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The doping sites in Eu^{2+}-doped $A^{I}B^{II}PO_4$ phosphors and their consequence on the photoluminescence excitation spectra

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ABSTRACT

The energy corresponding to the excitation edge in Eu^{2+}-doped phosphate phosphors of the type $A^{I}B^{II}PO_4$ (A^{I} = monovalent cation, B^{II} = divalent cation) is calculated from the knowledge of two crystal-structure-related factors he(X(i)) and Fc(X(i)) which are connected respectively to the crystal field splitting (CFS) and the centroid energy (Ec) of the excited $4f^{6}5d^{1}$ electron configuration of Eu^{2+}. The calculation is carried out for each cation site X(i) available for Eu^{2+} in 25 different compositions of $A^{I}B^{II}PO_4$ including $NaZnPO_4$-Eu^{2+} for which the luminescence is firstly reported. Our results indicate (1) that is it possible to identify the nature of the cation site that contributes to the excitation edge of Eu^{2+} in $A^{I}B^{II}PO_4$ within an accuracy of ± 1000 cm^{-1} and (2) that the method can be used as a tool for the predictive design of $A^{I}B^{II}PO_4$ - Eu^{2+} phosphors applicable in solid state LED-based lighting.

1. Introduction

Eu^{2+}-doped phosphates belonging to the $A^{I}B^{II}PO_4$ family, where A^{I} and B^{II} are monovalent and divalent cations respectively, have been the subject of extensive research in recent years owing to their attractive photoluminescence properties upon blue or near-UV LED excitation [1,2]. The $A^{I}B^{II}PO_4$ family includes many members with many possible crystal structures and doping sites, depending on the nature of A^{I} (typically Li^{+}, Na^{+}, K^{+}, Cs^{+}, Rb^{+}, Ag^{+}, NH_4^{+}) and B^{II} (typically Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}). To date, the luminescence properties of Eu^{2+} are far from having exhaustively been explored in this family. The luminescence in these systems results from allowed electron transitions between $4f^{7}$ and $4f^{6}5d^{1}$ configurations of Eu^{2+} giving rise to intense band-like luminescence signals. Basically, the Eu^{2+} ions can be inserted either in the A^{I} or B^{II} sites of the $A^{I}B^{II}PO_4$ lattice. In both cases, the states belonging to the $4f^{6}5d^{1}$ configuration undergo an energy downshift through the combined action of the nephelauxetic effect and the crystal field splitting that result from the surrounding of the Eu^{2+} ions. In the free Eu^{2+} ion, the energy barycenter of the $4f^{6}5d^{1}$ configuration is located at 46,340 cm^{-1} (≈ 216 nm) [3] and the lowest $4f^{7} \rightarrow 4f^{6}5d^{1}$ transition is positioned at 34,000 cm^{-1} (≈ 294 nm) [4]. From this wavelength, a relatively moderate depletion is required to shift the low-energy excitation edge to the violet (400 nm) or the blue (450 nm) spectral region and therefore match the emission output of commercial LEDs. This justifies the tremendous interest on Eu^{2+} for solid-state lighting applications. The photoluminescence excitation edge, defined in the present work as the wavelength where the excitation has lost 50% of its lowest-lying maximum intensity, marks the limit above which the excitation in the first spin and dipole allowed $4f^{7} \rightarrow 4f^{6}5d^{1}$ transition of Eu^{2+} becomes inefficient. Browsing the literature, we found that the excitation edge of $A^{I}B^{II}PO_4$:Eu^{2+} phosphors vary by more than 100 nm, depending on the polymorph and on the nature of atoms A^{I} and B^{II}. This is considerable. Important discrepancies in the edge position also exist for a few lattices where A^{I} and B^{II} are fixed. In $CsMgPO_4$:Eu^{2+}, for instance, the excitation edge is reported either at 395 nm [5] or at 460 nm [6], which makes an unexplained mismatch of 65 nm. In $NaMgPO_4$:Eu^{2+}, the excitation edge is found at 377 nm for a corresponding blue emission [7] or close to 500 nm for a corresponding red emission [8], depending on the preparation method. The lack of information on the luminescence-structure relationships in $A^{I}B^{II}PO_4$:Eu^{2+} strongly limits our understanding of the above behaviors and furthermore restricts the design of $A^{I}B^{II}PO_4$:Eu^{2+} phosphors for LED-based lighting to trial-error procedures that are matter and time-consuming. Our motivation, in this context, is to identify the nature of the sites (A^{I} or B^{II}) that contribute to the excitation edge of the photoluminescence spectra of a given $A^{I}B^{II}PO_4$ lattice doped with Eu^{2+} by introducing a method enabling the calculation of the corresponding energy. This will be done by merging two semi-empirical models that have been introduced in the years 2000 to formalize

