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Theoretical assessment of emission efficiency of Eu²⁺-doped phosphors based on alkaline-earth network

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This paper presents the methodology for the estimation of the emission efficiency of Eu^{2+} -doped phosphors based on their structural information. It was figured out from the electronic structures of CaAlSiN₃:Eu²⁺ and SrSiN₂:Eu²⁺ that the lowest unoccupied molecular orbital (LUMO), which is mainly consisted of Eu 5d orbital, is a key factor to show high efficiency of Eu^{2+} emission. Large contribution of Eu 5d orbital to LUMO is found when there is a strong atomic orbital interaction between alkaline earth atoms and Eu^{2+} atoms. According to the fact, we defined alkaline earth network (ANet) to represent the magnitude of the interaction of alkaline earth atoms with Eu^{2+} atoms in the host crystal. We calculated ANet for 10 Eu^{2+} doped phosphors and correlated them with the experimental values of internal quantum efficiency. ANet has an inversely relationship with internal quantum efficiency. ANet is a good index for qualitatively searching a high efficient Eu^{2+} -doped phosphor because it is calculated only from the structural information of targeted phosphors.

Key words: Eu²⁺-doped phosphor, Alkaline-earth network, (n-1)d orbital, Symmetry, Emission efficiency, Computation.

Introduction

New type of phosphors, nitride and oxy-nitride, has been paid much attention because market of white light emitting diode is growing [1]. Phosphors for cathode ray tube, fluorescent lamp, and plasma display had been actively researched. There are various types of crystal structures of phosphors have been reported, however, most of them were not used in market. This would be because these phosphors did not have suitable performance, e.g. an emission wavelength, excitation source, and emission efficiency for targeted applications. Therefore, prediction method for a performance of phosphor from its crystal structure accelerates phosphor development, which enables to improve their emission properties to be suitable for particular application.

Prediction of emission properties of phosphors is difficult because it is strongly affected by a combination of types of emission center and host material. In particular, emission properties of Eu^{2+} and Ce^{3+} -doped phosphors which emit lights with 4f-5d electron transition are significantly changed by type of host crystal. This is because a magnitude of energy level change of Eu 4f orbital, which is located near nuclear, is smaller than that of Eu 5d orbital.

There were some studies on the prediction of emission properties of phosphors. Crystal field theory and ligand field theory have been widely used to calculate energy level split of d-orbitals. Quantum chemistry calculation was used to study electronic structures of phosphors [2, 3]. We have studied interactions between emission center and host crystals by evaluating their electronic structures using tightbinding calculations for relative large-scale crystal models. It is suggested that the interaction, indicating the degree of overlap of atomic orbital, between Eu 5d orbital and alkaline-earth(A) (n-1)d orbitals is important to characterize emission property of the Eu²⁺-doped phosphors [4].

Quantum chemistry reveals the relationship between electronic structure and crystal structure, however, it needs much computational time to treat whole structure of host crystal so that to obtain meaningful insight helpful for improvement of phosphors is difficult in practice. For phosphor developments, the short time estimation based on crystal structure is required. Dorenbos studied the relationship between crystal field strength and emission wavelength of Eu²⁺-doped phosphors [5]. Ulitert proposed an empirical equation to predict emission wavelength of Eu²⁺- and Ce³⁺-doped phosphors on the baseis of crystal field strength [6]. Our group proposed a structure index for representing a

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local orbital interaction between a crystal structure around Eu atom on the basis of electronic structure calculations [7]. A good relationship was found between the structure indexes and the emission wavelength of Eu^{2+} -doped oxides, meaning the importance of the consideration of the interaction with A atoms on emission properties.

There has been scarcely reported on the prediction methodology for emission efficiency of Eu^{2+} and Ce^{3+} -doped phosphors. There is a common perception that Eu^{2+} -doped nitrides and oxynitrides phosphors show high quantum efficiency. It is not clearly revealed what kind of crystal structure shows high efficiency as Eu^{2+} -doped phosphor. Phonon is known to be one of the important factors to determine quantum efficiency of phosphor emission because some of excited energy would be lost by emitting phonon. Many researchers studied the relationship between phonon and emission lifetime, in particular phosphors emitting visible lights with 4f-4f transition [8]. We discussed the effects of phonon on Eu^{2+} emission efficiency in the part of the results and discussion.

In this paper we aimed to find a correlation between crystal structure and emission efficiency of phosphors. Electronic structures of high and low efficiency phosphors are calculated to study a relationship between crystal structure and emission efficiency. Based on quantum chemistry calculation, we defined alkalineearth network (ANet) representing strength of atomic orbital interaction between A atoms, which shows a good correlation to internal quantum efficiency in the case of Eu^{2+} -doped phosphors. Therefore, we proposed ANet as indicator for prediction of emission efficiency of Eu^{2+} -doped phosphors.

