Development of New Calculation Method for Rare Earth Element and Large Scale Electronic Structure Calculation of Blue Phosphor BaMgAl₁₀O₁₇:Eu²⁺

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1. Introduction

Much attention has been paid to the development of advanced luminescent materials for applications such as flat panel displays, mercury-free lamps and X-ray imaging systems. Among the various types of flat panel displays, Eu^{2+} doped BAM (BaMgAl₁₀O₁₇:Eu²⁺) is commonly used blue-emitting phosphor in plasma display panels due to its availability and high quantum efficiency. The characteristic feature of the blue luminescence can be coordinated with the strong crystal field strength, a high degree of covalency of the host lattice and the allowed 5d-4f transition of Eu²⁺. The structure of BAM consists of two spinel blocks $[MgAl_{10}O_{16}]$ separated by a conduction layer [BaO], in which different activation ions can be structurally substituted for cation sites. Luminescence properties of BAM:Eu²⁺ are strongly affected on their host crystal structures. Therefore, large scale electronic structure calculations will provide effective guidelines for theoretical design of rare earth containing phosphors.

In the present study, we report a new quantum chemical calculation method for rare earth 4f orbitals and applied the method to the electronic structure calculation of bulk BAM:Eu²⁺. In addition, we have also studied the influences of oxygen defects and particle surfaces on the luminescence properties of BAM:Eu²⁺.

2. Computational Details

Tight-binding quantum chemical calculations

We have developed a tight-binding quantum chemical molecular dynamics program, "Colors" [1]. This program was used for electronic structure calculations. The total energy is expressed by:

$$E = \sum_{i=1}^{n} \frac{1}{2} m_i v_i^2 + \sum_{k=1}^{n} \varepsilon_k + \sum_{i=1}^{n} \sum_{j=i+1}^{n} \frac{Z_i Z_j e^2}{R_{ij}} + \sum_{i=1}^{n} \sum_{j=i+1}^{n} E_{ij}^{repul}(R_{ij})$$
(1)

where m_i , v_i , e and R_{ij} is the atomic weight, the atomic velocity, the elementary electric charge and the internuclear distance, respectively. In order to decrease the computation time, parameters for ionization potential, ζ values of Slater-type orbital, resonance integrals, two-center

electron-repulsion integrals, and exchange–repulsion integrals were used. They were determined on the basis of density functional theory (DFT) calculation. Because DFT is well-known to underestimate the band gap energies, we referred to experimental results only for band gap energies. *New calculation method for rare earth 4f orbitals*

4*f* orbitals of rare earth elements are strongly attracted by nuclei therefore they are localized at rare earth element and are degenerated. We developed a new algorithm for rare earth 4*f* orbitals on the assumption of their degeneration. This novel method is changes of seven molecular orbitals (MOs) with large distribution of rare earth 4*f* atmic orbitals (AOs). Coefficients of 4*f* AOs for these MOs are changed to unity and coefficients of other AOs (*s*, *p* and *d*) are changed to zero. In addition, occupation numbers of these changed seven MOs are changed to unity; for example, if a calculation system has one Eu^{2+} ion, the occupation numbers of their MOs are changed to one as it makes possible high-speed calculations and large system calculations included luminescence center environments.

3. Results and Discussion

Validations of the calculation method

In order to validate our calculation methods we compared the calculation results with those obtained by DFT as well as with experiments. In the present method, we employed an ideal crystal model with 464 atoms, Ba₁₅EuMg₁₆Al₁₆₀O₂₇₂, while for DFT calculation an ideal crystal model with 116 atoms, Ba₃EuMg₄Al₄₀O₆₈, was used. Eu concentration in 464 atoms model is almost same as realistic BAM:Eu²⁺. Although three Eu sites are suggested, i.e., Beevers-Ross (BR) site, anti-BR site and mid-oxygen site [2], Eu was positioned at BR site in this study as neutron powder diffraction analysis revealed BR site for Eu [3]. Since the luminescence in BAM: Eu^{2+} is based on electron transition between Eu 4f and 5d orbitals. We believe that the changes of Eu 4f and 5d orbitals in ground states would provide some insights into luminescence properties. Therefore we have calculated the ground states using parameters which were determined to conform to luminescence of BAM:Eu²⁺.