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relationships between the host environment and the crystal field splitting (CFS) or the centroid energy (Ec) of the $4f^{n-1}5d^1$ electron configuration of broad band emitting ions like Eu^{2+} [9,10]. These methods arise from the dielectric theory of electronegativity [11–13] that has been applied successfully to a wide variety of physical problems in the years 60–70 before being extended to phosphors at the end of the 90's [9,10,14,15]. Following these models, it is assumed (1) that Ec is determined mostly by the fractional covalence of the chemical bonds between the central ion and the nearby anions, the effective charge Q of the neighboring anions, the coordination number and the chemical bond volume polarizability and (2) that the magnitude of a cubic CFS is determined mostly by the homopolar part of the average energy gap separating the bonding and anti-bonding states in the chemical bond, the coordination number of the central ion, the fractional bond ionicity between the central ion and the nearby anions and Q. For convenience, the above parameters are combined in the calculation of two “environmental factors” *he(X(i))* and *Fc(X(i))* that can be calculated for any cation site X(i) of the host lattice from the knowledge of the crystal structure. From these values, the energy $E_{fd}(X(i))$ of the first spin and dipole allowed $4f^7 \rightarrow 4f^65d^1$ transition of Eu^{2+} in site X(i) can be determined. This energy is assimilated to the excitation edge defined above. In the present work, these calculations are carried out for each cation site X(i) contained in 25 $A^IB^{II}PO_4$ lattices, including 12 lattices in which the luminescence properties of Eu^{2+} have already been described in the literature and the member $NaZnPO_4$-Eu^{2+} whose luminescence properties are firstly described. From these data, we show (1) that is it possible to identify the nature of the cation site that contributes to the excitation edge of Eu^{2+} within an accuracy of ± 1000 cm^{-1} and (2) that the method can be used as a tool for the predictive design of $A^IB^{II}PO_4$ - Eu^{2+} phosphors applicable in solid state LED-based lighting.

2. Experimental

2.1. Synthesis

$NaZnPO_4$:Eu^{2+} was prepared by standard solid state method using Na_2CO_3 (ACROS, > 99.6%) as the alkaline source, $NH_4H_2PO_4$ (Sigma-ALDRICH, > 98.5%) as the phosphate source, $Zn(NO_3)_2$, $6H_2O$ (Acros, > 98%) as the zinc source and Eu_2O_3 (PURATREM, 99.99%) as the dopant source. The nominal doping rate was 1 mol%. The reagents were homogeneously mixed in stoichiometric proportions presence of ethanol. The mixtures were dried at 80 °C, heated at 300 °C in air for 15 h, thoroughly grinded and heated again at 850 °C for 6 h under Ar/H_2 – 95/5 flow.

2.2. Characterization methods

The crystal structure and microstructure of the materials were checked respectively by X-ray diffraction using an X-pert Pro diffractometer (Panalytical) with Cu anode and by electron scanning microscopy using a JSM-5910 LV microscope from Jeol operated at 15 kV. The steady state excitation and emission spectra were collected at 77 K using a setup consisting of two Jobin-Yvon/Horiba TRIAX 180 and TRIAX 550 monochromators operated with a 450 W CW xenon lamp. The powders were conditioned in ultrapure quartz tubes and immersed in liquid nitrogen. The excitation spectra were spectrally corrected using sodium salicylate.

3. Theoretical backgrounds and methodology

In the frame of the dielectric theory of electronegativity, the complex crystal under investigation needs first to be decomposed into a linear combination of binary units consisting of a central cation surrounded by oxygen neighbors. Let us illustrate this decomposition on a phosphate with general formula $A_aB_bP_pO_o$. To individuate the crystallographic sites (i = 1, 2, ..., n) that may be occupied by the cations and anions in the crystal structure, the compound will be reformulated as: “$A(i)_{a_i}B(i)_{b_i}P(i)_{p_i}O(i)_{o_i}$” where $a_i = m_i(A)/Z$, $b_i = m_i(B)/Z$, $p_i = m_i(P)/Z$, $o_i = m_i(O)/Z$ and $\sum_{i=1}^{n} a_i = a, \sum_{i=1}^{n} b_i = b, \sum_{i=1}^{n} p_i = p, \sum_{i=1}^{n} o_i = o$.

