

Theoretical Study of PDP Materials

**Akira Miyamoto^{1,2}, Hiroaki Onuma¹, Hiromi Kikuchi¹, Hideyuki Tsuboi¹,
Michihisa Koyama¹, Akira Endou¹, Hiromitsu Takaba¹, Momoji Kubo^{1,3},
Carlos A. Del Carpio¹, Parasuraman Selvam^{2,4}, and Hiroshi Kajiyama⁵**

¹Department of Applied Chemistry, Graduate School of Engineering,
Tohoku University, 6-6-11-1302 Aoba Aramaki, Aoba-ku, Sendai 980-8579, Japan

²New Industry Creation Hatchery Center, Tohoku University,
6-6-10 Aoba Aramaki, Aoba-ku, Sendai 980-8579, Japan

³PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho,
Kawaguchi, Saitama 332-0012, Japan

⁴Department of Chemistry, IIT-Bombay, Powai, Mumbai 400-076, India

⁵Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba,
Meguro-ku, Tokyo 153-8505, Japan

Phone: + 81-22-795-7233, E-mail: miyamoto@aki.che.tohoku.ac.jp

Abstract

A novel quantum chemical molecular dynamics program, 'Colors' was developed to simulate the electronic structure of rare earth-doped phosphor materials as well as the destruction processes of MgO protecting layer in plasma display panel (PDP). We have also developed a quantitative prediction method based on Monte Carlo simulation technique to evaluate the electrical conductivity of insulators, semiconductors, and metals as well as the spatial distribution of electron density by Colors code. All these original simulators enable us to study theoretically a variety of materials related to PDP.

1. Introduction

Plasma display panel (PDP) has attracted much attention for a high definition TV because its intrinsic characteristics such as flat, thin, and large area display. Despite numerous experimental efforts, the display performance is quite unsatisfactory. One of the serious issues of PDP is the degradation of the blue phosphor material, BaMgAl₁₀O₁₇:Eu²⁺ (BAM:Eu²⁺), and that the crystal structure may play a key role for such behavior. Therefore, in order to design and develop new phosphor materials that possess much higher durability in terms of degradation, the development of novel theoretical approach that considers the whole crystal structure is inevitable. Yet another closely related problem is the degradation of MgO protecting layer. The

latter may be due to the charge accumulation on MgO surface as a consequence of sputtering of energetic particles (ion bombardment) under the plasma condition. However, the experimental observation such an effect is highly difficult. In order to overcome this difficulty, a theoretical approach is strongly demanded. In this context, we have developed a unique tight-binding quantum chemical molecular dynamics (QCMD) program, 'Colors' [1-4], which can simulate large-scale electronic structure of rare earth-doped phosphor materials such as BAM:Eu²⁺ as well as to obtain electronic and atomic states dynamics of MgO protecting layer of PDP under applied electric field. In addition, we have also developed a novel electrical conductivity simulator based on Monte Carlo (MC) method, which refers to the spatial distribution of probability density of electrons obtained by Colors program [5]. In this presentation, we review our recent successful applications some of these new simulators to PDP materials.

2. Methods

Our original accelerated quantum chemical molecular dynamics program is based on tight-binding approximation, and the total energy of a system is described as:

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

where the first, second, third, and fourth terms refer to the kinetic energy of atom, orbital energy, Coulombic energy, and exchange-repulsion energy, respectively. To solve the Schrödinger equation (in Colors), the parameters for Hamiltonian are derived from the first-principles calculations based on the density functional theory are applied.

We have also developed a novel electrical conductivity simulator, which uses spatial distribution of probability density of electrons obtained by Colors [5]. In this simulation, the following procedures were adopted to calculate the electron mobility, μ : (i) the data pertaining to molecular orbital of a system is calculated by Colors program; (ii) the three-dimensional mesh model for the system is constructed; (iii) the probability density distribution of electrons of the system calculated from the data of molecular orbital is assigned to the three-dimensional mesh model; (iv) the probability of movement of an electron to the adjacent mesh point is assumed to be proportional to the probability density of electrons; (v) an electron is moved using MC method according to the assumption described in the previous procedure; (vi) the number of electrons reached at the goal plane is counted as the input condition. The flow chart of the present method of calculating electrical conductivity is illustrated in Fig. 1.

