Fluorescence Spectra of Pr\textsuperscript{3+} Ions in Phosphate Materials Calculated by the DVME Method

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Recently fluorescence spectra of rare-earth ions in oxide materials are very attractive for the applications of the optical amplification in optical fiber communications and white LED etc. However, it has been difficult to calculate the fluorescence spectra of rare-earth ions by the first principle method. In this study, we used the relativistic discrete-variational multi-electron (DVME) method, which is a configuration-interaction (CI) calculation program using the molecular orbitals obtained by the relativistic DV-X\alpha method. We applied this method to the calculation of the fluorescence spectrum of the Pr\textsuperscript{3+} ions in phosphate materials. The transition probability of the fluorescence was calculated in the same manner of the absorption. The obtained theoretical
fluorescence spectrum was good agreement with the experimental one, though the intensity of each peak was deeply dependent on the configuration of the surrounding structural units. The results suggested that the DVME method was useful for the calculation of not only absorption but also fluorescence spectra of rare-earth ions in oxide materials.

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1. Introduction

Rare-earth ion doped oxide glasses have been attractive for their application to white LED, the fiber-LASER amplification, and displays, etc. Many people have made effort to study about the absorption and luminescence spectra of these glassy materials. [1-4]

In these studies, theoretical analyses of the electronic state of rare-earth ions in oxide glasses are very important. Usually the absorption and fluorescence spectra of these glasses were analyzed by
the empirical method.[5-9] There are several empirical methods to analyze 4f-4f transition spectra of rare-earth ions. But in these methods, we need the experimental parameters to obtain the results. Recently the relativistic DVME method, which is one of the first principles configuration interaction method was developed and there have been already many studies about electronic state of rare-earth ions in solid state materials.[10-15] However, there are a few studies about fluorescence spectra of rare-earth ions in the oxide materials. In this study, we have calculated fluorescence spectra of Pr$^{3+}$ ions in phosphate matrices by the relativistic DVME method. The Pr$^{3+}$ ion doped phosphate materials have been expected as new laser materials for various applications because of their good fluorescence efficiency in the visible and infrared region.

2. Calculation method

We have used relativistic DV-Xα method to obtain the molecular orbitals, named SCAT coded by Adachi et al.[16] After one electron approximation calculation, the fully relativistic DVME method, which is based on a CI calculation program.[17] In this method, Slater determinants corresponding to all the possible electronic configurations are constructed using the four-component fully relativistic molecular spinors obtained by the relativistic DV-Xα cluster calculations. In the present
work, only electrons occupying the molecular spinors mainly composed of Ln-4f states in the grand
state were treated explicitly. Then by diagonalization of the many-electron Hamiltonian, the
multiplet energies were obtained as eigenvalues and the many-electron wave functions were obtained
as linear combination of the Slater determinants. The relativistic many-electron Hamiltonian is
expressed as

\[
H = \sum_{i=1}^{n} \left[ c \alpha p_i + \beta c^2 - \frac{Z_v r_i}{|r_i - R_v|} + V_0(r_i) + \sum_{\mu} \frac{Z^\text{eff}_\mu r_i}{|r_i - R^\mu|} \right] + \sum_{i=1}^{n} \sum_{j>i}^{n} \frac{1}{|r_i - r_j|}
\]

(1)

where \(\alpha, \beta\) are the Dirac matrices, \(c\) the velocity of light, \(r_i, p_i\) the position and the momentum
operator of the \(i\)th electron, \(Z_v\) and \(R_v\) the charge and position of the \(v\)th nucleus, \(Z^\text{eff}_\mu\) and \(R^\mu\) the
effective charge and position of the \(\mu\)th ion outside the model cluster, \(n\) the number of explicitly
treated electrons. \(V_0(r_i)\) is the potential from the remaining electrons. [18]

The oscillator strengths of electric dipole transitions in the absorption spectra were calculated as
follows:
\[ I_{if} = 2\Delta E \left| \left< \Psi_f \sum r_k \cdot e^{\Psi_i} \right> \right|^2 \] 

(2)

\( \Psi_i \) and \( \Psi_f \) are the initial and final states with energies of \( E_i \) and \( E_f \), respectively. In the case of fluorescence spectra, the transition probabilities of electric dipole transitions were obtained by the following equation:

\[ I_{if} = 2\Delta E^3 \left| \left< \Psi_f \sum r_k \cdot e^{\Psi_i} \right> \right|^2 \]

In this calculation, the higher energy state was adopted as the initial state of the fluorescence spectra and usually the grand states was the final state. We could obtained the transition probabilities of the fluorescence spectra in the same manner as the absorption spectra.

