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Crystal field splitting of $4f^{n-1}5d$-levels of Ce^{3+} and Eu^{2+} in nitride compounds

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ABSTRACT

Recently a lot of Ce^{3+}/Eu^{2+}-activated nitride and oxonitride phosphors have been explored due to potential or practical application for white-light LEDs. In this paper, data of crystal field splitting of the $4f^{n-1}5d$-levels of Ce^{3+} and Eu^{2+} in nitride compounds is collected and analyzed. The relationship between the crystal field splitting and the coordination polyhedron around the Ce^{3+} and Eu^{2+} is revealed, showing that crystal field splitting is related to coordination number, polyhedron shape and size, while being irrelevant of the anion types. In addition, the crystal field splitting of Ce^{3+} and Eu^{2+} in the nitride compounds is correlated by a multiplication factor 0.76, which is in consistent with those in halides, sulfides and oxides. This paper makes it possible to predict luminescence properties of Ce^{3+}- or Eu^{2+}- doped nitride compounds.

1. Introduction

Recently Ce^{3+}/Eu^{2+}-activated nitride and oxonitride phosphors have received much attention because of their unique luminescent properties and fine potential for using in phosphor-converted white LEDs (pc-LEDs) [1]. The phosphors play a significant role in quality of pc-LEDs, such as luminous efficiency, color rendering index (CRI), correlated color temperature (CCT), and lifetime. The general requirements for LED phosphors include as follows: broad excitation spectrum matching well with the emission spectrum of blue LED chips; suitable emission spectrum; high quantum efficiency; small thermal quenching (temperature quenching) and high chemical stability [2,3]. The unique luminescent properties of Ce^{3+}/Eu^{2+}-activated phosphors are originated from $4f^n$–$4f^{n-1}5d$ (*f–d*) transition of rare earth ions. This transition is a parity-allowed electric dipole transition and therefore broad and high efficient emission can be achieved. In addition, energy positions of absorption and emission can be modulated by the host lattice due to the strong interaction of the *5d*-electron with the neighbouring anion ligands.

Generally there is a large energy gap between the 4*f* ground state and the lowest 5*d* excited state for a free rare earth ion, such as ~4.216 eV (34,000 cm^{-1}) for Eu^{2+} and ~6.118 eV (50,000 cm^{-1}) for Ce^{3+} ions [3]. Dorenbos has carried out a systematic study of the energies of the lowest $4f^{n-1}5d^1$ states of Ce^{3+}/Eu^{2+} ions in different hosts [4,5]. The effect of the host crystal on the *5d* energy levels can be expressed as their energy red-shift (D), which includes the centroid shift ε_c and the crystal field splitting ε_{cfs}. Centroid shift ε_c is defined as the downward shift of the average position of the five *5d*-levels relative to the free ion value. The ε_c represents the nephelauxetic effect, which is related to covalency between the central lanthanide ion and the anion ligands of host lattice. The bonding types of most inorganic compounds lie intermediately between the simple ionic and covalent extremes. The increase in the covalent character usually causes an increase of ε_c value [5]. In a host lattice, the degenerate *5d*-levels will split into at most five *5d* states. The difference between the lowest and highest *5d*-level is defined as the crystal field splitting. The ε_{cfs} is generally related to the shape and size of Ce^{3+}/Eu^{2+} coordination polyhedral [6,7].

The bonding in nitrides is significantly more covalent than that in oxides, because of the higher formation energy of N^{3-} from atomic N (+2300 $kJmol^{-1}$) than that of O^{2-} from atomic O (+700 kJ mol^{-1}) [8]. As compared to oxide hosts, nitride and oxonitride hosts can make *5d* energy levels downward shift more, i.e. a larger centroid shift ε_c. So the Ce^{3+}/Eu^{2+}-doped nitride phosphors can effectively absorb blue LED radiation and emit longer-wavelength visible light, and thus they are very suitable for use in pc-LEDs. In addition, an important class of nitrides/oxonitrides is nitridosilicates and their derived compounds. Their structures typically consist of SiN_4 tetrahedra, where a partial nitrogen/silicon can be substituted by oxygen/aluminum to form Si/Al $[O/N]_4$ tetrahedra. These tetrahedron units are stacked together by sharing their corners to form a condensed framework, usually resulting in a structural rigidity contributing to chemical and thermal luminescence stability [9]. Furthermore, these tetrahedron units have different

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connecting ways providing the Ce^{3+}/Eu^{2+} with rich and different ligand environments, and can efficiently adjust the emission and absorption wavelengths. Therefore, currently, nitrides/oxonitrides and their derivatives are exploited as the key phosphors for using in pc-LEDs, such as (Sr, Ca)$AlSiN_3:Eu^{2+}$, $M_2Si_5N_8:Eu^{2+}$ (M = Ca,Sr,Ba), $SrLiAlN_3:Eu^{2+}$, $La_3Si_6N_{11}:Ce^{3+}$, α-sialon:Eu^{2+}, β-sialon:Eu^{2+}, and $MSi_2O_2N_2:Eu^{2+}$, etc. [10–23].