Method: electronic structure calculation

We calculated the electronic structures using periodic quantum chemistry (QC) calculations based on the density functional theory (DFT). The DMol³ program implemented in the Materials Studio version 3.2 was used. Geometry optimizations were performed at the local density approximation level employing the VWN functional [9]. We optimized only the atomic positions in the calculation model and the cell sizes were not optimized. The electronic structure calculations for the detailed analysis of the optimized structures were performed at the generalized gradient approximation level employing the PBE functional [10]. The double numerical with polarization basis sets and effective core potentials were used for all the calculations. The supercell model of CaAlSiN₃:Eu²⁺ (CASN:Eu²⁺) and SrSiN₂:Eu²⁺ are constructed and their lattice parameters are listed in Table 1.

Method: definition of ANet

ANet is defined as a deviation in the distance from the structure in which the positions of A atoms are

Table 1. Calculation model.

		Lattice length (Å)		
Phosphor	Composition	а	b	С
CaAlSiN ₃ :Eu ²⁺	$Ca_{15}EuAl_{16}Si_6N_{48}$	9.80	11.30	10.13
SrSiN ₂ :Eu ²⁺	$Sr_{31}EuSi_{32}N_{64}$	11.95	14.57	10.99



Fig. 1. Calculation flow of ANet.



Fig. 2. Examples of ANet calculation: (a) crystal structure of $BaSi_7N_{10}:Eu^{2+}$, (b) crystal structure of $Ca_2Si_5N_8:Eu^{2+}$, (c) extracted atoms of $Ca_2Si_5N_8:Eu^{2+}$, and (d) extracted atoms of $Ca_2Si_5N_8:Eu^{2+}$.

completely symmetric in the terms of the center of Eu²⁺ atom. A calculation flow of ANet is shown in Fig. 1. Fig. 2 illustrates the examples of ANet calculations. The symmetry is calculated by setting the Eu^{2+} as the center. The Eu²⁺ site in the crystal structure is selected from A (A = Car or Ba or Sr) site which is the most stable site for the replacement [7]. Local atoms around the Eu²⁺ atom in the phosphor crystal are extracted by following two rules: 1) A atoms which make angle of Eu-X-A less than 90° are extracted. X represents all atoms except Eu²⁺. 2) A and X atoms which make angle of Eu-X-A less than 120 ° are extracted if there is no A atom being satisfied with the condition of 1). Then symmetry of cluster constructed by extracted atoms is determined with an allowance of the distance of 1.0 Å. Hence, ANet is an index for indicating the deviation from the perfect symmetry. C_s and C_n symmetry are considered in this study. ANet was calculated for 10 phosphors [11-15].



Fig. 3. Computed electronic structure: (a) $CASN:Eu^{2+}$ and (b) $SrSiN_2:Eu^{2+}$.

Results and Discussion

Electronic structures of Eu^{2+} -doped phosphors were calculated to find a key interaction to determine their quantum efficiencies. We selected CASN: Eu^{2+} and SrSiN₂: Eu^{2+} as high and low efficiency phosphor, respectively. Fig. 3 shows the calculated partial density of state for two phosphors.

Obtained electronic structures for CASN: Eu^{2+} and SrSiN₂: Eu^{2+} are similar. The top of valence bands are consisted of N 2p orbitals. The bottom of conduction bands are composed of Ca/Sr (n-1)d with Al and Si 3s/3p orbitals. The Eu 4f orbitals appear in forbidden bands.

A difference of electronic structures of two phosphors was found in characteristics of the lowest unoccupied molecular orbital (LUMO). The LUMOs are consisted of Eu 5d orbitals for both phosphors, however, the contribution of Sr 4d orbitals in the lowest Eu 5d orbital of SrSiN₂:Eu²⁺ is higher than that of Ca 3d orbitals of CASN:Eu²⁺. In the case of BAM:Eu²⁺, the largest component of LUMO is the lowest Eu 5d orbital [4]. Electronic structure calculation suggests that a significant contribution of Eu 5d orbital to LUMO is one of a key factor to show high emission efficiency. The detailed discussion is presented in the next section.

Electronic structure calculations suggest that one of the key factors for high efficiency of Eu^{2+} -doped phosphors are able to explain by the feature of LUMO. High efficiency phosphor has LUMO which are mainly consisted of Eu 5d orbital. In this section, we discussed what kind of crystal structures is a good applicant for high efficiency Eu^{2+} -doped phosphors from the view point of a relationship between crystal structure and electronic structures. The Eu 5d orbitals are more stable than the A (n-1)d orbitals. It means that if Eu^{2+} is doped in a host crystal which has the bottom of conduction band consisted of A (n-1)d orbital, the Eu 5d orbital contributes to LUMO. A crystal with high symmetric structure in terms of A atoms would form the bottom of conduction band from the contribution of

Table 2. Calculated ANet and internal quantum efficiency for Eu^{2+} -doped phosphors from the experiments [10-14].

