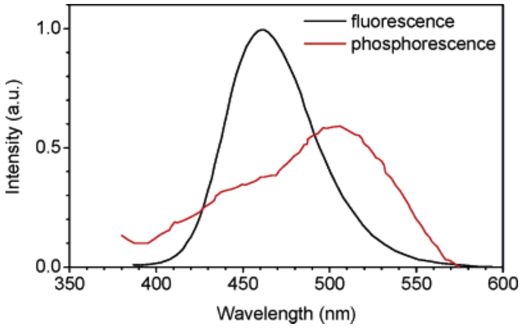

Figure 7. Evolution of the emission spectrum of $SrMgAl_{10}O_{17}:Eu^{2+}_{0.01}$ measured under (black) and after (red) irradiation at 304 nm (adapted from ref 26).

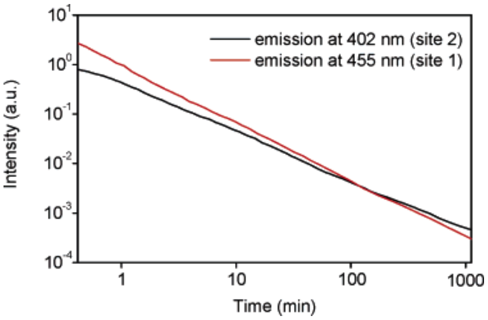

Figure 8. Evolution of the intensity of the two emission bands peaking at 402 and 455 nm, attributed to two crystallographically distinct Ce activators in $BaAl_2O_4:Ce^{3+}_{0.01}$, as a function of time after removal of the excitation (UV mercury lamp; adapted from ref 28).

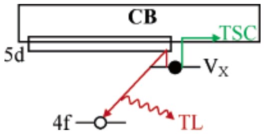

Figure 9. Mechanisms controlling TL and TSC in Eu^{2+}- or Ce^{3+}-containing phosphorescent materials, where V_X refers to an anion vacancy level.

Dy^{3+}.[4] As a result of the contracted nature of the f orbitals, no direct electron−hole recombination can be expected from the trapped electron. The thermo-activated return of the trapped electron to the photo-oxidized europium cation would occur directly to its 5d orbitals (Figure 6).

Absorption measurements show that the activators Tb^{3+} and Pr^{3+} in glass $Ca_{59}Mg_7Al_{54}Si_7O_{161}$ are oxidized to Tb^{4+} and Pr^{4+}, respectively, under UV irradiation.[20] Whereas hole traps are also detected, electron paramagnetic resonance (EPR) measurements show that electrons are well-trapped in glasses $Ca_2Al_2SiO_7:Ce^{3+}$, $Sr_4Al_6Si_3O_{19}:Eu^{2+},Dy^{3+}$, and $Ca_{59}Mg_7Al_{54}Si_7O_{161}:Tb^{3+}$.[21−24] The improvement of phosphorescence with increasing the $[Al^{3+}]/[Si^{4+}]$ ratio in $Sr_4Al_6Si_3O_{19}:Eu^{2+},Dy^{3+}$ [25] suggests strongly that the traps are the V_O vacancies. The proximity of these electron traps to the luminescent centers Eu^{2+} or Ce^{3+} in this aluminosilicate series is supported by several experiments:

(1) The emission spectra of $SrMgAl_{10}O_{17}:Eu^{2+}$,[26] $SrAl_2O_4:Eu^{2+}$,[22] and $CaAl_2O_4:Eu^{2+}$ [27] vary largely between fluorescence and phosphorescence (Figure 7). Thus, the environment of an activator for fluorescence differs from that for phosphorescence. Similarly, the Ce^{3+} ions of $BaAl_2O_4:Ce$ located at the two nonequivalent barium crystallographic sites show a different time dependence of their luminescence intensities (Figure 8).[28] These phenomena are possible only if each activator Eu^{2+} or Ce^{3+} is coupled to an electron trap close to it.

