博士論文

$\text{LnF}_3: \text{Eu}^{3+}$ ($\text{Ln} = \text{La, Gd}$) ナノ粒子の母材制御と発光特性

2011年2月

張小婷
Host Control and Photoluminescence Properties of LnF₃:Eu³⁺(Ln=La, Gd) Nanoparticles

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Chapter 5. Summery
Chapter 1. Introduction

1.1 General introduction

Phosphors play important roles in our society for their wide applications in industry, in military and in everyday life. Whether one engages in laser surgery with a neodymium-YAG laser or one enjoys 3D movies without any eyewear at home, the development of these materials is scientifically of great interest.

Phosphors are formed from host-crystal and activator ingredients which are isostructural. Typical activators are rare-earth or transition-metal ions. In contrast to transition metals, rare-earth (RE) ions have the unique properties: a large number of possible energetic states of partially filled 4f\(^n\) electron shell \(1<n<14\), screening effect produced by their completely filled 5s\(^2\)5p\(^6\) electron shells (which weakens the influence of external electric and magnetic fields on 4f electrons) and small stabilization due to crystal-field effect. These unique properties make them very attractive activator ions in solid state lasers and phosphors covering a wide spectral range from infrared (IR) to ultraviolet (UV) and vacuum ultraviolet (VUV) spectral regions.

Lanthanide trifluorides (LnF\(_3\)) are very suitable hosts for doping RE ions because the lanthanide ions could be substituted easily with RE ions with the same valence, and more significantly, they have low phonon energy that makes it possible to reduce the nonradiative de-excitation probability of the luminescent RE ions by the multiphonon relaxation.

Recently, many studies on rare-earth ions doped LnF\(_3\) luminescent materials have focused on the preparation of various kinds of nanoparticles in controlled shape, size, and crystal structure and thus to tailor their luminescence properties\(^1\)\(^-\)\(^3\). LnF\(_3\) with different size and morphologies such as fullerene-like nanoparticles\(^4\), bundle-like particles\(^5\), and nano-plates\(^6\) exhibited different optical properties. EuF\(_3\) with hexagonal structure shows stronger luminescence intensity than that with orthorhombic structure was also reported\(^7\). It is well known that the optical properties of luminescent nanomaterials are enormously affected by their shapes, sizes and structures\(^8\)\(^-\)\(^10\), but the mechanism of how particle
size and crystal structure influence luminescence properties of doped rare-earth ions are still far from being well understood. In order to obtain phosphors with higher efficiencies and strong luminescence intensity it is necessary to know how the host size and structure affect activator luminescence properties. This thesis focused on investigating the roles of host structures (particle size, particle shape, polytype and activator location) playing in activator luminescence properties. These basic studies of host structure will be a guiding principle to synthesize high performance rare-earth ions doped LnF₃ materials.

Lanthanum fluoride (LaF₃) is an excellent host matrix for luminescent materials because of its low phonon energies and has been used as an extreme pressure and antiwear additive in grease and as solid lubricant under high temperature because of its fairly low hardness, high melting point, and good resistance to thermal and chemical attack. RE-doped LaF₃ (nanocrystals) NCs have received much attention for their wide applications in optics and optoelectronics (e.g., lighting and displays, optical amplifiers, and lasers), microelectronics and especially biological labels and have been prepared via various chemical methods such as modified precipitation, polyol, and solvothermal method. A synthesis method of size tunable LaF₃:Eu³⁺ nanocrystals with cetyltrimethylammonium bromide (CTAB) as size control agent via a hydrothermal rout was developed in order to illustrate the correlation between particles size, Eu³⁺ ions located position and luminescence properties. In LnF₃ materials, the medial SmF₃, EuF₃ and GdF₃ undergoing the phase transition between hexagonal and orthorhombic, GdF₃ is also a good alternative for LaF₃. Because of the 4f energy-level overlap between the ⁶P₁ states of Gd³⁺ and the ⁵H₄ states of Eu³⁺, energy transfer from Gd³⁺ to Eu³⁺ is possible. So, polytype GdF₃:Eu³⁺ nanocrystals were selected to illustrate the effect of host polytypes on luminescence properties of doped Eu³⁺ ions.

In Chapter 1, general properties of the Eu ion used as activator and the structure of LaF₃ (GdF₃) used as host in this work are discussed. Theories of Rietveld method and Förster resonance energy transfer mechanism are introduced.

In Chapter 2 a new method to analyze Eu³⁺ ions location in host particle is described. This method is based on Eu³⁺ ions typical luminescence properties. Via analyzing ⁵D₀ - ⁷F₁₂ decay curves in Eu³⁺ ions with double exponential function by a least-square fitting method, fractions of doped Eu³⁺ ions located in different sites in host particles can be estimated. This method is used throughout this thesis.
Chapter 3 describes the development of synthesis method of size tunable LaF\textsubscript{3}:Eu\textsuperscript{3+} nanoparticles and the characterization of their size, crystals structure and luminescence properties. Size effects on luminescence properties of these samples were investigated. It is pointed out that the Eu\textsuperscript{3+} ion location depends on particle size, and how the location changes was also discussed.

Chapter 4 introduces a novel simple method to prepare polytype (hexagonal and orthorhombic) GdF\textsubscript{3}:Eu\textsuperscript{3+} nanoparticles crystals. The polytype structures and morphologies are characterized by XRD patterns, SEM and TEM images, their luminescence properties are discussed based on the photoluminescence (PL), photoluminescence excitation (PLE) and decay curves spectra, how the polytype structures influence luminescence properties is described.

A summery was described in Chapter 5.

In this study, by analyzing Eu\textsuperscript{3+} luminescence properties in size tuned LaF\textsubscript{3}:Eu\textsuperscript{3+} nanoparticles it was found that Eu\textsuperscript{3+} ions prefer to locate in a high symmetric site in LaF\textsubscript{3} lattice matrix as their particle size increased. It means that in large particles most of Eu\textsuperscript{3+} ions were situated in the environment with few defects, which engaged strong PL. Polytype studies of Eu\textsuperscript{3+} doped GdF\textsubscript{3} nanoparticles indicated that the interatomic distances between Gd\textsuperscript{3+} ions in the hexagonal structure were shorter than those in the orthorhombic structure. Much more efficient energy transfer is expected from Gd to Eu in the hexagonal structure than that in the orthorhombic structure as the most of Eu ions (about 70%) in both polytype GdF\textsubscript{3}:Eu\textsuperscript{3+} occupied Gd sites.

1.2 Eu ion luminescence properties

Being special important rare-earth ions, Eu ions energy levels of 4f orbitals are not degenerate because of electronic repulsion, spin-orbit coupling, and (in a coordination environment) the ligand field. The strongest interaction, the electronic repulsion between the electrons, disrupts the degeneracy of the 4f energy levels and yields terms with separations in the order of $10^4$ cm\textsuperscript{-1}. Spin-orbit coupling is the interaction between the magnetic moments of the electrons due to their spin (spin angular momentum) and the magnetic moments due to their movement around the nucleus (orbital angular momentum). This causes further splitting of the energy levels into so call J-states. The splitting of these
Energy levels is in the order of $10^3 \text{ cm}^{-1}$. The J-degeneracy is partially removed in a coordination environment by the ligand field. These splittings are in the order of $10^2 \text{ cm}^{-1}$ (see Figure 1-1).

![Energy Levels Diagram](image)

**Figure 1-1** Splitting of the 4f energy levels of Eu$^{3+}$ as a result of electronic repulsion, spin-orbit coupling, and the ligand field.

Eu$^{3+}$ luminescence can be structures-probe apart from its application in phosphor materials. This is possible for the reason that Eu$^{3+}$ has several structure-dependent transitions enabling one to gain insight about the site that it occupies in a given host. The optical transitions of Eu$^{3+}$ are a special case in the theory of induced electric dipole transitions. The induced electric dipole transitions have an additional selection rule ($\Delta J = \pm 2, \pm 4, \ldots$). If the initial level has J = 0, as is the case for Eu$^{3+}$ ($^5D_0$): transitions to odd J are forbidden. This generally results in the following emission spectrum $^{16}$ (in Figure 1-2):

$^5D_0 \rightarrow ^7F_0$ (~580 nm): extremely weak, induced electric dipole ($J = 0$ to $J' = 0$ is forbidden).

$^5D_0 \rightarrow ^7F_1$ (~590 nm): magnetic dipole emission.

$^5D_0 \rightarrow ^7F_2$ (~613 nm): hypersensitive induced electric dipole emission.

$^5D_0 \rightarrow ^7F_3$ (~650 nm): extremely weak, induced electric dipole emission.

$^5D_0 \rightarrow ^7F_4$ (~700 nm): weak, induced electric dipole emission.
Figure 1-2 Emission spectrum from $^5D_0$ level of Eu$^{3+}$ ion in LaF$_3$ particles.