Dorenbos addressed that spectroscopic polarizablility α_{sp} should be regarded as a phenomenological parameter representing the nephelauxetic effects, and related the energy of the *5d* configuration of Ce^{3+} with anion polarizability and cation electronegativity and obtained the relationship in oxides and fluorides [24]. Our previous work collected information on *5d* levels of Ce^{3+} in nitrides and obtained a linear relationship between the anion polarizability and the inverse square of the average electronegativity of the cations [25]. Based on the above relation, we can predict the centroid shift due to the covalent effect not only in nitrides but also in oxynitrides. Furthermore, if the crystal field splitting data of *5d* energy levels in nitride hosts can be accessed, we can estimate the characteristic data on its luminescence properties, especially on excitation spectra.

The crystal field splitting of the $4f^{n-1}5d$-levels of Ce^{3+} and Eu^{2+} in fluoride, chloride, bromide, iodide, oxide, sulfide, and selenide compounds has been studied by Dorenbos [26–29]. By selecting the compounds with the same shape of coordination polyhedron around Ce^{3+} and Eu^{2+}, the crystal field splitting appears to behave as

$$\varepsilon_{cfs} = \beta^{Q}_{poly} R_{av}^{-2} \tag{1}$$

where β^{Q}_{poly} is a constant depends on the type of coordination polyhedron, irrespective of the lanthanide valence (trivalent, Q = 3+ or divalent, Q = 2+). R_{av} is defined as

$$R_{av} = \frac{1}{N}\sum_{i=1}^{N}(R_i - 0.6\Delta R) \tag{2}$$

where R_i are the individual bond length to the N coordinating anions in the unrelaxed lattice.$\Delta R \equiv R_M - R_{Ln}$, where R_M is the ionic radius of the cation which is replaced by the lanthanide Ln with ionic radius R_{Ln}. $0.6\Delta R$ is an estimation of the bond length relaxation. By fitting the data through Eq. (1), the value of the β_{poly} can be obtained. For example, β_{octa} is $1.36{\cdot}10^5 eV\ pm^2$ for Eu^{2+}. β_{octa}: β_{cubal}: β_{cubo} equals 1: 0.89: 0.44 for both Ce^{3+} and Eu^{2+} [30]. It reveals that higher coordination number tends to reduce the crystal field splitting. And the type of the anion, whether it is F, Cl, Br, I, O, S or Se, makes no difference [30]. From comparing Eu^{2+} data with Ce^{3+} data it follows that $\beta_{poly}(Eu^{2+}) = 0.81\beta_{poly}(Ce^{3+})$ and $\varepsilon_{cfs}(7, 2+, A) = 0.77\varepsilon_{cfs}(1, 3+, A)$ [3]. However, the crystal field splitting of Ce^{3+} and Eu^{2+} in nitrides hasn't been studied in detail, as far as we know.

This work deals with data on the crystal field splitting of the $4f^{n-1}5d$-levels of Ce^{3+} and Eu^{2+} in nitride compounds by using the model proposed by Dorenbos. The relationship between the crystal field splitting and the shape and size of the coordination polyhedron in nitride compounds is obtained, and it is in good coincidence with the result of Dorenbos in fluorides, chlorides, bromides, iodides, oxides, sulfides, and selenides. Following the relationship, the crystal field splitting of the Ce^{3+} and Eu^{2+} can be predicted based on different nitride compounds. Comparison of the crystal field splitting of the $4f^{n-1}5d$-levels of Ce^{3+} with Eu^{2+} in the same nitride compound shows a linear relationship, which makes it possible to predict emission and absorption wavelengths of Eu^{2+} from information available on Ce^{3+} or vice versa.

2. Data on 5d-level positions in nitride compounds

Along with the development of nitride compounds recently, many spectral data have been reported. The structural and spectral data of most reported nitride compounds doped with Ce^{3+} and $Eu^{2+}$are summarized in Tables 1 and 2 respectively.

Table 1

Crystallographic and spectroscopic properties, crystal field splitting ε_{cfs} in Ce^{3+} doped nitrides. *N* is the number of the coordinating anions and R_{av} is the average bond length to the coordinating anions in the polyhedron.