(2) A nitridation, which replaces three oxygen atoms with two nitrogen atoms, hence, creating oxygen vacancies, and a bombardment by electrons and ions do not improve the phosphorescence of a recently patented material containing Eu^{2+} as an activator.[29] Even when anion vacancies were created in the phosphor, the absence of annealing does not allow the defects to migrate near the Eu^{2+} activators to become electron traps.

(3) The detection of cross-relaxation effects in the optically detected EPR for the scintillator $BaFBr:Eu^{2+}$ (i.e., a phosphor with a large trap depth) shows[30] that the Eu^{2+} activator is close to the probable electron traps V_F and/or V_{Br}. Given that electron traps are closely coupled to the most used activators in phosphorescent materials (i.e., Eu^{2+} and Ce^{3+}), it becomes possible to explain why the peaks of TL lie in general at a lower temperature than do those of thermo-stimulated conductivity (TSC).[31] As depicted in Figure 9, we propose that the TL peaks arise from the direct electron transfer from the trap to the 5d levels of the activator, and the TSC peaks arise from the electron transfer from the trap to the CBs. As long as the bottom of the 5d block levels of the activator lies below the CB bottom, the TL peaks would occur at a lower temperature than the TSC peaks. The previous explanation, which assigned the TSC peaks to thermally disconnected traps (i.e., traps too deep to be de-trapped at the temperatures applied),[31] is unrealistic.

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(20) Kinoshita, T.; Hosono, H. *J. Non-Cryst. Solids* **2000**, *274*, 257.

(21) Yamaga, M.; Tanii, Y.; Kodama, N.; Takahashi, T.; Honda, M. *Phys. Rev. B* **2002**, *65*, 235108.

(22) Qiu, J.; Shimizugawa, Y.; Kojima, K.; Tanaka, K.; Hirao, K. *J. Mater. Res.* **2001**, *16*, 88.

(23) Kinoshita, T.; Yamazaki, M.; Kawazoe, H.; Hosono, H. *J. Appl. Phys.* **1999**, *86*, 3729.

(24) Hosono, H.; Kinoshita, T.; Kawazoe, H.; Yamazaki, M.; Yamamoto, Y.; Sawanobori, N. *J. Phys.: Condens. Matter* **1998**, *10*, 9541.

(25) Qiu, J.; Shimizugawa, Y.; Kojima, K.; Tanaka, K.; Hirao, K. *J. Mater. Res.* **2001**, *16*, 88.

(26) Lin, Y.; Tang, Z.; Zhang, Z.; Wang, X.; Zhang, J. *J. Mater. Sci. Lett.* **2001**, *20*, 1505.

(27) Hölsa, J.; Jungner, H.; Lastusaari, M.; Niittykoski, J. *J. Alloys Compd.* **2001**, *323−324*, 32.

(28) Jia, D.; Wang, X.; van der Kolk, E.; Yen, W. *Opt. Commun.* **2002**, *204*, 247.

(29) Clabau, F. Ph.D. Thesis, Université de Nantes, Nantes, 2005 (Restricted distribution until 2010).

(30) Koschnick, F.; Spaeth, J.; Eachus, R. *J. Phys.: Condens. Matter* **1992**, *4*, 8919.

(31) McKeever, S. *Thermoluminescence of Solids*; Cambridge University Press: Cambridge, 1988.