In these expressions, $m_i(A)$, $m_i(B)$, $m_i(P)$ and $m_i(O)$ are the multiplicity of the different Wyckoff sites (i) occupied by atoms A, B, P and O, respectively and Z is the number of formula units per unit cell. The compound can then be expressed as a sum of oxo-units $A(i)a_i\frac{N_{O(i)-A(i)}}{N_{A(i)}}O(i)o_i\frac{N_{A(i)-O(i)}}{N_{O(i)}}$,$B(i)a_i\frac{N_{O(i)-B(i)}}{N_{B(i)}}O(i)o_i\frac{N_{B(i)-O(i)}}{N_{O(i)}}$ and $P(i)a_i\frac{N_{O(i)-P(i)}}{N_{P(i)}}O(i)o_i\frac{N_{P(i)-O(i)}}{N_{O(i)}}$, where $N_{A(i)\text{-}O(i)}$, $N_{B(i)\text{-}O(i)}$ and $N_{P(i)\text{-}O(i)}$ indicate the number of oxygen atoms O(i) surrounding A(i), B(i) and P(i), respectively, while $N_{O(i)\text{-}A(i)}$, $N_{O(i)\text{-}B(i)}$ and $N_{O(i)\text{-}P(i)}$ indicate the number of cations A(i), B(i) and P(i) surrounding oxygen O(i), respectively. $N_{A(i)}$, $N_{B(i)}$ and $N_{O(i)}$ are the coordination numbers of the considered atoms in the lattice. The environmental factors *he(X(i))* and *Fc(X(i))* are then calculated for each cation site X(i) in these binary units. In the present work, we have ignored the calculations for P sites that are not available for Eu^{2+} dopant. For a given binary crystal $X(i)_mO(i)_n$, the two factors *he(X(i))* and *Fc(X(i))* for site X(i) are calculated as:

$$he(X(i)) = \sqrt{\sum_{1}^{N_{X(i)}} f_{c(X(i)-O(i))}\alpha_{(X(i)-O(i))}Q^2_{O(i)}} \tag{1}$$

and

$$Fc(X(i) = \frac{39.74Q_O f_{i(X(i)-O)}}{N_{X(i)}d^{2.48}_{(X(i)-O)}} \tag{2}$$

In Eq. (1), $fc_{(X(i)\text{-}O(i))}$ and $\alpha_{(X(i)\text{-}O(i))}$ represent respectively the fractional covalency and the volume polarization of each X(i)-O(i) bond in the unit. $Q_{O(i)}$ is the effective charge carried by the oxygen atoms in site (i) of the binary unit. For a given $X(i)_mO(i)_n$ unit, $Q_{O(i)}$ is calculated as $Q_{O(i)} = \frac{m}{n}Q_{X(i)}$, where $Q_{X(i)}$ is the effective charge of cation X in site X(i). This charge was taken as the bond valence sum of atom X(i) in its polyhedron and was obtained from the crystal structure of the host lattice (cif file) using VESTA software [16]. The necessary values of bond valence parameters were obtained from [17]. In Eq. (2), $fi_{(X(i)\text{-}O)}$ is the fractional iconicity between X(i) and all nearby oxygen atoms in the polyhedron. It is evaluated as the average value of the fractional iconicity $fi_{(X(i)\text{-}O(i))}$ of each individual X(i)-O(i) bond in the polyhedron. Similarly, $d_{(X(i)\text{-}O)}$ is the corresponding average X(i)-O distance in the considered polyhedron and Q_O is the average value of the effective charge carried by the oxygen atoms. Values of $fc_{(X(i)\text{-}O(i))}$ and $fi_{(X(i)\text{-}O(i))}$ are calculated from: $f_{c(X(i)-O(i))} = E^2_{h(X(i)-O(i))}/(E^2_{h(X(i)-O(i))} + C^2_{(X(i)-O(i))})$ and $f_{i(X(i)-O(i))} = C^2_{(X(i)-O(i))}/(E^2_{h(X(i)-O(i))} + C^2_{(X(i)-O(i))})$, where $E_{h(X(i)\text{-}O(i))}$ and $C_{(X(i)\text{-}O(i))}$ are respectively the homopolar and heteropolar parts of the energy gap separating the bonding and anti-bonding states in each individual X(i)-O(i) bond. These energies come from the interaction of dipole moments and other multiple moments and account for bond covalency [18]. Their calculation (in eV) is described in details in the Appendix A section. The quantity $39.74d^{-2.48}_{X(i)-O}$ in Eq. (2) represents the average value of $E_{h(X(i)\text{-}O(i))}$ in the oxo polyhedra related to site X(i).

The volume polarization $\alpha_{(X(i)\text{-}O(i))}$ of each X(i)-O(i) bond is obtained using:

$$\alpha_{(X(i)-O(i))} = \nu_{(X(i)-O(i))}\frac{3}{4\pi}\frac{\varepsilon_{(X(i)-O(i))}-1}{\varepsilon_{(X(i)-O(i))}+2} \tag{3}$$

where $\upsilon_{(X(i)\text{-}O(i))}$ is the volume (in cm^3) of the X(i)-O(i) bond and $\varepsilon_{(X(i)\text{-}O(i))}$ is the dielectric constant of this bond. Details on the calculation of these parameters are given in the Appendix A section.

As described in [9,10], the centroid energy (in cm^{-1}) of the $4f^65d^1$ configuration in Eu^{2+}-doped inorganic solids follows the empirical equation [9]:

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