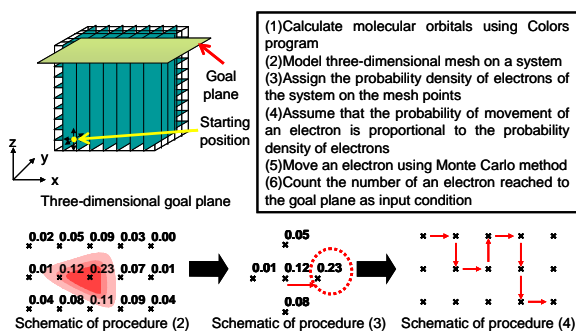


Fig. 1. Schematic representation of computation flow in electrical conductivity simulator.

The number of thermally excited electrons in the molecular orbital is evaluated by Fermi distribution at 300 K. The electrical conductivity, σ of each molecular orbital is calculated according to Drude model:

$$\sigma = ne\mu$$

where n is electron density, e is the elementary electric charge, and μ is the mobility of an electron calculated by the present MC method. The total electrical conductivity of the system is given by the summation of the electrical conductivity of each of the molecular orbital.

3. Results and Discussion

3.1 Large-Scale Electronic Structure Calculation of BAM:Eu²⁺

Our original simulator, Colors was applied to calculate the electronic structure of BAM:Eu²⁺. In this study, we implemented a novel algorithm to reproduce the electronic configuration of Eu²⁺ ion obtained by the first-principles quantum chemical calculation in which: (i) seven MOs consisting of mainly 4f AO of Eu²⁺ are searched; (ii) for the searched MOs, the coefficients of s , p , d , and f AOs of Eu²⁺ to 0, 0, 0, and 1, are converted; (iii) the overlap integrals between 4f 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 the localized 4f AO of Eu²⁺ at the searched MOs. The introduction of the third part of the present algorithm is to avoid difficulty in getting the convergence for the electronic structure calculation owing to the presence of rare earth ion. This can be justified by the fact that the electronic configuration of Eu²⁺ (in BAM:Eu²⁺) calculated by the first-principles method is 4f⁷5d⁰. This also implies that the covalent overlap of 4f-AO of Eu²⁺ with the other AOs of the ions surrounding Eu²⁺ may be negligible.

Fig. 2 shows the calculated partial density of states (PDOS) of BAM:Eu²⁺ model consisting of 464 atoms. This figure clearly indicates that the Colors program with the new algorithm for rare earth ion is successfully reproduces the 4f-5d energy gap (2.8 eV) of Eu²⁺ emission center corresponding to 450 nm of wavelength for blue light. Subsequently, the effect of oxygen defect on the electronic structure of phosphor materials was also studied. An oxygen defect model with 463 atoms was constructed by removing one of nearest oxygen atoms in the structure. Two defect levels are formed between the valence band (VB) and the conduction band (CB) in the host material. We observed that Eu-5d orbital was shifted to deeper level in energy leading to a narrower 4f-5d

energy gap as a consequence of the presence of the oxygen defect in the structure. This implies that the red shift of the luminescence is attributed to the structural defects of BAM:Eu²⁺ phosphor.

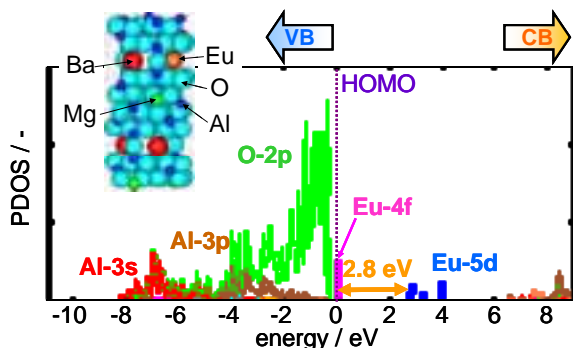


Fig. 2. PDOS of BAM:Eu²⁺ obtained by Colors program. HOMO of this structure model was defined as 0 eV of energy level.