The Ln^{3+} co-dopants capable of improving the phosphorescence of the alkaline-earth aluminates, silicates, or aluminosilicates doped with Eu^{2+} would be those whose IPs are lower than that of the host alkaline-earth cation, because the propensity of Eu^{2+} to attract and stabilize anion vacancies would be then enhanced by Ln^{3+} cations, which in turn are attracted to Eu^{2+} because of their charge deficiency. In the calcium and strontium aluminates, silicates, or aluminosilicates, the more appropriate ions satisfying this criterion well are Nd^{3+} and Dy^{3+} with IP = 40.5 and 41.5 eV, respectively (to be compared with IP = 51.0 and 43.7 eV for Ca^{2+} and Sr^{2+}, respectively).[9] These ions indeed give rise to the best phosphorescence properties.[32] For the barium aluminates, silicates, or aluminosilicates, only Ce^{3+} has an IP lower than that of Ba^{2+} (36.8 vs 37.4 eV)[9] and should improve the phosphorescence properties. However, Ce^{3+} has to be excluded from consideration because of its tendency to be in the oxidation state Ce^{4+} (that is, Ce^{3+} may totally give up one electron due to its ability to acquire the oxidation state of +4, which would induce a significant local structural rearrangement with a partial population of the electron trap before photo-excitation and an overall increase in the activator−electron trap distance. As expected, co-doping with Ce^{3+} cations in a recently patented phosphorescent material[29] increases the concentration of electron traps, but these traps have a lower depth than do those before co-doping with Ce^{3+}.[29] The latter stems from the intrinsic high stability of Ce^{4+}). The IP of Co^{2+} (33.6 eV [9]) is lower than that of Ba^{2+}. However, Co^{2+} induces no charge deficit, so this ion is not attracted to the Eu^{2+} activator. As a result of a few Co^{2+} ions that are located near Eu^{2+}, therefore, a weak phosphorescence is observed in BaMgAl$_{10}$O$_{17}$:Eu^{2+},Co^{2+}.[16]

At this point, we note a new model that has been recently proposed to explain the persistent luminescence in Eu^{2+} and Dy^{3+} co-doped aluminates.[33] This model is based on the photogeneration of electrons with the concomitant oxidation of Eu^{2+} cations into Eu^{3+} as in ref 4 and suggests that the electron traps consist of Dy^{3+} cations. However, this model did not consider the chemical instability of Dy^{2+} species and the specific phosphorescence mechanism of un-co-doped SrAl$_2$O$_4$:Eu^{2+} samples whose afterglow lasts several hours.

4.2. Phosphorescence Associated with 3d → CB Excitations. The transition-metal-ion luminescent centers such as Cu$^+$ (3d^{10}) and Mn^{2+} (3d^5) can be ionized into Cu^{2+} and Mn^{3+}, respectively. Under excitation, one of their electrons can be easily released toward the host and become trapped by anion vacancies. As discussed in section 3, the 3d orbitals of Cu^{2+} and Mn^{3+} are spatially extended enough to favor a direct radiative transition from an occupied anion vacancy level to their empty 3d levels when the activator and the vacancy are close (Figure 10). Thus, the electron traps, that is, the vacancy levels leading to phosphorescence, are only those anion vacancies remote from the activators. The latter is the opposite to what is found for oxidizable rare-earth activators, as already discussed. The localized or delocalized character of the trapping process depends on the chemical nature of the activator via the spatial extension of its d orbitals (e.g., the 5d orbitals of rare earth are more extended than the 3d orbitals of first-row transition elements).

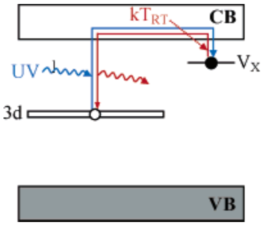

Figure 10. Phosphorescence mechanism for the Cu$^+$ or Mn^{2+} based phosphors, where V$_X$ refers to an anion vacancy level.

In a phosphor containing Mg^{2+} (IP = 80.2 eV) ions with an activator Mn^{2+} (IP = 33.7 eV),[9] the positively charged anion vacancies will be first stabilized in the proximity of Mn^{2+}. Any co-dopants Ln^{3+}, having lower IPs than that of Mg^{2+} and being attracted toward Mn^{2+} cations, should contribute to the attraction of the anion vacancies toward Mn^{2+} and would diminish phosphorescence properties. This is indeed what is observed for MgGeO$_3$:Mn^{2+} [34] (the phosphorescence of MgGeO$_3$:Mn^{2+} is decreased when co-doped by any rare-earth element except for Yb, which probably exists in the reduced form Yb^{2+} in contrast to its Ln^{3+} congeners). To enhance the phosphorescence of a phosphor with Mn^{2+} as the activator, it is necessary to co-dope the phosphor with a cation whose charge favors its migration toward Mn^{2+} centers (attractive as a result of their low IP) and whose IP is higher than that of the host cation to minimize the attraction of the anion vacancies by Mn^{2+}. The Al^{3+} and Ga^{3+} ions (IP = 120.2 and 64.4 eV, respectively),[9] when substituted for Zn, indeed slightly improve the phosphorescence of Zn$_3$(PO$_4$)$_2$:Mn^{2+} (IP = 39.8 eV for Zn^{2+}).[35] Following this observation, it should be pointed out that the fluorescence of ZnS:Cu$^+$ co-doped with Al^{3+} (i.e., the lack of afterglow compared to ZnS:Cu,Co) is caused most probably by the high concentration of the co-dopants and thus by a strong decrease in the total number of the V$_S$ vacancies.