Partial density of states (PDOS) calculated by present method is in good agreement with those calculated by DFT

(Fig. 1). As canbe seen from this figure that the O-2p orbitals are dominant at the top of valence band (V.B.) and the metal orbitals are dominant at the bottom of conduction band (C.B.). Atomic charges obtained by our method are also in good agreements with those obtained by DFT method (Table I). Band gap of the host material obtained by present method was 6.9 eV, which is in good agreement with the experimental value of 7.0 eV [4]. The Eu 4f and 5d orbitals gap calculated by present method is 2.8 eV, corresponding to luminescence peak, 453 nm [4].

Effects of defects and surfaces on luminescence properties Realistic particles have structural defects, surfaces and grain boundaries. It is widely considered that they influence on luminescence properties of phosphors. For example, BAM:Eu²⁺ phosphors are treated in reducing atmosphere so as to maintain a divalent state. The heat treatment may lead to the formation of oxygen defects. Thus, we have calculated the electronic structures of both the crystal model with one oxygen defect and the particle model to study their influences for luminescence.

The electronic structure of oxygen defect model was calculated with 463 atoms that was constructed by removing one of the nearest oxygen atoms in the structure. New two defect levels are formed between host V.B. and C.B. (Fig. 2a). From present calculation, it was found that Eu-5d orbitals are shifted to deeper level in energy and it leads to the narrower 4f-5d gap due to the existence of the oxygen defect. This result suggests that the red shift of luminescence is invoked by structural defects. We have also calculated the electronic structures of the 348 atoms particle model, Ba₁₁EuMg₁₂Al₁₂₀O₁₉₂. Surface levels are formed between host V.B. and C.B. (Fig. 2b) and widely spread on the particle surface. In that case, Eu exists near the surface of particle: Eu-5d orbitals are largely hybridized with surface levels. This result suggests that Eu existed at near the surface of particle has few relation to luminescence. Our results supported the common tendency of phosphors that the smaller particle size weaker brightness [5].

4. Conclusions

We have developed a new calculation method for rare earth 4f orbitals and succeeded the electronic structure calculation of the large scale model with rare earth element. This is in good agreements with DFT calculation as well as experimental results. We have also successfully calculated the electronic structure for oxygen defect model and particle model. Oxygen defect model shows two defect levels that are considered as traps for excited electrons. Particle model possesses many surface levels, which may lead to descent brightness.

Our present method was effectively applied to the electronic structure calculation for more practical system, and is hoped to shed light on the theoretical design of novel rare earth phosphors.

References

[1] K. Sasata, T. Yokosuka, H. Kurokawa, S. Takami, M. Kubo, A.

Imamura, T. Shinmura, M. Kanoh, P. Selvam and A. Miyamoto, Jpn. J. Appl. Phys. 42 (2003) 1859

- [2] K. C. Mishra, M. Raukas, A. Ellens, K. H. Johnson, J. Lumin. 96 (2002) 95
- [3] W. B. Im, Y. Kim, D. Y. Jeon, Proc. 12th. Int. Display Workshops (2005) 543
- [4] T. Jüstel, H. Lade, W. Mayer, A. Meijerink, D. U. Wiechert, J. Lumin. 101 (2003) 195
- [5] H. Huang, G. Q. Xu, W. S. Chin, L. M. Gan, C. H. Chew, *Nanotechnology*. 3 (2002) 318



Fig. 1 Model and PDOS using (a) Colors and (b) DFT

Table I. Atomic charges on the ideal crystal models	
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Atom	0	Al	Mg	Ba	Eu
Colors	-0.46	0.50	0.53	0.78	0.68
	~ -0.33	~ 0.57		~ 0.80	
DFT	-0.37	0.38	0.39	0.64	0.70
	~ -0.22	~ 0.60			0.70



Fig. 2 Schematic of PDOS of (a) the oxygen defect model and (b) the particle model