Fig. 1 shows model clusters used in the present study. Cluster 1 shown in Fig. 1 (a) is the simplest model cluster, which includes only center Pr\(^{3+}\) ion and the first neighboring O\(^{2-}\) ions. In the calculation of the cluster 1, we have used the Madelung potential. The atom positions of the cluster 1 were determined from Pr(PO\(_3\)_3) crystal structure.[19] Cluster 2 shown in Fig. 1 (b) is a larger
model for Pr(PO₃)₃. This cluster includes 7 surrounding PO₄ units terminated with H ions for the neutrality of the cluster. In this case, Madelung potential have not used for the calculation of the relativistic DV-Xα method. Though the cluster 2 is a model cluster for Pr(PO₃)₃ crystal, it can be applied to the calculation of glassy materials because this model has no long-range structure.

3. Results and discussion

Fig. 2 is the experimental fluorescence spectrum of Pr(PO₃)₃ crystal under excitation in the ⁴P₂ multiplet at 444 nm.[19] In this spectrum, there are two intense peaks around 480 and 630 nm, assigned to the transitions from ³P₀ to ¹H₄ and from ³P₀ to ³F₂. Fig. 3 shows the theoretical spectrum of the cluster 1 (a) and 2 (b). In the spectrum of the cluster 1, there are intense peak around 600 nm, which is corresponding to ³P₀ to ³F₂ peak in the experimental one. The profile of the spectrum, however, is not similar to the experimental spectrum. In the case of the cluster 2, the profile of the spectrum is similar to that in the cluster 1, that is, this spectrum doesn’t agree with the experimental one. The theoretical spectra in both model clusters didn’t agree with the experimental spectrum. In Dieke diagram [20], the Pr³⁺ ion has several possible energy levels of initial state of fluorescence near 3 eV. In the experimental spectrum, however, only ³P₀ was used as the initial state for the
assignments of the peaks. It means that there was possibility of the other initial states for the fluorescence of the Pr\(^{3+}\) ion. Figs. 4 (a)-(d) show the results of the each initial state, \(^3P_2\), \(^3P_1\), \(^3P_0\) and \(^1I_6\) of the cluster 2. The main peaks in the visible region are observed around 360, 580, 580 and 550 nm in the spectra of \(^3P_2\), \(^3P_1\), \(^3P_0\) and \(^1I_6\), respectively. Thus each spectrum has different feature and all of them are not the same as the experimental spectrum shown in Fig. 2. This result suggests that there might be simultaneously several initial states in the actual fluorescence spectrum. Then we have summed these four spectra and obtained the theoretical fluorescence spectrum of Pr\(^{3+}\) ion in phosphate matrices. The result is shown in Fig. 5. In the theoretical spectrum, there are two intense peaks around 350 and 570 nm. The peak positions shift slightly smaller wavelength but the relative positions of these major peaks are corresponding to those in the experimental spectrum. Furthermore, the relative peak intensities are also similar to those in the experimental spectrum. However, the assignments of the peaks shown in the figure are very complicated. For an example, the assignments of the intense peaks around 550-610 nm are several transitions from \(^3P_2\), \(^1I_6\), and \(^3P_1\) to \(^3F_3\), and from \(^1I_6\) to \(^3F_4\), though the corresponding peaks around 600-650 nm in the experimental spectrum were assigned to the transitions from \(^3P_0\) to \(^3H_6\) and \(^3F_2\). This result suggests that there were several initial states in the fluorescence of Pr\(^{3+}\) ion in phosphate matrices, and it is very difficult
to make assignment of the peaks by only the empirical method. This result also shows the relativistic
DVME method is very useful to analyze fluorescence spectra of rare-earth ions in phosphate matrices
and the first principles calculation is necessary to analyze the fluorescence spectra of rare-earth ions.

4. Conclusion

The theoretical fluorescence spectra of rare-earth ions in phosphate matrices were calculated by the
relativistic DVME method, which is one of the first principles CI calculation methods. The model
cluster with surrounding PO₄ units, H₁₈PrPₒ₂₈ was suitable to obtain the fluorescence spectra, rather
than PrO₅ cluster which includes only the first neighboring oxide ions. The theoretical spectra with
several initial states were good agreement with the experimental one, though the spectra with only
one initial state were not. These results suggested that the relativistic DVME method was very
useful and necessary to analyze fluorescence spectra of rare-earth ions in phosphate matrices.

References


Figure captions

Fig 1 Cluster models for the Pr\(^{3+}\) ions in phosphate materials (a) PrO\(_8\) cluster, (b) H\(_{18}\)Pr\(_7\)P\(_{28}\) cluster.

These figures were drown with VESTA developed by K. Momma and F. Izumi

Fig. 2 Fluorescence spectrum of the Pr(PO\(_3\))\(_3\) crystal reported by A. Jouini et al. in ref. [19].

Fig. 3 Theoretical fluorescence spectra of (a) cluster 1 and (b) cluster 2.

Fig. 4 Theoretical fluorescence spectra of cluster 2 with different initial state, (a) \(^3\)P\(_2\), (b) \(^3\)P\(_1\), (c) \(^3\)P\(_0\).

(d) \(^1\)I\(_6\).  

Fig. 5 Theoretical fluorescence spectrum of cluster 2 with several initial states. (a) theoretical spectrum, (b) experimental spectrum reported by A. Jouini et al. in ref. [19].