



Luminescence of Eu^{3+} in $\text{La}_{1-x}\text{Eu}_x\text{Ta}_7\text{O}_{19}$ ($0 < x \leq 1$) solid solution

Shun-ichi Kubota^a, Tadashi Endo^{a,*}, Hirotsugu Takizawa^b, Masahiko Shimada^b

^aDepartment of Molecular Chemistry and Engineering, Faculty of Engineering, Tohoku University, Aoba, Aoba-ku, Sendai, Miyagi 980, Japan

^bInstitute for Advanced Materials Processing, Tohoku University, Katahira, Aoba-ku, Sendai, Miyagi 980, Japan

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Abstract

The luminescence properties of Eu^{3+} in $\text{La}_{1-x}\text{Eu}_x\text{Ta}_7\text{O}_{19}$ solid solution were examined systematically. In the structure the nearest neighbours of La^{3+} sites doped with Eu^{3+} ions are arranged two-dimensionally with proper separations of about 0.62 nm. An intense emission peak is observed at 610 nm together with supplementary weak peaks. All the peaks can be ascribed to ${}^5\text{D}_j \rightarrow {}^7\text{F}_{j'}$ ($j=0,1; j'=0,1,2,3,4$) transitions of Eu^{3+} . The emission of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition becomes intense and saturates with the Eu^{3+} concentration. As a result, the profile of the concentration quenching implies that energy migration of excited Eu^{3+} hardly takes place in $\text{La}_{1-x}\text{Eu}_x\text{Ta}_7\text{O}_{19}$ solid solution.

Keywords: Luminescence; Energy migration; Quenching

1. Introduction

Many investigations have been performed on the emission properties of concentrated Eu^{3+} -doped compounds, e.g. $\text{EuMgB}_5\text{O}_{10}$ [1], $\text{Li}_6\text{Eu}(\text{BO}_3)_3$ [2], EuP_3O_9 [3], NaEuTiO_4 [4], etc. These phosphors display a high critical concentration for quenching in comparison with conventional Eu^{3+} -doped compounds such as $\text{YAlO}_3:\text{Eu}^{3+}$ [5]. This is due to the long separations and low dimensional arrangements of Eu^{3+} ions in La^{3+} sites [6,7].

Recently Gatehouse [8] demonstrated that $\text{CeTa}_7\text{O}_{19}$ consists of a layer of $(\text{Ce}^{3+}, \text{Ta}^{5+})\text{-O}^{2-}$ polyhedra interstratified in a double layer of $\text{Ta}^{5+}\text{-O}^{2-}$ polyhedra. Since $\text{EuTa}_7\text{O}_{19}$ is isomorphous with $\text{CeTa}_7\text{O}_{19}$, Eu^{3+} ions are separated by a shortest distance of about 0.62 nm and displaced two-dimensionally. In addition, each layer involves Eu^{3+} sites set about 1.0 nm apart.

The interesting luminescence properties of the rare earth polytantalates [9–12] have been examined extensively. Very recently, the present authors reported on the luminescence properties of $\text{La}_{1-x}\text{Tm}_x\text{Ta}_7\text{O}_{19}$ [13] and $\text{Y}_{1-x}\text{Tm}_x\text{Ta}_7\text{O}_{19}$ [14,15]. Most of the data indicated that the emission intensity changes peculiarly with the Tm^{3+} concentration. Ustimovich et al. [9] reported that an intense emission of Eu^{3+} is obtained at $n=7$ in the

$(\text{La}_{1-x}\text{Eu}_x)_2\text{O}_3\text{-}n\text{Ta}_2\text{O}_5$ system. However, the results were not sufficient to understand the luminescence properties of $\text{La}_{1-x}\text{Eu}_x\text{Ta}_7\text{O}_{19}$ solid solution. As described above, the crystal structure involves the La^{3+} sites doped with Eu^{3+} . In addition, the separations between La^{3+} sites seem to be favourable to avoid the quenching phenomenon due to interaction between Eu^{3+} ions. In this paper the luminescence properties of $\text{La}_{1-x}\text{Eu}_x\text{Ta}_7\text{O}_{19}$ are examined and discussed on the basis of the characteristics of activated Eu^{3+} sites.