With luminescent centers such as Cu$^+$ and Mn^{2+}, the agglomeration between activators and anion vacancies leads to a loss of traps because it induces a direct recombination. This process is probably responsible for the underestimation observed in the dating of potteries by TL.[31] A slow, natural migration of vacancies toward luminescent centers with very low IP would cause a direct and premature recombination of trapped charge carriers.

4.3. Phosphorescence Associated with 4f → 4f Excitations. The rare-earth cation luminescent centers such as Eu^{3+}, Tm^{3+}, and Sm^{3+} can exist in their reduced states Eu^{2+}, Tm^{2+}, and Sm^{2+}, respectively, so one of their holes can be trapped by cation vacancies. As the phosphorescence is caused by a $(4f)^{n*} \rightarrow (4f)^{n}$ transition, a direct recombination is not easy even when a vacancy is close to an activator as a result of the strongly localized nature of the 4f orbitals so that only recombination via the bands of the host lattice is expected (Figure 11). Thus, both cation vacancies close to and far away from activators may play the role of hole traps.

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[32] Zhang, J.; Zhang, Z.; Wang, T.; Hao, W. *Mater. Lett.* **2003**, *57*, 4315.

[33] Dorenbos, P. *J. Electrochem. Soc.* **2005**, *152*, H107.

[34] Iwasaki, M.; Nam Kim, D.; Tanaka, K.; Murata, T.; Morinaga, K. *Sci. Technol. Adv. Mater.* **2003**, *4*, 137.

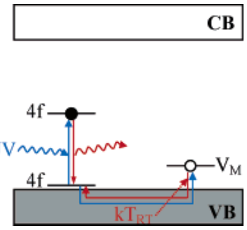

Figure 11. Phosphorescence mechanism for the Eu^{3+}, Tm^{3+}, or Sm^{3+} based phosphors, where V_M refers to a cation vacancy level.

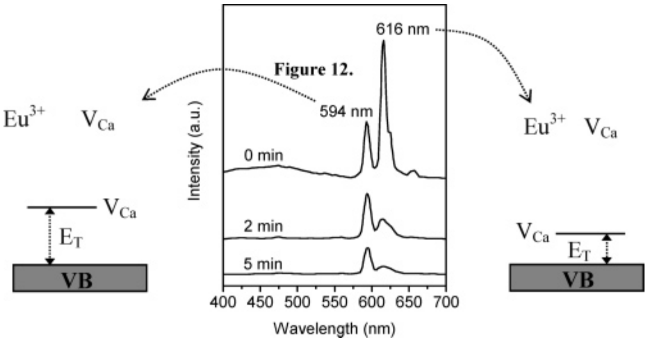

Figure 12. Emission spectra of $Ca_{0.9995}O:Eu_{0.0005}$ before and 2 min and 5 min after the removal of excitation at $\lambda_{exc} = 254$ nm (adapted from ref 36), where V_{Ca} refers to a Ca vacancy level. The rapid decay time of the $^5D_0 \rightarrow {}^7F_2$ transition peaking at 616 nm is attributed to Eu^{3+} ions close to Ca vacancies, and the long decay time of the $^5D_0 \rightarrow {}^7F_1$ transition peaking at 594 is attributed to Eu^{3+} ions far away from Ca vacancies. This difference results because the hole trap depth depends on the distance between the activator and the Ca vacancy as indicated.

