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Development of Accelerated Large-Scale Electronic Structure Calculation Program for Designing of Rare Earth Phosphors

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1. Introduction

BaMgAl₁₀O₁₇:Eu (denoted as BAM:Eu²⁺) is a practically used as a blue phosphor in plasma display panels (PDPs). A critical issue regarding BAM:Eu²⁺ blue phosphor has been the degradation caused by vacuum ultra violet photon in PDP and by heating processes in the fabrication of PDP. These may lead to the formation of defects in phosphor materials. Experimentally, thermoluminescence spectrum has been used to study the defect levels of BAM [1]. However, the detailed information of defects of BAM:Eu²⁺ in the electronic/atomic levels seems to be difficult to clarify by only experimental methods. Quantum chemical method such as first-principles calculation is one of powerful tools to understand electronic structures of materials. It is expected that large-scale models of BAM:Eu²⁺ are required for the electronic structure calculations when the structural defect, for instance, O²⁻ vacancy, is considered. However, the first-principles method is often limited to use relatively small models consisting of *ca* 100 atoms, due to its extremely expensive computation. In addition, it is anticipated that the difficulty in getting good convergence of electronic states increases when the rare earth element is included in the calculation system.

On the other hand, we have developed an original accelerated quantum chemical molecular dynamics program, 'Colors', based on our original tight-binding approximation. This program is 5,000 times faster than traditional first-principles quantum chemical method, and has been successfully applied to various systems such as semiconductors and ceramics [2-4]. In the present study, we have extended Colors program so as to calculate rare earth phosphors materials with good convergence of electronic states.

2. Method

Our original accelerated quantum chemical molecular dynamics program, 'Colors', is based on our original tight-binding approximation. In this program, the total energy of a system is described as follows:

$$E = \sum_{i=1}^N \frac{1}{2} m_i v_i^2 + \sum_{k=1}^{OCC} n_k \mathbf{e}_k + \sum_{i=1}^N \sum_{j=i+1}^N \frac{Z_i Z_j e^2}{R_{ij}} + \sum_{i=1}^N \sum_{j=i+1}^N E_{REP}(R_{ij})$$

where the first, second, third, and fourth term on the right-hand side refers to the summation of kinetic energy of atom, molecular orbital (MO) energy, Coulombic energy, and exchange-repulsion energy, respectively. To solve the Schrödinger equation in Colors program, parameters for Hamiltonian matrix are used, which are derived from the first-principles calculation results based on the density functional theory.

In this study, we implemented a novel algorithm to reproduce the electronic configuration of Eu²⁺ ion obtained by the first-principles quantum chemical calculation. This consists of three parts: (1) seven MOs consisting of mainly 4*f* atomic orbital (AO) of Eu²⁺ are searched, (2) the coefficients of *s*, *p*, *d*, and *f* AOs of Eu²⁺ to 0, 0, 0, and 1, for the searched MOs, are converted, and (3) the overlap integrals between 4*f* AO of Eu²⁺ and the other AOs of the other ions are neglected. The first part of the new algorithm is achieved to evaluate the square of a matrix element of eigenvectors. The second part corresponds to localize only 4*f* AO of Eu²⁺ at the searched MOs. The reason of introduction of the third part of the present algorithm is to avoid difficulty to get convergence for electronic structure calculation due to the existence of rare earth element. This will be justified by the fact that the electronic configuration of Eu²⁺ in BAM:Eu²⁺ calculated by the first-principles method is (4*f*)⁷(5*d*)⁰, as described in the next section. This implies that the covalent overlap of 4*f* AO of Eu²⁺ with the other AOs of the ions surrounding Eu²⁺ may be negligible.

3. Results and Discussion

First, we calculated the electronic structure of BAM:Eu²⁺ phosphor using the first-principles quantum chemical calculations. The model consists of 116 atoms and is shown Fig. 1(a). Three possibilities have been reported as the occupation site of Eu²⁺ ions, i.e., Beevers-Ross (BR), anti-BR, and mid-oxygen sites [5]. In this study, BR site is chosen as the occupation site of Eu²⁺. Calculated charges

on Eu, O, Al, Mg, and Ba ions of the present model shown in Fig. 1(a) are listed in Table I. From this first-principles calculation, it is found that the electronic configuration of Eu^{2+} is $(4f)^7(5d)^0$. We determined the parameters used in Colors program (ζ coefficients of Slater-type orbital, valence state ionization potential, and Wolfsberg-Helmholz parameters) in order to reproduce the electronic structures obtained by the first-principles quantum chemical calculations. Charges on ions of the present model (Fig. 1(a)) calculated by Colors program is also shown in Table I. From Table I, it is clear that the order of charges obtained by our Colors program is in well accordance with those obtained by the first-principles method. We also confirmed that the electronic configuration of Eu^{2+} derived from Colors program was $(4f)^7(5d)^0$, which reproduces the first-principles result. Fig. 1(b) shows the visualized MO of the present BAM:Eu²⁺ model where the contribution from only 4f AO of Eu²⁺ ion is found. These results indicate that our novel algorithm works fairly.