2. Experimental details

Descriptions of the preparation of samples and the experimental set-up are given in Refs. [13,15].

3. Results and discussion

$\text{EuTa}_7\text{O}_{19}$ was prepared by the solid state reaction of Eu_2O_3 and Ta_2O_5 at 1200 °C in air. Fig. 1 shows a scanning electron microscope (SEM) photograph of the $\text{EuTa}_7\text{O}_{19}$ powder produced. The grains are 0.2–2 μm in size and irregular in shape. This observation was independent of the Eu^{3+} concentration in $\text{La}_{1-x}\text{Eu}_x\text{Ta}_7\text{O}_{19}$. From the powder X-ray diffraction patterns, all samples can be regarded as being single

*Corresponding author.

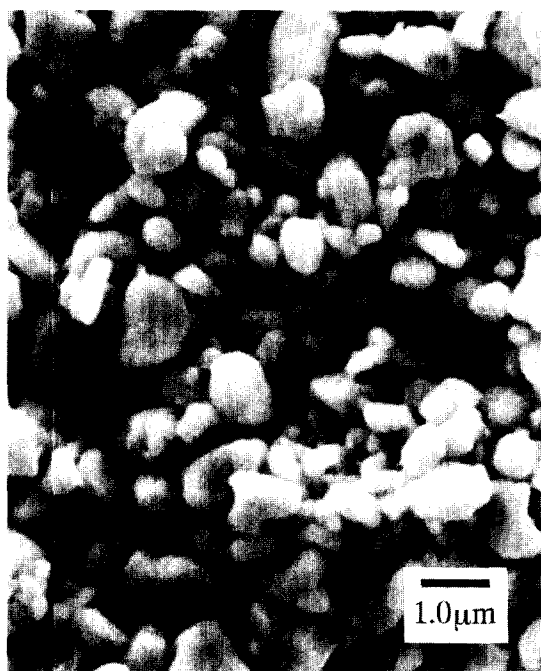


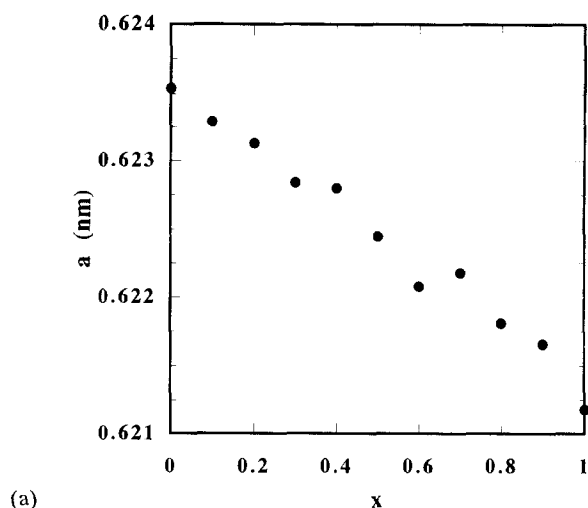
Fig. 1. SEM photograph of $\text{EuTa}_7\text{O}_{19}$.

phase. According to the data reported by Ustimovich et al. [9], $\text{La}_{1-x}\text{Eu}_x\text{Ta}_7\text{O}_{19}$ is transformed from the $\text{LaTa}_7\text{O}_{19}$ structure type (orthorhombic) to the $\text{EuTa}_7\text{O}_{19}$ structure type (tetragonal) at $x=0.05$. However, we were able to index according to hexagonal symmetry for all Eu^{3+} concentrations, as reported in Refs. [16,17].