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Phosphor	ANet (-)	Internal quantum efficiency		Ref.
Ca ₂ Si ₅ N ₈ :Eu ²⁺	0.202	$50\sim 55\%$	(Eu = 2 mol%)	10
$Sr_2Si_5N_8{:}Eu^{2+}$	0.000	75%	(Eu = 10 mol%)	11
$Ba_2Si_5N_8{:}Eu^{2+}$	0.000	79%	(Eu = 10 mol%)	11
BaSi ₇ N ₁₀ :Eu ²⁺	0.091	$55\sim 60\%$	(Eu = 20 mol%)	12
CaAlSiN ₃ :Eu ²⁺	0.000	91%	(Eu = 0.5 mol%)	11
CaSiN ₂ :Eu ²⁺	0.307	39%	(Eu = 0.1 mol%)	11
SrSiN ₂ :Eu ²⁺	0.486	25% v.s. YAG*1	(Eu = 2 mol%)	12
BaSiN ₂ :Eu ²⁺	0.000	40% v.s. YAG^{*1}	(Eu = 2 mol%)	12
$CaSi_2O_2N_2{:}Eu^{2+}$	0.150	76%	(Eu = 2 mol%)	13
BaSi ₂ O ₂ N ₂ :Eu ²⁺	0.000	71%	(Eu = 2 mol%)	13
Ba ₃ Si ₆ O ₉ N ₄ :Eu ²⁺	-	-	(Quenching at RT ^{*2})	14

 *1 YAG is Y₃Al₅O₁₂:Ce³⁺.

*2RT means room temperature.

Table 3. Phonon frequency of host crystal and internal quantum efficiency of Eu^{2+} in host crystal [16-19].

Phosphor	Phonon frequency (cm ⁻¹)	Internal quantum efficiency (%)
α -Sialon:Eu ²⁺	1129 [16]	60~70 [17]
SrS:Eu ²⁺	284 [18]	35 [19]

A (n-1)d orbitals because high symmetric structure means that atomic orbital interaction continues over the whole of crystal structure. Therefore, we defined the ANet, which represents the magnitude of local symmetry of Eu and A atoms, as an indicator for quantum efficiency of Eu^{2+} -doped phosphors.

Calculated ANet for Eu2+-doped phosphors and their internal quantum efficiencies are summarized in Table 2. Eu concentrations of the phosphors are also listed in Table 2 because quantum efficiency depends on Eu concentration. The Eu concentrations in this table are the concentrations when the phosphors showed the highest efficiency. It is found that ANet has an inverse relationship to internal quantum efficiency of Eu²⁺doped phosphors. For example, ANet are calculated as 0.0 for high efficiency phosphors: CASN:Eu²⁺ and Sr₂Si₅N₈:Eu²⁺. On the other hand, low efficiency phosphors, e.g. SrSiN₂:Eu²⁺ and Ba₃Si₆O₉N₄:Eu²⁺, have higher ANet values. Because ANet is defined from the symmetry of local structure surrounding the center of Eu²⁺, our results suggest that host crystals having high symmetry around Eu²⁺ have a possibility to show high quantum efficiency.

In general, quantum efficiency is determined by a balance of phonon emission rate and lifetime of excited state. Phonon is emitted when energy levels of the excited state and the ground state are crossed, therefore, phonon emission rate may relate to phonon frequency. Because this contribution has not been considered in our methodology, we would like to discuss briefly this effect in the following sentences. Good relationships between phonon frequency and emission efficiency of 4f-4f transition phosphor, for example, Y_2O_3 :Eu³⁺ [8], have been reported. This is because the lifetime of 4f-4f transition rate, which order is $10^{-6} \sim 10^{-3}$ sec, is much slower than the phonon emission rate, which order is $10^{-13} \sim 10^{-12}$ sec. On the other hand, the order of 4f-5d transition rate is 10⁻ $^{9} \sim 10^{-6}$ sec, meaning a difficulty in the discussion of emission efficiencies of Eu²⁺- and Ce³⁺-deped phosphors based on the phonon frequency. Table 3 lists quantum efficiencies of Eu2+-doped phosphors and phonon frequency of host crystals [16-19]. Ca--sialon:Eu²⁺ shows higher quantum efficiency than SrS:Eu²⁺ although SrS:Eu²⁺ shows smaller phonon frequency. It suggests that phonon frequency is not major factor to determine quantum efficiency of Eu²⁺-doped phosphors, supporting our discussion of the relationship between ANet and quantum efficiency.

Summary

This paper studied relationship between crystal structures and quantum efficiencies of Eu²⁺-doped phosphors and proposed ANet as an indicator to judge the quantum efficiencies is high or not. By calculations and comparison of electronic structures of CASN:Eu²⁺ and the SrSiN₂:Eu²⁺, one of the requirements for showing high efficiency is suggested; LUMO is mainly consisted of Eu 5d orbitals. Local symmetric structure of A atoms are important to make LUMO with large contribution of Eu 5d orbital, therefore we defined ANet as the index to judge magnitude of local symmetry of Eu and A atoms. The calculated ANet values of Eu²⁺-doped phosphors showed a correlation to their internal quantum efficiencies; a crystal having small ANet value shows high internal quantum efficiency. From our discussion on the effects of phonon on Eu^{2+} quantum efficiency, it is concluded that the phonon is not major factor for demining quantum efficiency. Our discussion also supports that ANet is a reasonable indicator to assess quantum efficiency of Eu²⁺-doped phosphors. ANet is only calculated from the host structure and would be useful to find better candidates of host crystals.

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