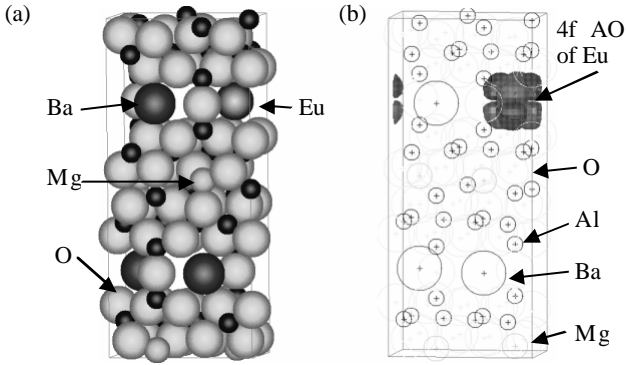


Fig.1 Computer graphics of (a) 116 atoms model of BAM:Eu²⁺ and (b) localized 4f atomic orbital (AO) of Eu²⁺ ion.

Table I. Charges obtained for 116 atoms model of BAM:Eu²⁺.

Ion	First-Principles	Present method
Eu ²⁺	+0.70	+0.68
O ²⁻	-0.37 ~ -0.27	-0.46 ~ -0.33
Al ³⁺	+0.38 ~ +0.60	+0.50 ~ +0.57
Mg ²⁺	+0.39	+0.53
Ba ²⁺	+0.64	+0.78 ~ +0.80

Next, we performed the electronic structure of BAM:Eu²⁺ phosphor model consisting of 464 atoms, using our Colors program. Table II shows the charges and spin densities on individual ions including BAM:Eu²⁺ model. The charge on ions shown in Table II resemble to those shown in Table I. This suggests that a large-scale electronic structure calculation is succeeded by using our Colors program. Spin density is defined as the difference of the number of α electron with that of β electron. From Table II, it is evident that seven α electrons localize at Eu²⁺ ion. This also stresses that the electronic configuration of Eu²⁺ ion is $(4f)^7(5d)^0$. Fig. 2 shows the contours of MOs consisted of mainly 5d AO of Eu²⁺ ion. From Fig. 2(a), not only the contribution of 5d AO of Eu²⁺ but also that of 2p AO of O²⁻

ion is slightly confirmed. We can also see the relatively small contributions from the 2p AO of O²⁻ ions and 3p AO of Al³⁺ ions to the MOs. The origin of blue luminescence of BAM:Eu²⁺ is considered as the electron transition from 5d AO to 4f AO of Eu²⁺ ion. From the present results, it is considered that the ideal crystal structure of BAM is convenient for 5d AO of Eu²⁺ ion in the sense of the realization of effective light emission. In other words, it is anticipated that the significant changes in atomic structure, for instance the formation of O²⁻ defect, lead to the loss of efficiency of luminescence because of the change in the spatial distribution of MO consisting mainly 5d AO of Eu²⁺.

Table II. Charges obtained for 464 atoms model of BAM:Eu²⁺.

Ion	Charges	Spin density
Eu ²⁺	+0.68	7.00
O ²⁻	-0.46 ~ -0.34	0.00
Al ³⁺	+0.50 ~ +0.57	0.00
Mg ²⁺	+0.53	0.00
Ba ²⁺	+0.78 ~ +0.80	0.00

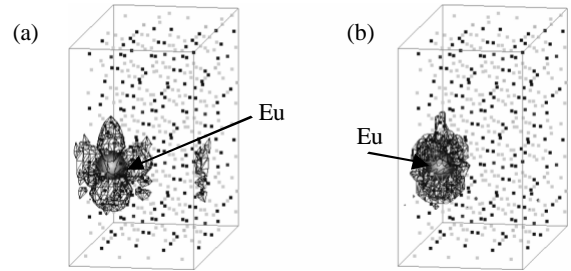


Fig. 2 Contours of MOs regarding 5d atomic orbital (AO) of Eu²⁺ obtained for 464 atoms of BAM:Eu²⁺: (a) 5d AO of Eu²⁺ + 2p AO of O²⁻ and (b) 5d AO of Eu²⁺ + 2p AO of O²⁻ + 3p AO of Al³⁺.

4. Conclusions

We have extended our original accelerated quantum chemical molecular dynamics program, 'Colors', in order to carry out the electronic structure calculations for rare earth phosphor materials easily. The implemented algorithm for the rare earth element works as expected. We can utilize the advantage of Colors program in order to address the difficulty in calculating large-scale and defective phosphor material doped rare earth element.

References

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