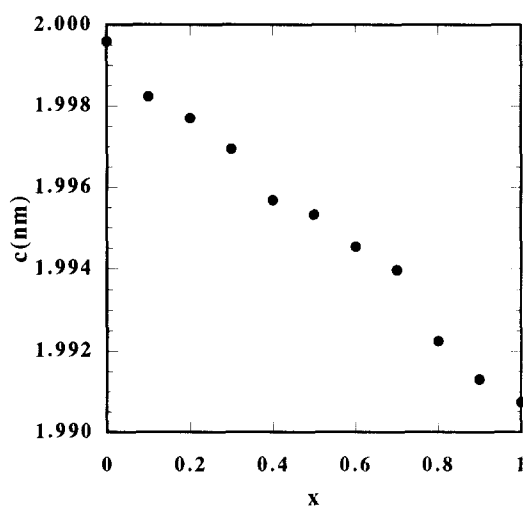
Fig. 2 shows the unit cell parameters a and c plotted against the x value of $\text{La}_{1-x}\text{Eu}_x\text{Ta}_7\text{O}_{19}$. The unit cell parameters have a tendency to decrease linearly with increasing x because of the difference in ionic radius between La^{3+} (0.118 nm for eight coordination) and Eu^{3+} (0.107 nm) [18]. The result implies that Eu^{3+} ions are successively substituted for La^{3+} ions in the two-dimensional networks of $(\text{La}^{3+}, \text{Ta}^{5+})\text{-O}^{2-}$ polyhedra.

Fig. 3 shows the UV-visible diffuse reflection spectrum of $\text{EuTa}_7\text{O}_{19}$. It is seen that the absorbing edge is located around 270 nm (4.59 eV), which is similar to the value for $\text{LaTa}_7\text{O}_{19}$. The additional peaks can be ascribed to transitions from ${}^7\text{F}_{0,1}$ to each excited state of Eu^{3+} as indicated in the figure. There is a probability that a band due to charge transfer from O^{2-} to Eu^{3+} ions will be observed near 300 nm. However, no such band was observed in this spectrum.

Fig. 4 shows the emission spectra of $\text{La}_{0.9}\text{Eu}_{0.1}\text{Ta}_7\text{O}_{19}$ and $\text{EuTa}_7\text{O}_{19}$ under excitation at 396.3 nm measured at room temperature. The emission spectra consist of a main peak at 610 nm and several supplementary peaks. These peaks can be identified as ${}^5\text{D}_j \rightarrow {}^7\text{F}_{j'}$ ($j=0, 1; j'=1, 2, 3, 4$) transitions. Similar spectra were observed for all Eu^{3+} concentrations with some changes in intensity. In Fig. 4 the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (electric dipole transition)



(a)



(b)

Fig. 2. Concentration dependence of unit cell parameters of (a) a and (b) c of $\text{La}_{1-x}\text{Eu}_x\text{Ta}_7\text{O}_{19}$.

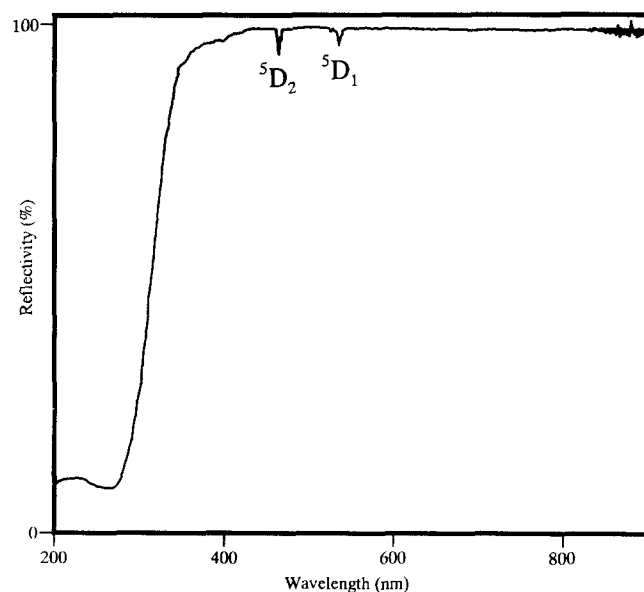


Fig. 3. UV-visible diffuse reflection spectrum of $\text{EuTa}_7\text{O}_{19}$.