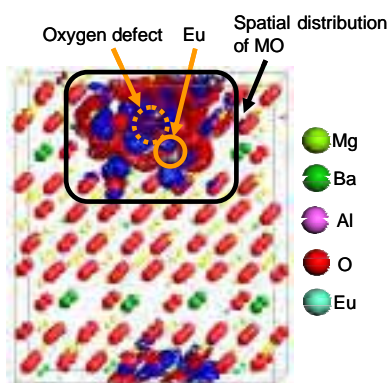


Fig. 3. Spatial distribution of a MO consisting of Eu-5d AO and the other AOs of surrounding atom.

Fig. 3 depicts a MO contour corresponding to one of the defect levels as result of the oxygen vacancy. This figure indicates a widespread distribution of MO, which consists of Eu-5d AO and the other AOs of the atoms surrounding oxygen vacancy. These results clearly suggest that the obtained defect levels may work as electron trap levels. By using our present method, we have also succeeded to calculate not only a large-scale crystal model consisting of 464 atoms but also a model with O²⁻ vacancy. At this juncture, it is noteworthy that such calculations are extremely difficult by the traditional first-principles method because of its huge computation cost and poor convergence.

3.2 Effect of Oxygen Vacancy in MgO surface on the Stability

The oxygen vacancy in MgO protecting layer is considered as one of the important factors to influence the stability. We have employed our Colors program to investigate the effect of the oxygen vacancy in the MgO (001) surface on the stability of the MgO protecting layer. Fig. 4 illustrates the destruction process of MgO (001) surface with one oxygen vacancy under an applied electric field of 0.15 V/Å. We observed a destruction dynamics of MgO (001) surface under the influence of the electric field. In contrast, under the same (electric field) condition, the destruction does not take place for the MgO (001) surface without the oxygen vacancy [1]. Thus it is suggested that the oxygen vacancy in the structure decreases the stability of MgO protecting layer.

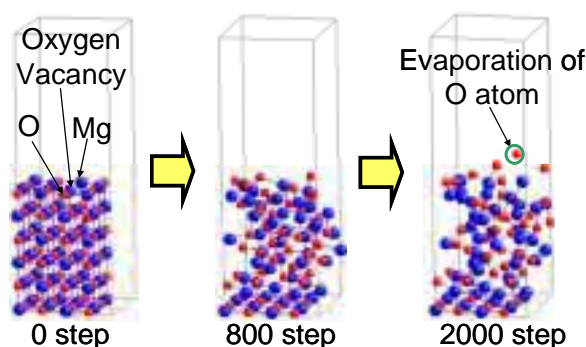


Fig. 4. Snapshots of the destruction process of MgO (001) surface with one oxygen vacancy under an applied electric field of 0.15 V/Å.

3.3 Effect of Dopants in MgO on the Secondary Electron Emitting Ability

In PDP, MgO films are widely used as a protective layer because of their high durability, good protection characteristics against ion bombardment and high secondary electron emission coefficient. Additionally, a high secondary electron emission coefficient plays an important role in lower the firing voltage. Hence, it is desirable that the dopants do not decrease the secondary electron emitting ability of the MgO and that an increase in the emitting ability is preferred. Thus, we have investigated the dopants effect on the secondary electron emitting ability using Colors program. We have chosen Mg₃₁M₁O₃₂ (M = Ca, Si or Sr) model for the study.

Table 1 presents the energy difference (ΔE) between the energy level due to the dopants and the top of valence band of $Mg_{31}M_1O_{32}$ model. From this table, it is clear that the calculated ΔE values are in agreement the experimental value. Fig. 5 shows the dopant levels in cases of $Mg_{31}CaO_{32}$ and $Mg_{31}SrO_{32}$ models, and we can confirm the spatial distributions of MO are spread at dopant atoms. These results suggest that the dopants Sr and Ca work as the electron traps.