With the help of the above postulate, all experimental results carried out for the phosphorescence of $CaO:Eu^{3+}$ [36] and $Y_2O_2S:Eu^{3+}$, Mg^{2+},Ti^{4+}[13−15] can now be explained. The phosphorescence of $CaO:Eu^{3+}$ changes from red to orange in color during the luminescence decay, that is, the emission spectrum initially dominated by the 616 nm peak becomes more and more dominated by the 594 nm peak (Figure 12).[36] It is known that the $^5D_0 \rightarrow {}^7F_1$ transition at 594 nm is most intense when the Eu^{3+} site is centro-symmetric, whereas the $^5D_0 \rightarrow {}^7F_2$ transition at 616 nm appears when the Eu^{3+} site is non-centro-symmetric.[2] Thus, the variation of the luminescence spectrum implies that the activators with a centro-symmetric environment emit longer than do those with a noncentro-symmetric environment. The centro-symmetric site of Ca^{2+} and, hence, that of Eu^{3+}, becomes non-centro-symmetric by having point defects near this site. To ensure the charge balance, the Eu^{3+} co-doping introduces negatively charged V_{Ca} vacancies, which would have a tendency to migrate toward Eu^{3+} for electrostatic reasons. The immediate chemical environment of a V_{Ca} vacancy can accept one hole to get stabilized. Just as an anion vacancy tends to migrate toward an electron donor, a cation vacancy would be attracted to an electron acceptor cation.

It is expected that Ca forms a stronger ionic bond with oxygen than does Eu. Thus, according to the inductive effect,[37] the ionic character of a Ca−O bond would be stronger in the neighborhood of Eu than distant from Eu. Because the trap depth is proportional to the strength of a chemical bond, the hole traps distant from Eu^{3+} would have a greater depth (i.e., a greater E_T) than those close to Eu^{3+}. Thus, the activators at the centro-symmetric sites (i.e., those distant from V_{Ca}) would emit for a longer time (under the probable assumption that a hole is preferentially captured by the trap close to Eu^{3+}). When the alkaline earth is changed, the intensity and the decay time of the phosphorescence increase in the order $Ba^{2+} \ll Sr^{2+} < Ca^{2+}$.[36] This is understandable because the electronegativity of the alkaline earth increases from Ba to Sr and Ca so that the strength of the M−O bond increases as M changes from Ba to Sr to Ca, and the depth of a hole trap distant from Eu^{3+} would increase in the order $Ba^{2+} < Sr^{2+} < Ca^{2+}$. It is worthwhile to note that these expectations agree well with the trend in the IPs of the alkaline earth ions; the higher the IP, the higher the E_T.

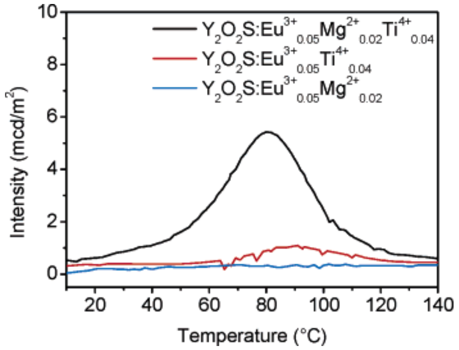

Figure 13. TL curves of $Y_2O_2S:Eu_{0.05},Mg_{0.02}$ (blue), $Y_2O_2S:Eu_{0.05}Ti_{0.04}$ (red), and $Y_2O_2S:Eu_{0.05},Mg_{0.02},Ti_{0.04}$ (black) measured after 5 min of irradiation at 365 nm with a heating rate of 2.5 °C/min (adapted from ref 14).