The emission band centered around at 590 nm, corresponding to $^5D_0 \rightarrow ^7F_1$ transition that is magnetic dipole in character, is relatively strong and independent of the local symmetry of the Eu$^{3+}$ ions $^{15}$. The electric dipole $^5D_0 \rightarrow ^7F_2$ transition centered around at 613 nm is hypersensitive and extremely sensitive to the local symmetry of Eu$^{3+}$ ions. Kirby and Richardson $^{17}$ established that the relative intensity of $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ emission is a good measure of the local environment of the Eu$^{3+}$ ion. In a high symmetric environment, the magnetic dipole $^5D_0 \rightarrow ^7F_1$ transition of Eu$^{3+}$ is dominating, whereas distortion of the symmetry around the ion causes an intensity enhancement of electric dipole transitions such as the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition. It is clear that the $I_{^7F_2}/I_{^7F_1}$ intensity ratio, called the asymmetry ratio, $A$, $^{18,19}$ give a measure of the local environment of the Eu$^{3+}$ ion. For this special characteristic, Eu$^{3+}$ ion was chosen as a doping rare-earth to investigate how the hosts particle size and polytype structure influence the luminescence properties of doped ions in our work.
1.3 LaF$_3$ and GdF$_3$ crystal structure

1.3.1 LaF$_3$ crystal structure

LaF$_3$ nanocrystal has received particular attention because of its good qualities: adequate thermal and environmental stability, low phonon energy (as low as 350 cm$^{-1}$), ability of being easily doped with rare-earth ions. All of these good qualities made LaF$_3$ nanocrystas become one of the most efficient host materials for luminescence materials.$^{20,21,22}$ Therefore, the study of LaF$_3$ nano-crystals has attracted considerable interest. Single-crystal studies by Mansmann (1965)$^{23}$, Zalkin, Templeton and Hopkins (1966)$^{24}$ and A. K. Cheetham and AND B. E. F. Fender (1975)$^{25}$ indicate the space group $P\overline{3}c1$, the result was supported by Raman measurements (Bauman and Porto, 1967$^{26}$). On the other hand the X-ray and neutron measurements of de Rango, Tsoucaris and Zelwer (1966)$^{27}$ have been interpreted in $P6_3cm$, while Afanasiev, Habuda and Lundin speculated $P6_3/mcm$ on the basis of other results on CeF$_3$, PrF$_3$ and NdF$_3$ (1972)$^{28}$. Recently, more and more study results (I. Brach, and H. Schulz, 1985$^{29}$, B. Winkler, K. Knorr, and V. Milman, 2003$^{30}$, T.J. Udovic, Q.Z. Huang, A. Santoro and J.J. Rush 2008$^{31}$) prefer to $P\overline{3}c1$ space group. In Table 1-1 list the structure parameters of LaF$_3$ reported by Udovic group.

### Table 1-1 Atomic parameters of LaF$_3$ in $P\overline{3}c1$ space group

<table>
<thead>
<tr>
<th>LaF$_3$</th>
<th>Cell dimensions: a=b=7.1907Å, c=7.3531Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td>La</td>
<td>0.6596</td>
</tr>
<tr>
<td>F(1)</td>
<td>0.3655</td>
</tr>
<tr>
<td>F(2)</td>
<td>0</td>
</tr>
<tr>
<td>F(3)</td>
<td>0.3333</td>
</tr>
</tbody>
</table>

Figure 1-3 shows a LaF$_3$ crystal structure with hexagonal lattice with $P\overline{3}c1$ space group. La$^{3+}$ ions in LaF$_3$ are situated at a site of C$_2$ symmetry, each La$^{3+}$ ion being surrounded by 11 F$^{-1}$ ions, the
coordination polyhedron is a distortion of a tricapped trigonal prism with two extra ligands on the 3-fold axis. There are six sites with identical electric environment oriented in three directions separated by angles of 60°. The z-axes of the C2 sites are perpendicular to the z-axis of the crystal and the x-axis of each site is parallel to the z-axis of the crystal.

![Diagram of LaF3 crystal structure](image)

Figure 1-3 Unit-cell structure of hexagonal LaF3 crystal (hexagonal).

In LaF3 hexagonal structure, there is no asymmetric center in it, so the electric dipole $^5D_0 \rightarrow ^7F_2$ transition of Eu$^{3+}$ ion doped in LaF3 matrix is not completely forbidden. The analysis of $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ luminescence decay curves can be used in the method of Eu$^{3+}$ ions located position estimation in host particle, which is mentioned in Chapter 3.

1.3.2 GdF3 crystal structure

For rare-earth ions, ionic radius decreased as atomic number increased from La to Lu. It is reported by Mansmann that in lanthanide trifluorides (LnF3) crystals when the ionic radius of the lanthanide earth $r_{\text{LN}}$ decreases, the fluorine ions tend to touch each other, resulting in a repulsive energy which induced the LnF3 structure change from hexagonal to orthorhombic. Zalkin et al. established the current accepted structure of the LaF3. Which was described as trigonal with space group P̅3c1 and $Z = 6$ as mentioned in Section 1.3.1. The light rare earths fluorides from La to Nd crystallize in this structure. All other rare earth fluorides crystallize at room temperature in the orthorhombic structure determined by Zalkin and Templeton for LnF3, also referred as $\beta$-YF3, space group Pnma and $Z = 4$. The orthorhombic structure of YF3 was showed in Figure 1-4. The unit cell is a distorted hexagonal LaF3 lattice, the basic unit of the orthorhombic structure YF3 is a tricapped prism with nine fluorine
ions surrounding the $Y^{3+}$ ion, six fluorine ions are at the corners of the irregular trigonal prism with a $Y$ ion at the center and the three other fluorine ions are in front of the three side faces of this trigonal prism.

![Figure 1-4 Unit-cell structure of orthorhombic YF$_3$ crystal (orthorhombic).](image)

The intermediate SmF$_3$, EuF$_3$ and GdF$_3$ have the polytype structures of hexagonal and orthorhombic. Recently, stronger luminescence from Eu$^{3+}$ in hexagonal EuF$_3$ than that in orthorhombic one is reported$^{34}$. This fact suggests that polytype control of matrix LnF$_3$ enables to increase light emitting probability of doped rare earth in LnF$_3$ by changing atomic coordination around the doped rare-earth.

GdF$_3$ luminescence material is a well-known wide band-gap material that has excellent luminescent properties in visible and vacuum ultraviolet regions. In this thesis GdF$_3$ was selected as the host to detect the correlation between the luminescence properties and crystals structures.

### 1.4 Förster Resonance Energy Transfer

Sensitization via energy transfer provides a means to deliver energy to a donor that inefficiently couples to the excitation source. The acceptor at first absorbs the excitation energy and then transfers it to the donor through a nonradiative process. This nonradiative energy transfer is generally called by the Förster resonance energy transfer whose practical description was first given by Förster in 1946$^{35}$. 

- 8 -
According to Förster resonance energy transfer theory, the energy transfer arises from a dipole-dipole interaction between the electronic states of the donor and the acceptor, and does not involve the emission and re-absorption of a light field. Resonant transfer occurs when the oscillations of an optically induced electronic energy on the donor are coherent with the electronic energy gap of the acceptor. The strength of the interaction depends on the magnitude of a transition dipole interaction, which depends on the magnitude of the donor and acceptor transition matrix elements, and the alignment and separation of the dipoles. The probability of energy transfer, $P_{AB}$, depends on the square of the energy overlap and inversely on sixth power of the distance between the donor and acceptor, expressed as below:

$$P_{AB} = 1.4 \times 10^{24} f_A f_B S / [\Delta E^2 R^6]$$  \hspace{1cm} \text{Eq.(1-1)}$$

$f_A, f_B$: Oscillator strengths of the donor and acceptor, respectively

$S$: Overlap of donor emission and acceptor absorption;

$\Delta E$: Transition energy;

$R$: Distance between the donor and acceptor.

Förster resonance energy transfer theory is used in chemical science, particularly in scintillators and chemical sensors. In polymer science, it is used to examine the interpenetration of polymer chains, phase separation, compatibility between polymers, interdiffusion of latex particles, interface thickness in blends of polymers, and light-harvesting polymers, among others. In this thesis, it is used to discuss how the polytype structures influence the Eu$^{3+}$ luminescence properties.

1.5 Rietveld refinement method

Rietveld refinement method is used for the characterization of crystalline materials from powder diffraction data and invented by Hugo M. Rietveld. Rietveld method is now widely recognized to be uniquely valuable for structural analyses of nearly all classes of crystalline materials from X-ray and neutron powder diffraction data.
Be a complete powder-diffraction-pattern fitting technique, the goal of the Rietveld method is to minimize the residual function using a non-linear least squares method:

\[
WSS = \sum_i w_i (I_i^{\text{exp}} - I_i^{\text{calc}})^2, \quad w_i = \frac{1}{\sqrt{I_i^{\text{exp}}}} \quad \text{Eq.(1-2)}
\]

The intensity of diffraction spectrum is calculated by the classical intensity equation:

\[
I_i^{\text{calc}} = S_F \sum_{j=1}^{N_{\text{phase}}} \frac{f_j}{V_j} \sum_{k=1}^{N_{\text{peaks}}} L_k |F_{k,j}|^2 S_j \left(2\theta_i - 2\theta_{k,j} \right) P_{k,j} A_j + \text{bkg}_i \quad \text{Eq.(1-3)}
\]

The spectrum (at a 2θ point i) is determined by background value (bkg_i), diffraction intensity \((S_F \sum_{j=1}^{N_{\text{phase}}} \frac{f_j}{V_j} \sum_{k=1}^{N_{\text{peaks}}} L_k |F_{k,j}|^2)\) which depend on the crystal structure, quantity, cell volume, texture, stress, chemistry etc and determines the height of the peaks and line broadening \(S_j(2\theta_i - 2\theta_{k,j})\) which determined the shape of the peaks. Every parameter written in term can be refined; from the refinement results microstructure parameters can be obtained.