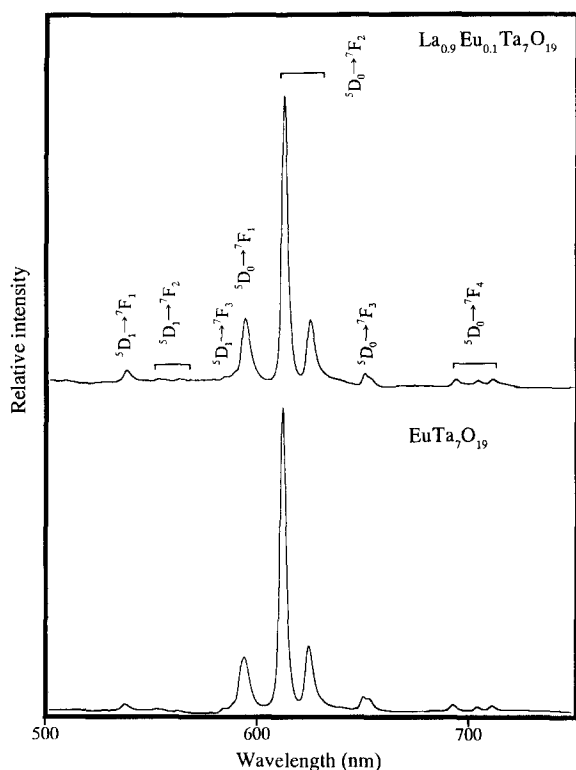


Fig. 4. Emission spectra of $\text{La}_{0.9}\text{Eu}_{0.1}\text{Ta}_7\text{O}_{19}$ and $\text{EuTa}_7\text{O}_{19}$ under excitation at 396.3 nm.

band is typically split into two or more bands. In comparison with the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (magnetic dipole transition) band, the substitution sites for Eu^{3+} are considered to have no inversion symmetry. In addition, most powder samples were homogeneously coloured pale pink with increasing Eu^{3+} concentration. Consequently, the colouring must be caused by the Eu^{3+} emission itself.

Fig. 5 shows the emission spectra of $\text{La}_{0.9}\text{Eu}_{0.1}\text{Ta}_7\text{O}_{19}$ and $\text{EuTa}_7\text{O}_{19}$ upon cathode ray (CR) excitation under conditions of 15 kV and $0.5 \mu\text{A}$. These emission profiles are very similar to those of UV excitation. However, the intensity of the ${}^5\text{D}_1$ emission hardly decreases with increasing Eu^{3+} concentration. This implies that no cross-relaxation occurs between ${}^5\text{D}_1 \rightarrow {}^5\text{D}_0$ and ${}^7\text{F}_0 \rightarrow {}^7\text{F}_3$ transitions owing to the long separation of Eu^{3+} ions.

The Eu^{3+} concentration dependence of the emission intensity was examined using the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition band at 610 nm under excitation at 396.3 nm in $\text{La}_{1-x}\text{Eu}_x\text{Ta}_7\text{O}_{19}$ as shown in Fig. 6. It can be seen that the observed plot deviates slightly from a proportional increase in emission intensity with Eu^{3+} concentration up to $x=1.0$. Saturation of the emission intensity is frequently observed in phosphors with a high critical concentration. For instance, in orthorhombic $\text{La}_{1-x}\text{Eu}_x\text{P}_3\text{O}_9$ [3] the Eu^{3+} sublattice consists of zigzag chains with an intrachain separation between Eu^{3+} ions of 0.42 nm and an interchain separation of 0.73 nm. Therefore energy migration of excited Eu^{3+} is

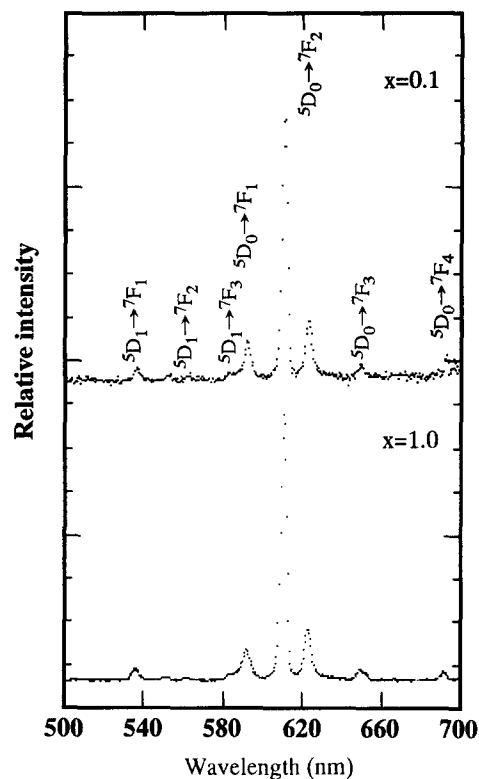


Fig. 5. Emission spectra of $\text{La}_{0.9}\text{Eu}_{0.1}\text{Ta}_7\text{O}_{19}$ and $\text{EuTa}_7\text{O}_{19}$ upon CR excitation under conditions of 15 kV and $0.5 \mu\text{A}$.