Table 1. Energy difference (ΔE) between the dopant level and the top of the valence band.

System	ΔE (eV)
Ca-doped MgO	4.85
Si-doped MgO	4.89
Sr-doped MgO	4.86
Experimental	~ 4.43

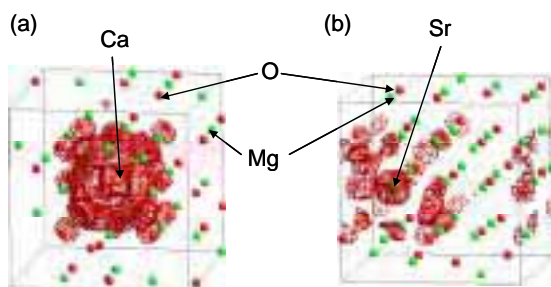


Fig. 5. Spatial distribution of the dopant levels: (a) $Mg_{31}CaO_{32}$ and (b) $Mg_{31}SrO_{32}$.

3.4 Electrical Conductivity Simulator based on MC and QCMD Methods

In the practical design of PDP, a careful selection of materials is needed to realize lower consumption of electric power. In this regard, the theoretical evaluation of electrical conductivity is quite useful. Table 2 sums up the calculated and experimental electrical conductivity values of Sn, Ge, Si, and C (diamond). In the present study, the calculated values of electrical conductivity are normalized with the experimental value of crystalline Si. It can also be noted from this table that the calculated electrical conductivities for Sn, Ge, Si, and C (diamond) are in line with those obtained by experiments. It is also noteworthy here that we have also successfully applied the present novel method to various materials such as polymers, oxides, and metals. Thus the new

simulator is hoped to be useful for the prediction of the complicated interfaces of PDP materials.

Table 2. Theoretical and experimental electrical conductivity values for Sn, Ge, Si, and C (diamond).

Material	Electrical conductivity (S/cm)	
	This study	Experimental
Sn	1.6×10^5	0.9×10^5
Ge	1.9×10^{-2}	1.9×10^{-2}
Si	4.3×10^{-6}	4.3×10^{-6}
C (diamond)	5.5×10^{-32}	$\sim 10^{-16}$

4. Conclusion

We have successfully developed a novel tight-binding quantum chemical molecular dynamics simulators, Colors, to investigate the electronic structure of rare earth doped phosphor and destruction processes of MgO protecting layer in PDP under the influence of applied electric field. We also developed a quantitative electrical conductivity simulator based on Monte Carlo method and calculated spatial distribution of electron density. In this study, we have also demonstrated that our original simulators are very effective theoretical tools to investigate PDP materials.

5. References

- [1] M. Kubo, K. Sasata, T. Yokosuka, T. Kusagaya, S. Takami, H. Kajiyama, A. Kato, A. Imamura, and A. Miyamoto, Proc. 9th IDW, 753-756 (2002).
- [2] M. Elanany, P. Selvam, T. Yokosuka, S. Takami, M. Kubo, A. Imamura, and A. Miyamoto, J. Phys. Chem. B 107, 1518-1524 (2003).
- [3] H. Zhong, X. Wang, M. Fushimi, A. Endou, M. Kubo, P. Selvam, A. Imamura, A. Miyamoto, Trans. Mater. Res. Soc. Jpn. 29, 3735-3738 (2004).
- [4] A. Miyamoto, R. Endou, H. Kikuchi, H. Tsuboi, M. Koyama, A. Endou, M. Kubo, C. A. Del Carpio, and H. Kajiyama, Proc. 12th IDW, 423-426 (2005).
- [5] H. Tsuboi, H. Setogawa, M. Koyama, A. Endou, M. Kubo, C. A. Del Carpio, and A. Miyamoto, Jpn. J. Appl. Phys. 45, 3137-3143 (2006).