In Rietveld refinement process will adjust the finable parameters until the residual (Eq.(1-2)) is minimized in some senses, that is, a “best fit” of the entire calculated pattern to the entire observed pattern will be obtained. There are several criteria R-factors now commonly used, where \(I_k\) is the intensity assigned to the \(k\)th Bragg reflection at the end of the refinement cycles, \(y_i\) is the intensity at the ith step.

\[
R_F = \frac{\sum_{k} \left( (I_k^{\text{obs}})^{1/2} - (I_k^{\text{calc}})^{1/2} \right)^2}{\sum (I_k^{\text{obs}})^{1/2}} \quad \text{(R- structure factor)} \quad \text{Eq.(1-4)}
\]

\[
R_B = \frac{\sum |I_k^{\text{obs}} - I_k^{\text{calc}}|}{\sum I_k^{\text{obs}}} \quad \text{(R-bragg factor)} \quad \text{Eq.(1-5)}
\]

\[
R_P = \frac{\sum |Y_i^{\text{obs}} - Y_i^{\text{calc}}|}{\sum Y_i^{\text{obs}}} \quad \text{(R-pattern)} \quad \text{Eq.(1-6)}
\]
\[ R_{wp} = \left( \frac{\sum W_i (Y_{i(obs)} - Y_{i(calc)})^2}{\sum W_i (Y_{i(obs)})^2} \right)^{1/2} \quad \text{(R-weighted pattern)} \quad \text{Eq.(1-7)} \]

\[ R_{exp} = \left( \frac{(N-P)}{\sum_{i=1}^{N} [W_i \tilde{I}_{i}^{exp}]^2} \right)^{1/2} \quad \text{(R-expected factor)} \quad \text{Eq.(1-8)} \]

\[ S = \frac{R_{wp}}{R_{exp}} \quad \text{(good fitness factor)} \quad \text{Eq.(1-9)} \]

Among these factors, \( R_{wp} \) is the most meaningful, because \( R_{wp} \) factor cannot be biased in favor of the model being used, since it best reflects the progress of the refinement. Above the R-factors, the “goodness of fit” factor \( S \) is another useful numerical criterion, a value about 1.3 is usually considered to be quite satisfactory and a value smaller than 1.5 indicate that the fitted model accounts for the data well.

In this thesis, the software program RIETAN-FP (Izumi and Ikeda, 2000) was used to refine the size-tunable LaF\(_3\) and polytype GdF\(_3\) structure.
1.6 References


Chapter 2. Analysis method of Eu$^{3+}$ location in host matrix on the basis of $^5D_0$ decay

In general, doped RE ions can locate three sites in host LnF$_3$ crystal, one is substitution site (replacing Ln by Eu in LnF$_3$ lattice) with high symmetry, the other two with low symmetry are surface site (at the particles surface) and interstitial site (in LnF$_3$ lattice), both of them are called distorted site. Doped RE ion position in LnF$_3$ host strongly influences RE luminescence properties. In this Chapter, a new method to estimate the location of doped Eu$^{3+}$ ions in host matrix is introduced. This method is based on the analysis of Eu$^{3+}$ $^5D_0 \rightarrow ^7F_{1,2}$ decay curves by least-square fitting method. This analysis method is illustrated by the case of LaF$_3$:Eu$^{3+}$ nanoparticles.

2.1 Experiment of LaF$_3$:Eu$^{3+}$ nanoparticles

Cetyltrimethylammonium bromide (CTAB, 99%) was obtained from SIGMA co.. All other reagents, La(NO$_3$)$_3$.6H$_2$O, NaF, and EuCl$_3$.6H$_2$O from ALDRICH co., were used as received.

LaF$_3$:Eu$^{3+}$ nanoparticles have been synthesized by a hydrothermal method as shown in Figure 2-1. 5 mmol La(NO$_3$)$_3$.6H$_2$O, 0.25 mmol EuCl$_3$.6H$_2$O and CTAB (0.006 mol/L) were dissolved in 150 mL deionized water. After being stirred mechanically for about 20 min. 15.75 mmol NaF was added drop by drop. A white suspension was gradually formed upon stirring. After stirred for 40 min. the mixture was transferred into a 250 mL autoclave, sealed, and heated at 140 °C for about 12 h. The system was then allowed to be cooled down to room temperature. The product was collected by centrifugation and washed subsequently with water and ethanol three times, respectively. After the centrifugation the particles were dried in an oven at 80 °C. The obtained nanocrystals were slowly calcined to 600 °C at a heating rate of 4 °C/min., annealed under a flow of N$_2$ gas for 2 h, and gradually cooled down to room temperature. The final product was a white powder of La$_{0.952}$Eu$_{0.048}$F$_3$ without CTAB.

The photoluminescence decay curves of $^5D_0 \rightarrow ^7F_{1,2}$ transitions were recorded by a time-resolved photoluminescence (TRPL) system (Oriel Instruments, InstaSpec™ V system) under the excitation by
N$_2$ laser (USHO, KEC-160; $\lambda_{ex} = 337.1$ nm, pulse width < 1 ns). All of the experiments were done at room temperature.

Figure 2-1 The flowchart of LaF$_3$:Eu$^{3+}$ nanoparticles preparation.

2.2 Results and discussion

2.2.1 PL spectrum and decay curves of Eu$^{3+}$ ions $^5$D$_0$-$^7$F$_{1,2}$ transitions in LaF$_3$:Eu$^{3+}$

Room-temperature (RT) photoluminescence spectra (PL) was presented in Figure 2-2. The luminescence lines are assigned according to Carnells' paper. As it was mentioned that Eu$^{3+}$ ion is a good probe for the chemical environment of the lanthanide ion; the relative intensities of $^5$D$_0$ $\rightarrow$ $^7$F$_1$ and $^5$D$_0$ $\rightarrow$ $^7$F$_2$ emission, which are typical magnetic and electronic dipole transitions in character, respectively, depend strongly on the local symmetry of the Eu$^{3+}$ ions. In a site with inversion symmetry the $^5$D$_0$ $\rightarrow$ $^7$F$_1$ magnetic dipole transition is dominant, while in a distorted site (without an
inversion symmetry) the $^5D_0 \rightarrow ^7F_2$ electric dipole transition is intensified in rate in comparison with the $^5D_0 \rightarrow ^7F_1$ transition. In the emission spectra of LaF$_3$:Eu$^{3+}$ nanocrystals (see Figure 2-2), the dominating emission at 592 nm corresponds to the $^5D_0 \rightarrow ^7F_1$ magnetic dipole transition, which indicates that Eu$^{3+}$ ions were mainly located in a higher symmetric site close to an inversion symmetry in LaF$_3$ matrix. The peak at 619 nm can be ascribed to $^5D_0 \rightarrow ^7F_2$ electric dipole transition, which is quite sensitive even to small changes in the chemical environment from an inversion symmetry surrounding Eu$^{3+}$ ion. It is clear that the $I(^5D_0 \rightarrow ^7F_2)/I(^5D_0 \rightarrow ^7F_1)$ intensity ratio, called the asymmetry ratio, $\Lambda$, gives a measure of the local environment of the Eu$^{3+}$ ion calculated about 0.310 indicating that Eu$^{3+}$ ions occupied a higher symmetric site.

![Photoluminescence spectra of LaF$_3$:Eu$^{3+}$ nanocrystals. (\(\lambda_{ex} = 397\) nm).](image)

Figure 2-3 shows the decay curves of the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ luminescence monitored at 592 nm and 619 nm, respectively. As mentioned in Chapter 1, the photoluminescence decay curve of doped Eu$^{3+}$ ions can offer the information on the change of the Eu$^{3+}$ ligand structure and on Eu$^{3+}$ clusters. We would like to start from an ideal system of Eu$^{3+}$ ligand with a perfect inversion symmetry, in which electric dipole transitions such as $^5D_0 \rightarrow ^7F_{2,4,6}$ are forbidden by a parity restriction of the $f$-$f$ transitions (Laporte rule), and negligible non-radiative effects. In the case, a dominant $^5D_0$ emission will be $^5D_0$-
\(7\text{F}_1\) of magnetic dipole, which is allowed by the selection rule \(\Delta J = 0, \pm 1\) (except \(0 \leftrightarrow 0\)) via the following formula for a line strength \(^3\),

\[
S_{\text{md}} = \frac{e^2 \hbar^2}{16\pi^2 m^2 c^3} \left| \left< f^N [\alpha S L] I J, L + 2S | f^N [\alpha' S' L'] J') \right> \right|^2 .
\]

\text{Eq.}(2-1)