In $Y_2O_2S:Eu^{3+},Mg^{2+},Ti^{4+}$, the emission spectrum does not vary during phosphorescence[14] because the Y^{3+} site is non-centro-symmetric. However, the phosphorescence of $Y_2O_2S:Eu^{3+},Mg^{2+},Ti^{4+}$ is enhanced when the Eu^{3+} concentration is low.[13] This suggests that the activators far away from the V_Y vacancies emit longer. (The lower the Eu^{3+} concentration, the longer the average activator−vacancy distance for a given concentration of V_Y.) Concerning the role of the co-dopants, TL measurements show that the Ti^{4+} co-doping creates traps, unlike the Mg^{2+} co-doping (Figure 13).[14] Formally, the replacement of Y^{3+} with Ti^{4+} creates cation vacancies as does the substitution of Ca^{2+} for Eu^{3+} in $CaO:Eu^{3+}$. However, the number of created V_Y vacancies appears very low, probably because titanium is mainly present in its Ti^{3+} form. The only way to force Ti^{4+} to exist in a large amount and tune the concentration of cation vacancies would be to co-dope the host lattice with a countercation of +2 oxidation state in lower concentration than the titanium cation concentration. As a result of the +4 oxidation state of Ti, the V_Y vacancies and this cation of the +2 oxidation state tend to approach Ti^{4+}. Then, being close to the trap, the cation of the +2 oxidation state should participate in the trap depth increase or should at least prevent the trap depth decrease. The cation of the +2 oxidation state with the largest IP is Mg^{2+}.

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(35) Wang, J.; Wang, S.; Su, Q. *J. Mater. Chem.* **2004**, *14*, 2569.
(36) Fu, J. *Electrochem. Solid State Lett.* **2000**, *3*, 350.
(37) Etourneau, J.; Portier, J.; Ménil, F. *J. Alloys Compd.* **1992**, *188*, 1.

5. Factors Influencing Phosphorescence

The various aspects of phosphorescence discussed in the previous sections lead one to consider three main factors affecting phosphorescence, that is, luminescent center, trap depth, and trap concentration. These considerations would be of use in formulating synthetic strategies toward new improved phosphorescent materials.

5.1. Luminescent Center. The hole trapping for the Eu^{3+}, Tm^{3+} and Sm^{3+} luminescent centers limits the number of host lattices that can give rise to phosphorescence and thus the possibility of finding an optimal trap depth. So far, only three Eu^{3+} containing compounds have been reported to give rise to phosphorescence, that is, CaO, Y_2O_3, and Y_2O_2S. In any event, this kind of phosphorescence requires a priori binary or pseudo-binary host lattices with only one type of cation, that is, a host lattice with no countercations. In host lattices containing weak chemical bonds between countercations and anions, the cation vacancies are due mainly to these countercations and form traps not deep enough to support phosphorescence.

The transition-metal ions Cu^+ and Mn^{2+} possess very low IPs (20.3 and 33.7 eV, respectively). Consequently, anion vacancies tend to agglomerate with them, thereby losing their role as traps. In addition, the anion vacancies acting as traps are not stabilized far away from the activators so that the trap depth remains relatively low. For instance, the intrinsic phosphorescence of $ZnS{:}Cu^+,Co^{2+}$ is insufficient for most commercial applications and requires the use of radioisotope co-dopant (^3H and ^{147}Pm) to achieve higher performance.

Phosphorescence of the luminescent centers Tb^{3+} and Pr^{3+} is due to a trapping of the electrons promoted to their 5d orbitals[19] so that the excitation energy should be very high, and, hence, the solar radiation cannot give rise to phosphorescence. Consequently, the use of these rare-earth elements to get phosphorescent materials is not recommended.

The low IPs of the luminescent centers Eu^{2+} and Ce^{3+} imply that the anion vacancies migrate naturally toward them and become traps. It should be noted that the emission of these luminescent centers is often blue or green in oxides, but the co-doping with Mn^{2+} makes possible yellow or red emission via energy transfer to manganese (e.g., $Ca_2Al_2SiO_7{:}Ce^{3+},Mn^{2+}$ or $MgSiO_3{:}Eu^{2+},Mn^{2+},Dy^{3+}$).[39] The activator Ce^{3+} has a higher IP and a higher charge than does the activator Eu^{2+}. Thus, Ce^{3+} is less attractive for the anion vacancies, and Eu^{2+} is the more efficient activator for phosphorescence.