Compound	*N*: R_{av}*(pm)*	*5d*-Excitation bands(nm)	$\varepsilon_{cfs}(eV)$	Ref.
$CaAlSiN_3$	5;249	259,313,370,421,483	2.2203	[60][a,b]
$Ca_2Si_5N_8$	6;259	261,329,365,397,423	1.8195	[34,37,61][a], [62][b]
$Ba_2Si_5N_8$	6;263	260,284,384,415	1.7813	[34,36][a], [62][b]
$Sr_2Si_5N_8$	6;264	260,276,330,387,425	1.8515	[34,36,61][a], [62][b]
$CaMg_3SiN_4$	7;272	302,484	1.5440	[52][a,b]
$La_3Si_6N_{11}$	8;265	300,350,385,455,474	1.5172	[14,63][a,b]
$SrMg_2Al_2N_4$	8;275	319,505	1.4317	[64,65]
$SrAlSi_4N_7$	8;277	306,336,417,462	1.3683	[31][a,b], [66][b]
$SrSiN_2$	8;277	298,330,399,443	1.3620	[40,41][a], [42][a,b]
$LaSi_3N_5$	9;278	260,282,313,332,354	1.2664	[67–69][a], [70][b]
$BaYSi_4N_7$	12;285	285,297,317,339	0.6930	[47][a,b]
$SrYSi_4N_7$	12;295	285,318,340	0.7038	[48][a,b]
$BaSi_7N_{10}$	12;309	284,306,325	0.5704	[71][a,b]

[a] The source of the crystallographic data.

[b] The source of spectroscopic data of Ce^{3+}.

Table 2

Crystallographic and spectroscopic properties, crystal field splitting ε_{cfs} in Eu^{2+} doped nitrides. N is the number of the coordinating anions and R_{av} is the average bond length to the coordinating anions in the polyhedron.

Compound	*N*: R_{av}*(pm)*	5d-Excitation bands(nm)	$\varepsilon_{cfs}(eV)$	Ref
$CaAlSiN_3$	5;259	310,335,450,500,564	1.8014	[10][a,b], [43][b]
$MgAlSiN_3$	5;260	296,352,423,478,505	1.7337	[44][a,b]
$SrAlSiN_3$	5;274	320,374,422,469,520	1.4903	[72][a], [45][b]
$Ca_2Si_5N_8$	6;269	315,374,401,486	1.3851	[34,37,73][a], [13,74,75][b]
$SrAlSi_4N_7$	6;271	315,358,412,460,512	1.3585	[32,33][a,b]
$Ba_2Si_5N_8$	6;273	312,334,402,472	1.3472	[36,61][a], [13,74][b]
$Sr_2Si_5N_8$	6;274	312,334,418,474	1.3583	[34,36,61][a], [13,74,76,77][b]
$SrLiAl_3N_4$	8;278	395,455,598	1.0657	[78][a], [49–51][b]
$SrSiN_2$	8;284	336,395,466	1.0295	[40,41][a], [42,79][b]
$SrMg_3SiN_4$	8;286	376,449,544	1.0184	[52][a,b]
$BaSiN_2$	8;289	334,395,464	1.0402	[40,41][a], [42][b]
$LaSi_3N_5$	9;274	338,404,456	0.9493	[67–69][a], [46][b]
$SrSi_6N_8$	10;302	354,374,419	0.5434	[53][a,b]
$BaYSi_4N_7$	12;286	342,386	0.4133	[47][a,b]
$SrYSi_4N_7$	12;296	340,390	0.4676	[48][a,b], [80][b]
$BaSi_7N_{10}$	12;309	296,332	0.4542	[71][a,b], [54][b]

[a] The source of the crystallographic data.

[b] The source of spectroscopic data of Eu^{2+}.

In the second column, *N* gives the coordination number, R_{av} expresses the average distance to the *N* coordinating anions in the relaxed lattice. Special attention should be devoted to multiple cation sites in Tables 1 and 2. In $SrAlSi_4N_7$ two different Sr^{2+} sites are identified, and they are coordinated by six and eight nitrogen atoms respectively [31–33]. Ruan et al. attribute the dominant Ce^{3+} emission to Ce^{3+} on the 8-fold coordinated Sr-site [31], and attribute the dominant Eu^{2+} emission to Eu^{2+} on the 6-fold coordinated Sr-site [33]. Here, we follow this assignment. As for $M_2Si_5N_8$, there exist two different M^{2+} sites for M = Ca, Sr, Ba. Combining the bond valence theory and the local coordination structure with the references by Ten Kate et al. [34], Li et al. [35] and Schlieper et al. [36], we consider that two Ca^{2+} sites are all coordinated by six nitrogen atoms, while two Sr^{2+} / Ba^{2+} sites are coordinated by six and seven nitrogen atoms, which is more rational than the coordination number of cation sites in $M_2Si_5N_8$(M = Ca, Sr, Ba) adopted by Wang et al. [12,37,38]. In those cases we choose the site with larger crystal field splitting, which has also less coordination number. For $CaAlSiN_3$, Ca^{2+} sites were considered to be fourfold by Piao et al. [39], and it was adopted by Wang et al. [25]. However, it