It is known that \(S_{\text{md}}\) is independent of host material. The other transitions from \(5\text{D}_0\) to \(7\text{F}_{0,3,5}\) (owing to \(J\)-mixing) are very small. The \(5\text{D}_0\) lifetime is therefore determined by the magnetic dipole transition probability \((5\text{D}_0\to 7\text{F}_J\) transition probability is denoted by \(W_{0,J}\)) \(^8\),

\[
W_{0-1} = A_{\text{md}} = \frac{64\pi^4 \nu^3}{3\hbar(2J + 1)} n^3 S_{\text{md}} ,
\]

\text{Eq.}(2-2)

where \(\nu\) is the wavenumber \((\text{cm}^{-1})\) of the transition and \(n\) is a refractive index of host material. The values corresponding to \(5\text{D}_0\rightarrow 7\text{F}_1\) were given by several authors: Risefeld et al. \(^9\) reported \(9.4 \times 10^{-8}\) as an oscillator strength. Axe et al. \(^10\) obtained the transition probability of \(43.3\ \text{sec}^{-1}\) for europium ethylsulfate. C. Görller-Walrand et al. theoretically calculated magnetic dipole strengths \(^11\) for \(5\text{D}_1\rightarrow 7\text{F}_0\), \(5\text{D}_0\rightarrow 7\text{F}_1\) and \(5\text{D}_2\rightarrow 7\text{F}_1\). In \(\text{LaF}_3:Eu^{3+} (n = 1.603)\) \(^12\) the value of \(W_{0-1}\) was obtained under the refractive index calibration and finally given to be \(54.3\ \text{sec}^{-1}\), which contributes, of an order of tenth milliseconds, to the \(5\text{D}_0\) lifetime.

![Figure 2-3](image)

Figure 2-3  Decay curve of \(5\text{D}_0\rightarrow 7\text{F}_{1,2}\) emission \(\text{LaF}_3:Eu^{3+}\) nanocrystals. The solid curves are obtained by a least-square fitting method.
However, in LaF$_3$ host there are the $^5$D$_0$-7F$_1$ and $^5$D$_0$-7F$_2$ transitions. It is due to the deviation from a perfect inversion symmetry but still an intense emission is given by $^5$D$_0$-7F$_1$ ($\lambda \sim 0.3$), that means the deviation is not very large. The other contributions of $^5$D$_0$-7F$_0$ and $^5$D$_0$-7F$_{3,6}$ are found to be very weak, as seen experimentally in the typical PL spectra of LaF$_3$:Eu$^{3+}$, and thus it can be accepted that these transition probabilities, $W_{0.0}$, $W_{0.3-6}$ are much less than $W_{0.1}$ and $W_{0.2}$. In the argument based on negligible non-radiative contribution to the $^5$D$_0$ lifetime in a host material with low phonon energy, the following equation is obtained for LaF$_3$:Eu$^{3+}$,

$$1/\tau \approx W_{0.1} + W_{0.2}$$

Eq.(2-3)

Strictly speaking, $W_{0.0}$ and $W_{0.3-6}$ have a few percentage of the contribution but is still small. $W_{0.2}$ is derived from odd terms of the ligand filed parameters, which is allowed as an electric dipole transition ruled by $\Delta J = 2$ and eventually result in the reduced $^5$D$_0$ lifetime via Eq.(2-3), of an order of a few milliseconds or submilliseconds. This is a basic status of our discussion. In the later part of this chapter, we shall focus on two transitions of $^5$D$_0$-7F$_1$ and $^5$D$_0$-7F$_2$ in our following analysis with a few percentages of errors.

Additionally, clustering of Eu$^{3+}$ ions leads to shorten the Eu$^{3+}$-Eu$^{3+}$ distances, fast energy transfer between Eu$^{3+}$ ions, luminescence quenching combined with a killer site, and hence $^5$D$_0$ decay time shortening. If the clustering effect is not negligible, the above equation should be modified as followed,

$$1/\tau = W_{0.1} + W_{0.2} + W_{CL}$$

Eq.(2-4)

Such a non-radiative transition probability ($W_{CL}$) related with Eu$^{3+}$ clustering influences the reduced $^5$D$_0$ lifetime as well. Thus, a longer $^5$D$_0$ decay time means that Eu$^{3+}$ ions are better dispersed in a higher symmetric site and less clustered. The initial decay rate ($\tau_{init}$) were determined within 1 ms of the $^5$D$_0$$\rightarrow$7F$_{1,2}$ decay curves and estimated as 10.8 ms and 2.6 ms for $^5$D$_0$$\rightarrow$7F$_1$ and $^5$D$_0$$\rightarrow$7F$_2$ emission, respectively.

The importance is that the lifetime observed is an order of 10 ms, which can be derived from Eu$^{3+}$ ions in a higher symmetric site via Eq.(2-4) with negligible $W_{0.2}$ and $W_{CL}$.
2.2.2 Calculation of Eu\textsuperscript{3+} fraction in high symmetry site

In one site model for Eu\textsuperscript{3+} luminescence the time evolution of \textit{5}D\textsubscript{0} emission under pulsed excitation is expressed by single exponential function and moreover each of \textit{5}D\textsubscript{0}-\textit{7}F\textsubscript{J} PL must have the same lifetime inversely proportional to the summation of the different transition probabilities from the \textit{5}D\textsubscript{0} to different \textit{7}F\textsubscript{J} levels. This case is as long as the luminescence given from the same excited \textit{5}D\textsubscript{0} level. However, as seen in Figure 2-3, the experimental decay curves of \textit{5}D\textsubscript{0}-\textit{7}F\textsubscript{1} and \textit{5}D\textsubscript{0}-\textit{7}F\textsubscript{2} were not identically the same, it means that the Eu\textsuperscript{3+} luminescence should be explained with more than two sites for Eu\textsuperscript{3+} ions.

A simple way to do it is to apply a two-site model to the data of Figure 2-3, which can be analyzed with double exponential function\textsuperscript{3} by a least-square fitting method:

\[ I(t)/I_0 = \alpha \exp(-t/\tau_f) + \beta \exp(-t/\tau_s), \quad \text{Eq}(2-5) \]

where \( \tau_f \) is the decay time of the fast component, \( \tau_s \) is the decay time of the slow component, and \( \alpha \) and \( \beta \) is the amplitude ratio of the fast and slow components, respectively (\( \alpha + \beta = 1 \)). Solid line in Figure 2-3 is the result of the fitting analysis for the LaF\textsubscript{3}:Eu\textsuperscript{3+} nanocrystals. The fairly good fitting result is obtained for the \textit{5}D\textsubscript{0}-\textit{7}F\textsubscript{1} decay curve. As for the \textit{5}D\textsubscript{0}-\textit{7}F\textsubscript{2} decay, an additional exponential function is needed for the fast component in order to obtain the satisfactory result.

Table 2-1 summarizes the decay times in the \textit{5}D\textsubscript{0} luminescence analysis using the above-mentioned fitting procedure. The slow decay is characterized by 10 ms lifetime, which directly means a very small \textit{5}D\textsubscript{0}-\textit{7}F\textsubscript{2} electric dipole transition probability, as mentioned in Section 3.3. The slow component must come from Eu\textsuperscript{3+} luminescence in a higher symmetric site (trigonal symmetric site for La\textsuperscript{3+}) of LaF\textsubscript{3} matrix. The lifetime for \textit{5}D\textsubscript{0} level is generally expressed by

\[ 1/\tau = W_{0-1} + W_{0-2} + W_{\text{MP}} + W_{\text{CL}}, \quad \text{Eq.}(2-6) \]

Where \( W_{0-1} \) is a magnetic dipole transition probability for \textit{5}D\textsubscript{0}-\textit{7}F\textsubscript{1} transition while \( W_{0-2} \) is an electric dipole transition probability for \textit{5}D\textsubscript{0}-\textit{7}F_2 transition. For the LaF\textsubscript{3}:Eu\textsuperscript{3+} nanocrystals heated at 600 °C, the multiphonon relaxation probability \( W_{\text{MP}} \) (because of the lower phonon energy) and PL quenching probability due to Eu\textsuperscript{3+} clustering \( W_{\text{CL}} \) as non-radiative processes are negligible. Thus, the decay time \( \tau_s \) of the slow component is approximately given through \( 1/\tau_s \sim W_{0-1} \). Here it has to be noted that the magnetic dipole probability \( W_{0-1} \) of \textit{5}D\textsubscript{0}-\textit{7}F\textsubscript{1} transition is almost constant, resulting from
insensitiveness to chemical environments around Eu\(^{3+}\) ions. On contrary, the fast decay times (\(\tau_f\) and \(\tau_B\)) are as short as \(~0.2\) ms and \(~1\) ms, respectively. Such a short lifetime is observed for Eu\(^{3+}\) in distorted sites (surface site or interstitial site).

Table 2-1 Summary of decay curve analysis for the photoluminescence decay of \(^{5}\text{D}_0-{ }^7\text{F}_{1,2}\) emission for LaF\(_3\):Eu\(^{3+}\) nanocrystals heated at 600 °C.