5.2. Trap Depth. The traps of the activator Eu^{2+} are anion vacancies, whose energy with respect to the CB bottom depends on the strength of the anion−cation bonds of the host lattice. When these bonds become stronger, the anion vacancy level is further lowered from the CB bottom. Thus, it is worthwhile to note that each oxygen of the scintillators $Gd_2SiO_5{:}Ce^{3+}$,[40] $YAlO_3{:}Ce^{3+}$,[41] and $Y_3Al_5O_{12}{:}Ce^{3+}$ [42] ($E_T \approx$ 1.5−2.0 eV) has at least four cations shorter than 2.5 Å, whereas each oxygen of the phosphors $SrAl_2O_4{:}Eu^{2+}$,[43] $Sr_4Al_{14}O_{25}{:}Eu^{2+}$,[44] and $Sr_2Al_2SiO_7{:}Eu^{2+}$ [45] ($E_T \approx 0.7$ eV) has only two or three cations shorter than 2.5 Å. In a given family of compounds, the trap depth depends on the structures and the substitutions. Indeed, the depth is defined with respect to the lowest-lying 5d levels of the activator (because the electron is not transferred via CB) and depends thus on the split of the 5d block levels by the crystal field, which is quantifiable from the energy of the 5d → 4f emission (Figure 6). The trap depth can again change by the co-doping with Ln^{3+}. The rare-earth cations whose IP is lower than that of the host cation increase the depth by slightly stabilizing the anion vacancy level. The co-doping by B^{3+} makes it finally possible to refine the trap depth slightly.[46]

5.3. Trap Concentration. The traps associated with Eu^{2+} are the anion vacancies close to the activator. One way of increasing the number of traps is to make the activator more attractive by increasing the difference in the IPs of the Eu^{2+} and the host cation, which increases in the order $Ba^{2+} < Sr^{2+} < Ca^{2+}$. Indeed, the compounds containing Ca^{2+} or Sr^{2+} possess much more outstanding phosphorescence properties than those containing Ba^{2+}.[47−49] Nevertheless, it is necessary in practice to find a compromise between the trap depth and the sensitivity of the human eye at a given wavelength. For instance, $SrAl_2O_4{:}Eu^{2+}$ (green emission) appears more strongly phosphorescent than $CaAl_2O_4{:}Eu^{2+}$ (blue emission), although it is intrinsically less powerful (i.e., shorter decay time) as a result of a higher sensitivity of the human eye in the green than in the blue region.[50] A second way of increasing the number of traps is to reinforce the attractive power of Eu^{2+} by associating with it a Ln^{3+} co-dopant whose IP is lower than that of the host cation. The number of useful rare-earth cations and the extent of their influence become greater with increasing the IP of the host cation. In the phases with Ca^{2+} and/or Sr^{2+}, the co-dopants Nd^{3+}, Dy^{3+}, and possibly Pr^{3+} are most prominent. A third way of increasing the number of traps is to prepare a phosphor under air and then anneal under reducing atmosphere[29] so as to slightly increase the number of residual Eu^{3+} ions. Thus, based on the aforementioned reasoning, the attractive power of Eu^{2+} (with regards to anion vacancies) located near Eu^{3+} ions should be reinforced. In the end, it is important that the total concentration of the anion vacancies is not a limiting factor, which is ensured by a possible slight cation under-stoichiometry.[29] Finally, it is noted that the synthesis by a solid route gives rise to a better phosphorescence than does the synthesis by soft chemistry.[51] This is so because there are

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(38) Lei, B.; Liu, Y.; Liu, J.; Ye, Z.; Shi, C. *J. Solid State Chem.* **2004**, *177*, 1333.

(39) Wang, X.; Jia, D.; Yen, W. *J. Lumin.* **2003**, *102*, 34.

(40) Smolin, Y. I.; Tkachev, S. P. *Kristallografiya* **1969**, *14*, 22.

(41) Vasylechko, L. O.; Matkovskii, A. O.; Savytskii, D.; Suchocki, A.; Wallrafen, F. *J. Alloys Compd.* **1999**, *291*, 57.