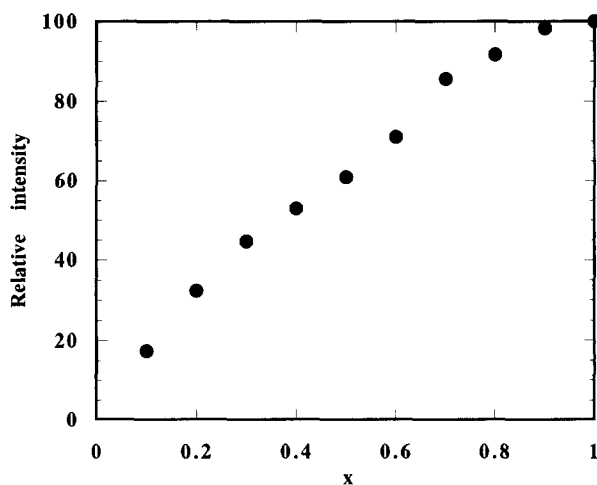


Fig. 6. Concentration dependence of Eu^{3+} emission (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition) intensity under excitation at 396.3 nm in $\text{La}_{1-x}\text{Eu}_x\text{Ta}_7\text{O}_{19}$.

apparently predominantly to neighbouring sites displaced one-dimensionally. On the other hand, in $\text{EuTa}_7\text{O}_{19}$ the EuO_8^{13-} polyhedra are isolated from each other by TaO_7^{9-} and TaO_8^{11-} polyhedra [8]. Also, the shortest distance between Eu^{3+} ions is estimated to be about 0.62 nm. As a result, the separation of Eu^{3+} ions is too long for interaction of the exchange type to occur in $\text{EuTa}_7\text{O}_{19}$. Consequently, the interaction between Eu^{3+} ions is considered to be of the dipole-dipole type.

Buijs and Blasse [1,3] reported that the type and strength of Eu^{3+} – Eu^{3+} interactions are fairly predictable from the arrangement of activated centres and the emission profile. The dipole–dipole interaction decreases abruptly with increasing separation of Eu^{3+} ions [6]. Energy migration to killer sites, resulting in concentration quenching, is restricted by the long separation and, as described in Ref. [7], the low dimensionality of the substituted Eu^{3+} sites. The dipole–dipole interaction of Eu^{3+} ions, where the strength depends on the oscillation strength of the ${}^5\text{D}_0$ – ${}^7\text{F}_0$ transition, is closely related to the intensity of the ${}^5\text{D}_0$ → ${}^7\text{F}_0$ emission [3]. The ${}^5\text{D}_0$ → ${}^7\text{F}_0$ emission intensity is relatively weak in $\text{La}_{1-x}\text{Eu}_x\text{Ta}_7\text{O}_{19}$. It seems that this fact is another reason why the concentration quenching is very weak in $\text{La}_{1-x}\text{Eu}_x\text{Ta}_7\text{O}_{19}$.

4. Conclusions

The results of the Eu^{3+} concentration dependence of the emission intensity indicate that energy migration between Eu^{3+} ions hardly occurs in $\text{La}_{1-x}\text{Eu}_x\text{Ta}_7\text{O}_{19}$. The long separation and low dimensionality of the La^{3+} sites doped with Eu^{3+} ions are eventually significant to avoid concentration quenching. Furthermore, the proper separation of Eu^{3+} results in no cross-relaxations. The emission spectrum of $\text{La}_{1-x}\text{Eu}_x\text{Ta}_7\text{O}_{19}$ is independent of the concentration of Eu^{3+} in shape, even upon CR excitation. Therefore $\text{EuTa}_7\text{O}_{19}$ can be regarded as one of the concentrated Eu^{3+} -doped compounds.

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