<table>
<thead>
<tr>
<th></th>
<th>(^{5}\text{D}<em>0-{ }^7\text{F}</em>{1}) emission</th>
<th>(^{5}\text{D}<em>0-{ }^7\text{F}</em>{2}) emission</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fast decay</td>
<td>slow decay</td>
</tr>
<tr>
<td>Decay time / ms</td>
<td>0.220</td>
<td>10.7(9)</td>
</tr>
<tr>
<td>Amplitude, (\alpha, \beta)</td>
<td>0.212</td>
<td>0.788</td>
</tr>
<tr>
<td>Luminescence Intensity</td>
<td>0.0466</td>
<td>8.49</td>
</tr>
<tr>
<td>Relative Contribution</td>
<td>0.5(5) %</td>
<td>99.4(5) %</td>
</tr>
<tr>
<td>Intensity Ratio</td>
<td>(=(\eta_f))</td>
<td>(=(\eta_s))</td>
</tr>
<tr>
<td></td>
<td>0.005(5)</td>
<td>0.994(5)</td>
</tr>
<tr>
<td>Microscopic</td>
<td>(\Lambda_{\text{fast}} = 12.0 ) (^{\text{*2}})</td>
<td>(\Lambda_{\text{slow}} = 0.25 ) (^{\text{*3}})</td>
</tr>
<tr>
<td>(W_{0-2})</td>
<td>(W_{0-2}^{\text{dis}} = 12.0W_{0-1})</td>
<td>(W_{0-2}^{\text{hs}} = 0.25W_{0-1})</td>
</tr>
</tbody>
</table>

*1) corresponding to the apparent asymmetric ratio \(\Lambda\) of 0.31 obtained from the luminescence spectrum in Figure 2-2.

*2) \(\Lambda_{\text{fast}} = \xi_f / \eta_f\),

*3) \(\Lambda_{\text{slow}} = \xi_s / \eta_s\)

The luminescence intensity can be calculated from multiplexing the decay time (ex. \(\tau_f\)) with the corresponding amplitude (ex. \(\alpha\)), which is also given in Table 2-1(\(\eta_f = \tau_f \times \alpha, \eta_s = \tau_s \times \beta\) for \(^{5}\text{D}_0-{ }^7\text{F}_{1}\); \(\xi_f = \tau_f \times \alpha, \xi_s = \tau_s \times \beta\) for \(^{5}\text{D}_0-{ }^7\text{F}_{2}\)). Figure 2-4 displays respective contributions of Eu\(^{3+}\) ions in different PL characters (\(\eta_f, \xi_f\), and \(\eta_s, \xi_s\) in Table 2-1) to \(^{5}\text{D}_0-{ }^7\text{F}_{1,2}\) luminescence intensities for the LaF\(_3\):Eu\(^{3+}\).
nanocrystals heated at 600 °C, which had the stronger luminescence intensity and the apparent lower asymmetric ratio $A$ of 0.310. As a result of the decay analysis, it can be seen that the over-all luminescence intensities come from two different phosphorous sites of Eu$^{3+}$ ions. One is a higher (trigonal) symmetric site in LaF$_3$ nanocrystal and the other is a much distorted site probably located at the surface of LaF$_3$ nanocrystals as described in Chapter 3. Additionally, we can calculate a microscopic asymmetric ratio, $A$ value, for each of inversion symmetric and distorted sites. The former has a value of 0.25, a little bit smaller than the apparent (macroscopic) $A$ of 0.31, and the latter has 12.0 (see Table 2-1 and Figure 2-4).

![Relative luminescence intensity of $^5D_0-^7F_{1,2}$ peak at 592 and 619 nm, respectively. The intensities can be decomposed with the fast and slow decay components given by the decay curve analysis.](image)

As it has been mentioned that the life times for $^5D_0$ level can be expressed by (see Eq. 2-6)

$$\frac{1}{\tau} = W_{0-1} + W_{0-2}$$

Eq. (2-6)

so the life times from disordered site and high symmetric site for $^5D_0$ level expressed as follows

$$\frac{1}{\tau_{\text{dis}}} = W_{0-1}^{\text{dis}} + W_{0-2}^{\text{dis}}$$

Eq. (2-7)

and

$$\frac{1}{\tau_{\text{hs}}} = W_{0-1}^{\text{hs}} + W_{0-2}^{\text{hs}}$$

Eq. (2-8)
In Table 2-1 it was estimated that $W_{0-2}^{\text{dis}}=12.0 \times W_{0-1}$ and $W_{0-2}^{\text{hs}}=0.25 \times W_{0-1}$, the Eq.(2-7) and Eq.(2-8) could be modified as

\[
\frac{1}{\tau^{\text{dis}}} = 13.0 \times W_{0-1} \quad \text{Eq. (2-9)}
\]

and

\[
\frac{1}{\tau^{\text{hs}}} = 1.25 \times W_{0-1} \quad \text{Eq. (2-10)}
\]

from the fitting result, it is known that $\tau^{\text{hs}}=10.8 \text{ ms}$ (see Table 2-1), $W_{0-1}$ can be calculated and the value was as 74.07 sec$^{-1}$, it was according well with the value (54.3 sec$^{-1}$) reported by C.Görllner-Walrand group. Taking into account the $W_{0-1}=74.07 \text{ sec}^{-1}$ in Eq.(2-9), $\tau^{\text{dis}}$ value was obtained and the value was about 1.0 ms, this value was coincided with the experimental data of the fast component of the lifetime (1.12 ms), it could be confirmed that the fitting result was reliable.

The large asymmetric ratio $\Lambda = 12.0$ indicates that the reduced $^5D_0$ lifetime of the fast component isn't a result from symmetric Eu$^{3+}$ in Eu cluster accompanying with PL quench. Furthermore, this microscopic consideration on Eu$^{3+}$ sites located in LaF$_3$ nanocrystals allows us to estimate the fractional number $N$ of Eu$^{3+}$ ions in a higher (trigonal) symmetric or distorted site. The luminescence intensity is proportional to

\[
N \times \frac{W_{0-1}}{W_{0-1} + W_{0-2}} \quad \text{Eq.(2-11)}
\]

and

\[
N \times \frac{W_{0-2}}{W_{0-1} + W_{0-2}} \quad \text{Eq.(2-12)}
\]

for $^5D_0-^7F_1$ and $^7F_2$ luminescence lines, respectively. For a higher (trigonal) symmetric site, an electric dipole transition probability $W_{0-2}$, denoted by $W_{0-2}^{\text{hs}}$, is closer to zero or very small (the factor of 0.25 in comparison with $^5D_0-^7F_1$ intensity) and so the $^5D_0-^7F_1$ luminescence intensity is approximately given by $N^{\text{hs}}$,

\[
I^{\text{hs}} \propto N^{\text{hs}} \times \frac{W_{0-1}}{W_{0-1} + W_{0-2}^{\text{hs}}} \approx N^{\text{hs}} \quad \text{Eq.(2-13)}
\]
One the other hand, Eu$^{3+}$ ions in a distorted site have a considerable value of $W_{0-2}$, denoted by $W_{0-2}^{\text{dis}}$, which can be calculated from the microscopic $\Lambda$ value, $\Lambda_{\text{fast}} = W_{0-2}^{\text{dis}} / W_{0-1} = \xi_f / \eta_f$. Hence, $W_{0-2}^{\text{dis}} = 12.0$ $W_{0-1}$ for a distorted site. The $^5D_0 - ^7F_1$ luminescence intensity of Eu$^{3+}$ ions in a distorted site is calculated to be

$$I_{\text{dis}} \propto N_{\text{dis}} \times \frac{W_{0-1}}{W_{0-1} + W_{0-2}^{\text{dis}}} = \frac{N_{\text{dis}}}{13.0}$$

Eq.(2-14)

The similar calibration must be applied in Eq.(2-11) for a higher (trigonal) symmetric site. Since $W_{0-2}^{\text{hs}} = 0.25 W_{0-1}$ from $\Lambda_{\text{slow}} = 0.25$ (see Table 2-1),

$$I_{\text{hs}} \propto N_{\text{hs}} \times \frac{W_{0-1}}{W_{0-1} + W_{0-2}^{\text{hs}}} = \frac{N_{\text{hs}}}{1.25}$$

Eq.(2-15)

$I_{\text{hs}}$ and $I_{\text{dis}}$ are proportionally related with $\eta_s$ and $\eta_f$, respectively, given in Table 2-1 and Figure 2-4 and therefore we can estimate the fractional number of Eu$^{3+}$ ions in each site in the LaF$_3$ nanocrystal. According to the results in Table 2-1, it can finally be concluded that 94.6 percentage (%) of Eu$^{3+}$ ions occupies a higher (trigonal) symmetric site while the other is in distorted sites (the detail is given in Table 2-1 and Table 2-2). At the present time, the distorted sites for Eu$^{3+}$ are speculated to be on the surface of LaF$_3$ nanocrystals. Figure 2-5 shows the low temperature (9 K) PL spectra of LaF$_3$:Eu$^{3+}$ ions excited at 578.4 nm. The directed excited spectra has a very high microscopic asymmetric ratio value ($\Lambda \approx 10$), which elucidated that the Eu$^{3+}$ ions located at very distorted sites were potentially excited and the $\Lambda$ value of Eu$^{3+}$ luminescence intensity ratio come from distorted sites estimated in decay curves analysis was valid.