(42) Nakatsuka, A.; Yoshiasa, A.; Yamanaka, T. *Acta Crystallogr., Sect. B* **1999**, *55*, 266.

(43) Schulze, A. R.; Mueller-Buschbaum, H. *Z. Anorg. Allg. Chem.* **1981**, *475*, 205.

(44) Wang, D.; Wang, M.-Q.; Lu, G.-G. *J. Mater. Sci.* **1999**, *34*, 4959.

(45) Kimata, M. *Z. Anorg. Allg. Chem.* **1984**, *167*, 103.

(46) Niittykoski, J.; Aitasalo, T.; Hölsa, J.; Jungner, H.; Lastusaari, M.; Parkkinen, M.; Tukia, M. *J. Alloys Compd.* **2004**, *374*, 108.

(47) Lin, Y.; Tang, Z.; Zhang, Z.; Nan, C. *J. Alloys Compd.* **2003**, *348*, 76.

(48) Lin, Y.; Nan, C.; Zhou, X.; Wu, J.; Wang, H.; Chen, D.; Xu, S. *Mater. Chem. Phys.* **2003**, *82*, 860.

(49) Matsui, H.; Xu, C.; Watanabe, T.; Akiyama, M.; Zheng, X. *J. Electrochem. Soc.* **2000**, *147*, 4692.

(50) http://www.nemoto.com

more anion vacancies and because the high preparation temperature enables the vacancy migration toward Eu^{2+}. This migration is enhanced by increasing the temperature and the duration of heating.[29]

6. Improvement of Fluorescence Properties

The conditions necessary for improving the fluorescence intensity of most phosphors are not yet fully understood, but it is certain that some of these conditions are the exact opposite to those required for the improvement of phosphorescence intensity. Consequently, our conclusions resulting from the model of defect conglomeration developed for phosphorescent materials may be easily adapted for some fluorescent compounds, especially when the activators may have the ability to be photoionized.

The improvement of fluorescence requires then a decrease in the number of traps and in their depth. As an example, let us consider the Eu^{2+} luminescent center. The traps are the anion vacancies located near the activator, and the fluorescence can be enhanced by rare-earth co-dopant cations with a high IP (e.g., Y^{3+}) that will push the V_O vacancies away from Eu^{2+}. Alternatively, one might use rare-earth cations that decrease the trap depth while continuing to attract the anion vacancies (Ce^{3+} or Tb^{3+}). The advantage of this type of doping is that it does not prevent the natural migration of V_O toward Eu^{2+}. In fact, a composition containing Ce^{3+} as co-dopants has been patented by Philips Corp. for the fluorescent phosphor $BaMgAl_{10}O_{17}:Eu^{2+}$.[52] Similarly, the Ce^{3+} ion is used to enhance the fluorescence over the phosphorescence in $Gd_3Ga_5O_{12}:Cr^{3+}$.[53]

7. Concluding Remarks

In understanding the role of dopant and co-dopant cations in phosphors, it is essential to recognize the presence of interactions between dopant cations and anion vacancies as well as how these interactions are affected by co-dopant cations. Our analysis shows that dopant and co-dopant cations have a preferential distribution around anion vacancies due to the associated energy stabilization. The anion vacancy level can be better stabilized when the anion vacancy is placed closer to a dopant cation of lower IP than that of the host cation. By employing the IPs of cations as a qualitative measure for their tendency to be close to an anion vacancy, it is possible to explain the phosphorescence of the most heavily used green phosphor $ZnS:Cu^{+}$, describe essential characteristics of three classes of phosphors, and suggest synthetic strategies toward new improved phosphors. Our analysis of the phosphorescence phenomenon also made it possible to account for how point defects affect fluorescence.

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(51) Lin, Y.; Zhang, Z.; Zhang, F.; Tang, Q.; Chen, Q. *Mater. Chem. Phys.* **2000**, *65*, 103.

(52) Philips Corporation. U.S. Patent 0,190,669, 2002.

(53) Blasse, G.; Grabmaier, B.; Ostertag, M. *J. Alloys Compd.* **1993**, *200*, 17.