Table 2-2 Estimation of the fractional number of Eu$^{3+}$ ions in LaF$_3$ lattice

<table>
<thead>
<tr>
<th>Microscopic $\Lambda$</th>
<th>Higher (trigonal) symmetric site</th>
<th>Disturbed site</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I(^5D_0 - ^7F_1)$</td>
<td>$N_{\text{hs}} / 1.25$</td>
<td>$N_{\text{dis}} / 13.0$</td>
</tr>
<tr>
<td>$\eta_{s,f}$</td>
<td>0.995(5)</td>
<td>0.005(5)</td>
</tr>
<tr>
<td>$N_{\text{hs, dis}}$</td>
<td>94.6 %</td>
<td>5.4 %</td>
</tr>
</tbody>
</table>
2.3 Conclusion

In this section, the method of analysis Eu$^{3+}$ located position in host matrix has been illustrated by the case of Eu$^{3+}$ ion doped in LaF$_3$ nanocrystals. In this method Eu$^{3+}$ $^5D_0$-$^7F_{1,2}$ decay curves were fitted by a least-square method and analyzed using double exponential functions. According to the fitting result, a fraction of Eu$^{3+}$ located in different site can be estimated. This method was used throughout this thesis and should be a useful method in rare-earth doped luminescence materials.


Chapter 3. Effect of LaF₃ particle size on luminescence properties of doped Eu ion

In this chapter, size tuned LaF₃:Eu³⁺ nanocrystals in hexagonal phase have been synthesized by a hydrothermal method with CTAB as a size-controlling agent. Different size samples were well characterized by X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM), photoluminescence excitation and emission spectral measurements. Sample synthesized with 0.006 mol/L CTAB and annealed at 600 °C with larger particle size and exhibited stronger Eu³⁺ luminescence intensity than other samples. The correlation between particle size and luminescence properties were discussed in this chapter

3.1 Introduction

Lanthanum trifluoride LaF₃ is an ideal host material for various phosphors because this material has very low phonon energy (~350 cm⁻¹), thus the multi-phonon relaxation of the excited state of rare-earth ions doped can be minimal. The preparation and luminescence of LaF₃:Eu³⁺ nanoparticles have been reported by several authors. J.-X. Meng et al. used La(NO₃)₃, Eu(NO₃)₃ and NH₄F as reactants to synthesize LaF₃:Eu³⁺ nanoparticles. Both La(NO₃)₃ and NH₄F is dissolvable significantly in water, while LaF₃ is an insoluble salt in water, so that solid LaF₃ precipitations can easily be obtained by the reaction of La³⁺ and F⁻ ions formed by the dissociation of La(NO₃)₆H₂O and NH₄F in an aqueous solution. However, since high La³⁺ and F⁻ ions concentration in an aqueous solution resulted in significantly high reaction rates, it is difficult to control the growth of LaF₃ crystalline. In materials science on nanophosphors, it is known that the size of very fine particles greatly influenced their luminescence properties. In this section, size tuned LaF₃:Eu³⁺ nanocrystals were synthesized via a hydrothermal method by using cetyltrimethylammonium bromide (CTAB) as an additive to control the particle growth. The influences of post-annealing temperature and CTAB concentration on the particles size as well as on the photoluminescence (PL) properties were studied. Particle size effects on doped Eu ions luminescence properties were discussed. It was found that in
large particles doped Eu ions prefer to locate in high symmetric site which induced strong luminescence intensity. LaF₃:Eu³⁺ nanoparticles growth mechanism also discussed in this section.

3.2 Experiment of size tunable LaF₃:Eu³⁺ nanoparticle

LaF₃:Eu³⁺ nanoparticles were prepared by the same procedures described in experiment of LaF₃:Eu³⁺ nanoparticles section of Chapter 2. In order to get particles with different size, CTAB concentration was changed from to 0 mol/L, 0.006 mol/L, 0.009 mol/L to 0.015 mol/L, post-annealing temperature was varied from 500 °C, 600 °C, 700 °C to 800 °C.

The crystalline data were obtained by X-ray diffractometer (XRD: Phillips X’pert system using Cu Kα; 45 kV, 40 mA). The data was collected by scanning between 2θ = 20 and 75 ° in 0.02 ° steps. Transmission electron microscopy (TEM) observation was done with a JEM-2010HR microscope (JEOL). The photoluminescence excitation (PLE) and photoluminescence (PL) spectra were obtained with F-7000 fluorescence spectrophotometer (Hitachi, co.). The photoluminescence decay curves of ⁵D₀ → ⁷F₁,₂ transitions were recorded by a time-resolved photoluminescence (TRPL) system (Oriel Instruments, InstaSpec™ V system) under the excitation by N₂ laser (USHIO, KEC-160; εₑₓ = 337.1 nm, pulse width < 1 ns). All of the experiments were carried out at room temperature.

3.3 Results and discussion

3.3.1 LaF₃:Eu³⁺ nanoparticles size analysis as the function of CTAB concentration

Figure 3-1 shows the variation of XRD pattern of samples depending on CTAB concentration. The good agreement of diffraction peak positions with the PDF Card No. 82-0684, indicates that the LaF₃:Eu³⁺ synthesized is in hexagonal structure ¹¹. From Figure 3-1, it can be found that a sample synthesized with 0.006 mol/L CTAB has the higher and sharper peaks than those with other CTAB concentrations. Particle size of the sample were estimated by applying the Scherrer formula to the full width at half maximum (FWHM) of the (111) diffraction peak. The calculated particle sizes indicated
in Figure 3-2 shows, it reaches to maximum value when 0.006 mol/L CTAB is used. The largest LaF$_3$:Eu$^{3+}$ particles were obtained with 0.006 mol/L CTAB concentration.

Figure 3-1 X-ray diffraction patterns of LaF$_3$:Eu$^{3+}$ nanocrystals synthesized with different CTAB concentrations. All the samples were heated at 600 °C.

Figure 3-2 Crystallite size of LaF$_3$:Eu$^{3+}$ nanoparticles synthesized with different CTAB concentrations, calculated with Scherrer's equation.
3.3.2 LaF$_3$:Eu$^{3+}$ nanoparticle size analysis as the function of annealing temperature

Figure 3-3 shows the variation of XRD pattern of samples depending on the annealing temperature. The diffractive peak positions also are in good agreement with the PDF Card No. 82-0684. From Figure 3-3 it can be found that a sample heated at 600 °C exhibited the higher and sharper peaks. When heated at 800 °C a small tiny peak near the (111) peak could be found. The small tiny peak was the (101) diffractive peak of LaOF (PDF Card No. 86-2377) phase. This is thought to result from partial oxidation of the LaF$_3$ nanoparticles, which is due to oxygen residues in the products. So the sample synthesized with 0.006 mol/L CTAB and heated at 600 °C has the good crystalline structure.

Figure 3-4 shows the crystallite size of the nanoparticles heated at different temperatures. The crystallite size was increased with increasing calcination temperatures up to 600 °C and once decreased down at 700 °C. However, at higher temperature the size was again increased. The crystallite size of the sample heated at 600 °C was calculated as 25.4 nm and for the sample heated at 800 °C was 32.6 nm.

![Figure 3-3 X-ray diffraction patterns of LaF$_3$:Eu$^{3+}$ nanocrystals heated at different temperatures. All the samples were synthesized with 0.006 mol/L CTAB.](image-url)
3.3.3 Particle growth mechanism

CTAB is a kind of cationic surfactants consisting of a polar hydrophilic head group and a non-polar hydrophobic tail as shown in Figure 3-5. The synthesis scheme of LaF₃:Eu³⁺ nanocrystals with aid of CTAB molecules is shown in Figure 3-6. When the concentration of CTAB was more than critical micelle concentration (CMC), corresponding to be about 0.006 mol/L in this experiment, a micelle structure begins to be formed where the size and morphology of CTAB micelle are influenced by CTAB concentration pH and salts. On the other hand, a lot of LaF₃:Eu³⁺ nucleus seeds were at first produced after the addition of NaF into the mixture of La³⁺/Eu³⁺ aqueous solution (see 3.2) and adsorbed by the hydrophobic tail of CTAB and finally located inside CTAB micelle. These LaF₃:Eu³⁺ nucleus seed can be served as nucleation centers, which was allowed to grow into LaF₃:Eu³⁺ single crystal (explained below) with an appropriate size in the hydrothermal process in autoclave. On the contrary, when the CTAB concentration is more than CMC, the number of CTAB micelles increases with the diameter of CTAB micelle decreased. And then the average number of LaF₃ nucleus seeds situated in a CTAB micelle will be decreased. Less nucleus seeds served as nucleation centers in a
CTAB micelle do not permit LaF$_3$:Eu$^{3+}$ to grow into a larger particle. This is why as the CTAB concentration increased the particle size was decreased.

![CTAB molecule configuration](image)

Figure 3-5 CTAB molecule configuration.

![Synthesis scheme of LaF$_3$:Eu$^{3+}$ nanocrystals in CTAB micelles](image)

Figure 3-6 Synthesis scheme of LaF$_3$:Eu$^{3+}$ nanocrystals in CTAB micelles.

3.3.4 TEM images and Selected Area Electron Diffraction (SAED) pattern of LaF$_3$:Eu$^{3+}$ synthesized with 0.006 mol/L CTAB concentration

Figure 3-7 shows TEM image of LaF$_3$:Eu$^{3+}$ nanocrystals synthesized with 0.006 mol/L CTAB and heated at 600 °C. The photograph shows that particle diameter was in the range of 20-30 nm and dispersed well. It is well corresponding to the value calculated by Scherrer formula from the XRD data.
The inset is selected area electron diffraction (SAED) pattern of LaF$_3$:Eu$^{3+}$ nanocrystal, indicating that it had a single crystal structure with hexagonal symmetry.

![SAED pattern](image)

Figure 3-7 TEM image and selected area electron diffraction pattern of sample synthesized with 0.006 mol/L CTAB and annealing at 600 °C.

3.3.5 Size distribution analysis of LaF$_3$:Eu$^{3+}$ particles synthesized with 0.006 mol/L CTAB

From TEM image shown in Figure 3-7, we analyzed size-distribution of LaF$_3$:Eu$^{3+}$ nanocrystals (Figure 3-8). It was found that the sample had a narrow size distribution and ~81% particles within the diameter range of 20~30 nm. It is well corresponding to the value calculated by Scherrer formula from the XRD data.
3.3.6 Photoluminescence spectra

Room-temperature photoluminescence spectra of samples synthesized with different CTAB concentration and annealing at different temperature are presented in Figure 3-9 and Figure 3-10, respectively. The luminescence lines are assigned according to Carnell’s paper\(^\text{15}\). The dominating emission at 592 nm corresponds to the \(5D_0 \rightarrow 7F_1\) magnetic dipole transition. The peak at 619 nm can be ascribed to \(5D_0 \rightarrow 7F_2\) electric dipole transition. Because of very low phonon energy of LaF\(_3\) crystal, luminescence form higher excited state of \(5D_1\) was also observed (See the region from 500 to 700 nm in). When the Eu\(^{3+}\) ion located in a La\(^{3+}\) site with C\(_2\) symmetry the electric and magnetic dipoles are allowed. Therefore, both the \(5D_0 \rightarrow 7F_1\) and the \(5D_0 \rightarrow 7F_2\) transitions of Eu\(^{3+}\) can be observed in LaF\(_3\):Eu\(^{3+}\) nanocrystals, this is also the reason why LaF\(_3\) was selected as host in this study. The strongest Eu\(^{3+}\) luminescence was \(5D_0-7F_1\) transition because of the site symmetry of La\(^{3+}\) in LaF\(_3\) lattice. Figure 3-9 clearly shows that the sample synthesized with 0.006 mol/L CTAB exhibited about 1.5 times higher \(5D_0-7F_1\) luminescence than without CTAB. On the other hand, for more CTAB concentration, the Eu\(^{3+}\) luminescence was monotonically decreased with increasing CTAB concentration. Figure 3-10 shows that heating at 600 °C increases PL intensity of LaF\(_3\):Eu\(^{3+}\) nanocrystals about twice.
Figure 3-9 PL spectra of LaF₃:Eu³⁺ nanocrystals with different CTAB concentrations (λ_ex = 397 nm). The all samples were annealed at 600 °C.

Figure 3-10 PL spectra of samples heated at different temperatures (λ_ex = 397 nm). The all samples were synthesized with 0.006 mol/L CTAB.
3.3.7 Correlation between particle size and luminescence intensity

As discussed above, the particle size was increased with increasing calcination temperature up to 600 °C, and once decreased down at 700 °C and then increased again. LaF$_3$:Eu$^{3+}$ nucleus grew into large particles (about 25 nm) by a help of CTAB micelle structure at 0.006 mol/L CTAB concentration, but LaF$_3$:Eu$^{3+}$ particle size was decreased by more increase of CTAB concentration. Figure 3-11 shows the LaF$_3$:Eu$^{3+}$ luminescence intensity as the function of particle size. It was found that Eu$^{3+}$ ions luminescence intensity was increased with the particle size except for the sample annealed at 800 °C. At 800 °C the particle size is largest however partial oxidations of the LaF$_3$ nanoparticles occurred and surface defects on LaF$_3$:Eu$^{3+}$ nanoparticles were produced. So it was confirmed that the large particle exhibited strong luminescence intensity regardless of CTAB concentration and annealing temperature if the oxidation did not occur.

![Figure 3-11](image-url)  
Figure 3-11 Intensity of the 592 nm emission of LaF$_3$:Eu$^{3+}$ nanocrystals as a function of particle size.
3.3.8 Decay curves of samples synthesized with different CTAB concentration

$^5\text{D}_0$ and $^5\text{D}_0$ Luminescence decay curves of Eu in samples synthesized with different CTAB concentrations were shown in Figure 3-12 and Figure 3-13 respectively. Black lines are fitting results of decay curves. The initial decay rates ($\tau_{\text{int}}$) are determined within 1.5 ms of the decay curves, as displayed in Table 3-1. The sample synthesized with 0.006 mol/L CTAB has a long lifetime for $^5\text{D}_0$ level, it means that Eu$^{3+}$ ions are well dispersed with high symmetric site in the nanocrystals synthesized with 0.006 mol/L CTAB and heated at 600 °C. This eventually leads to the stronger luminescence.

![Graph](image)

Figure 3-12 Variation of $^5\text{D}_0$→$^7\text{F}_1$ photoluminescence decay curves of Eu$^{3+}$ fluorescence of samples depending on the CTAB concentration. The excitation and monitoring wavelength are 337.1 nm and 592 nm, respectively.
Figure 3-13 Variation of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ photoluminescence decay curves of Eu$^{3+}$ fluorescence depending on CTAB concentration. The excitation and monitoring wavelength are 337.1 nm and 619 nm, respectively.

Table 3-1 Initial decay times $\tau_{\text{init}}$ of $^5\text{D}_0 \rightarrow ^7\text{F}_j (j = 1, 2)$ emission for LaF$_3$:Eu$^{3+}$ nanocrystals synthesized with different CTAB concentrations.

<table>
<thead>
<tr>
<th>CTAB concentration</th>
<th>$^5\text{D}_{0-1}$ (at 592 nm)</th>
<th>$^5\text{D}_{0-2}$ (at 619 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 mol/L</td>
<td>1.26 ms</td>
<td>0.70 ms</td>
</tr>
<tr>
<td>0.006 mol/L</td>
<td>10.8 ms</td>
<td>2.60 ms</td>
</tr>
<tr>
<td>0.009 mol/L</td>
<td>1.54 ms</td>
<td>1.22 ms</td>
</tr>
<tr>
<td>0.015 mol/L</td>
<td>1.73 ms</td>
<td>1.43 ms</td>
</tr>
</tbody>
</table>

3.3.9 Estimation of Eu ion fraction in high symmetric site

In Chapter 2, a new method to analyze Eu ion location in host matrix was introduced. According to this method possible positions of Eu$^{3+}$ ions located in LaF$_3$ matrix could be estimated from decay curve fitting results. The same methodology is applied and the estimations are summarized in Table 3-2. The fractional number of Eu$^{3+}$ ions in higher symmetric site-substitution site in LaF$_3$ lattice matrix is
obviously affected by CTAB concentration. After CTAB concentration reaches to 0.006 mol/L, it gets the maximum value of about 95%, and then decreases quickly with increasing CTAB concentration. This is because when the concentration of CTAB is more than critical micelle concentration (CMC), corresponding to about 0.006 mol/L in this experiment, a micelle structure begins to be formed, micelle helps synthesize large and well dispersed crystals. Figure 3-14 shows that with an increasing of CTAB concentration, Eu fraction in high symmetric site variation shows the same tendency as particle size. In the other word, large particle has the large Eu fraction in a high symmetric site. As shown in Figure 3-15, the fact that Eu luminescence intensity increased as surface/volume ratio decreased allows us to conclude that Eu ions distorted site is in the surface-state site, and thus the decreasing particle size must reduce the Eu$^{3+}$ luminescence since surface/volume ratio ( $\propto 1/D$ ) is increased and surface defects more greatly exhaust excitation energy of Eu$^{3+}$ ions doped in LaF$_3$ nanocrystals. In Chapter 2, it was mentioned that $^5D_0 \rightarrow ^7F_2$ emission decay curves was fitted by three exponential function, decay lifetime of the two fast components of $^5D_0 \rightarrow ^7F_2$ emission are 0.184 ms and 1.12 ms, so much short lifetimes are also confirmed that Eu ions distorted site is must be a surface-state site or a position close to particles surface. The sample synthesized with 0.006 mol/L CTAB and annealing at 600 °C has the smallest surface/volume (1/D=0.04 nm$^{-1}$) indicated that Eu faction located in surface-state site is small, Large particles have a low volume/surface ratio and lead to a low density of defects, resulting in the larger fractional number of Eu$^{3+}$ ions in substitution sites of LaF$_3$ matrix. The sample synthesized with 0.006 mol/L CTAB and annealing at 600 °C has the largest particles and about 95% of Eu$^{3+}$ ions could be positioned in the high symmetric site, which engaged in the strong luminescence intensity and long lifetime.
Table 3-2 Eu fraction in high symmetric site of LaF₃:Eu³⁺ nanoparticles synthesized with different CTAB concentration

<table>
<thead>
<tr>
<th>CTAB concentration (mol/L)</th>
<th>Fraction in high symmetric site (%)</th>
<th>Concentration in high symmetric (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>88.1</td>
<td>4.41</td>
</tr>
<tr>
<td>0.006</td>
<td>94.6</td>
<td>4.73</td>
</tr>
<tr>
<td>0.009</td>
<td>84.1</td>
<td>4.21</td>
</tr>
<tr>
<td>0.015</td>
<td>73.0</td>
<td>3.65</td>
</tr>
</tbody>
</table>

Figure 3-14 Eu fraction in high symmetric site and particle size of LaF₃:Eu³⁺ nanoparticles synthesized with different CTAB concentration.
On the basis of the XRD patterns, the crystal structures of the prepared samples were refined by the Rietveld refinement using the software program RIETAN-FP (Izumi and Ikeda, 2000)\(^\text{16}\). For fitting, space groups of LaF\(_3\) \(P\overline{3}c1\) (No. 165) were used\(^\text{17}\). The fitting result of sample synthesized with 0.006 mol/L CTAB is shown in Figure 3-16. The solid line and dots are the Rietveld fitting and observed XRD patterns, respectively. The fitted lattice parameters of LaF\(_3\):Eu\(^{3+}\) samples and commercial LaF\(_3\) and the difference between them were listed in Table 3-3. Comparing the Rietveld refinement results of commercial LaF\(_3\) and Eu\(^{3+}\)-doped samples, the lattice parameters of Eu\(^{3+}\)-doped samples are slightly smaller than those of Eu free sample. The lattice parameters of sample synthesized with 0.006 mol/L CTAB were the smallest, and the differences from Eu free sample are the largest.

3.3.10 XRD Rietveld refinement result of LaF\(_3\):Eu\(^{3+}\) synthesized with different CTAB concentration

![Graph showing the relationship between 5D\(_0\)−7F\(_1\) emission intensity and 1/D (≈ surface/volume ratio)](image.png)

Figure 3-15  \(5D_0−7F_1\) emission intensity as a function of reciprocal crystalline size (1/D), proportional to surface/volume ratio of LaF\(_3\):Eu\(^{3+}\) nanocrystals.

- 45 -
Figure 3-16 Rietveld fitting profiles for Eu free and LaF<sub>3</sub>:Eu<sup>3+</sup> nanoparticles. Solid line and dots represent the calculated and measured profiles, respectively. The residual intensities are shown at the bottom of figure (jagged line), stick marks below the profile indicated the positions of the Bragg reflections.

Table 3-3 Lattice parameters of Eu free and LaF<sub>3</sub>:Eu<sup>3+</sup> nanoparticles and the difference between them.

<table>
<thead>
<tr>
<th>Lattice Parameter (nm)</th>
<th>LaF&lt;sub&gt;3&lt;/sub&gt;:Eu&lt;sup&gt;3+&lt;/sup&gt; hexagonal</th>
<th>LaF&lt;sub&gt;3&lt;/sub&gt; hexagonal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CTAB 0.006 mol/L</td>
<td>CTAB 0.009 mol/L</td>
</tr>
<tr>
<td>(a=b)</td>
<td>0.718035 ± 0.000017</td>
<td>0.717966 ± 0.000014</td>
</tr>
<tr>
<td>(\Delta a=\Delta b)</td>
<td>(0.15%)</td>
<td>(0.17%)</td>
</tr>
<tr>
<td>(c)</td>
<td>0.734565 ± 0.0000011</td>
<td>0.734473 ± 0.000009</td>
</tr>
<tr>
<td>(\Delta c)</td>
<td>(0.1578%)</td>
<td>(0.17%)</td>
</tr>
</tbody>
</table>
Table 3-4 Summary of Eu concentration analysis in LaF₃: Eu³⁺ lattice matrix

<table>
<thead>
<tr>
<th>Lattice Parameter (nm)</th>
<th>CTAB Free</th>
<th>CTAB 0.006 mol/L</th>
<th>CTAB 0.009 mol/L</th>
<th>CTAB 0.015 mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δa=Δb</td>
<td>0.0011</td>
<td>0.0012</td>
<td>0.0011</td>
<td>0.0009</td>
</tr>
<tr>
<td>Δc</td>
<td>0.0012</td>
<td>0.0013</td>
<td>0.0012</td>
<td>0.0010</td>
</tr>
<tr>
<td>(Δa+Δc)/2</td>
<td>0.00115</td>
<td>0.00125</td>
<td>0.00115</td>
<td>0.00095</td>
</tr>
<tr>
<td>χ</td>
<td>0.0424</td>
<td>0.0461</td>
<td>0.0424</td>
<td>0.0350</td>
</tr>
</tbody>
</table>

Taking account of the linear relation between the lattice parameters and the lanthanide ion radius, an expected Eu ions concentration doped in LaF₃ lattice matrix can be calculated using the following function

\[
\chi = \frac{\Delta(d_{LaF_3} - d_{LaF_3:Eu})}{\Delta(d_{LaF_3} - d_{EuF_3})}
\]  

Eq.(3-1)

where \( d_{LaF_3:Eu} \): lattice constant of LaF₃:Eu
\( d_{LaF_3} \): lattice constant of LaF₃
\( d_{EuF_3} \): lattice constant of EuF₃ (\( a=b=0.692 \) nm, \( c=0.7086 \) nm)(JCPDS: 32-0373)
\( \chi \): Eu concentration in LaF₃:Eu³⁺.

The calculated results were listed in Table 3-4. Lattice constant of LaF₃ (\( a=b=0.7192 \) nm, \( c=0.7357 \) nm) obtained by Rietveld fitting in this study were used. The Eu concentration doped in LaF₃:Eu³⁺ lattice matrix for samples synthesized without CTAB, with 0.006 mol/L CTAB, 0.009 mol/L CTAB and 0.015 mol/L CTAB are 4.24 mol%, 4.61 mol%, 4.24 mol% and 3.50 mol%, respectively. So the concentration of Eu ions replacing La ions in LaF₃:Eu³⁺ is the highest in the sample synthesized with 0.006 mol/L CTAB among synthesized samples, which is well consisted with the analysis result of \( ^{5}D_{0}-^{7}F_{1,2} \) decay curves.
3.4 Conclusion

In this chapter, size tuned LaF₃:Eu³⁺ nanocrystals in hexagonal phase have been synthesized by a hydrothermal method with CTAB as a size-controlling agent. The measurements of photoluminescence and X-ray diffraction evidenced successful doping of Eu³⁺ ions in LaF₃ nanocrystals. The size plays important roles on the luminescence intensity. By XRD Rietveld refinement and the decay curve analysis, the luminescence intensity shows the same tendency as that of particle size. In large particles Eu³⁺ ions preferred to locate high symmetric site (substitution-state site), low ratio of surface/volume in large particles and low defects density inside particle induced strong luminescence intensity from doped Eu ions. When synthesized with 0.006 mol/L CTAB and heated at 600 °C LaF₃:Eu³⁺ nanocrystals reached to the largest size and exhibited the strongest luminescence among synthesized samples, which could be explained by well-dispersion of Eu³⁺ ions in a higher symmetric site in a trigonal prism without Eu³⁺ clustering accompanying with concentration quenching. It was found that the 94.6 % of Eu³⁺ ions were positioned in higher symmetric sites in a trigonal prism in LaF₃ lattice and engaged in this strong photoluminescence.
3.5 References


Chapter 4.  Effect of matrix GdF₃ polytype on luminescence properties of doped Eu ion

In this chapter, it is shown that GdF₃:Eu³⁺ nanophosphors with hexagonal or orthorhombic structure have been succeeded to be selectively synthesized at room temperature for the first time via a simple soft chemical route. The structure and morphology of GdF₃:Eu³⁺ nanophosphors were controlled by using different fluoride precursors. Hexagonal GdF₃:Eu³⁺ nanocrystals were formed when NaBF₄ was used as a fluoride precursor, while orthorhombic GdF₃:Eu³⁺ nanocrystals were obtained with NaF or NH₄F fluoride precursor. It was also experimentally revealed that hexagonal GdF₃:Eu³⁺ nanophosphors emitted essentially stronger Eu³⁺ luminescence than orthorhombic ones. The formation mechanism of GdF₃ nanocrystals and how the polytype structure influenced the luminescence properties were discussed.

4.1 Introduction

The lanthanide fluoride compounds LnF₃ and ALnF₄ (A = alkali metal, Ln = rare-earth element) have been widely used in many fields, such as optical telecommunication, lasers, new optoelectronic devices, diagnostics, and biological labels. The polytype engineering of these materials has recently attracted attention. In fact, polytype NaYF₄ (or NaGdF₄) with hexagonal and cubic structures have been well documented. However, studies of polytype LnF₃, including GdF₃, with hexagonal and orthorhombic structures are very few, most of which were focused on the phase transition mechanism at high temperatures. Recently, stronger luminescence from Eu³⁺ in hexagonal EuF₃ than in orthorhombic EuF₃ has been reported. This suggests that the polytype control of matrix LnF₃ makes it possible to increase the light-emitting probability of rare-earth-doped LnF₃ by the changing of atomic coordination around the doped rare earth.
4.2  Experiment of polytype GdF₃:Eu³⁺

All reagents were obtained from Aldrich Chem. Co. and used as received without further purification. Typical procedures for the synthesis of GdF₃:Eu³⁺ nanocrystals are described as follows (see in Figure 4-1). First, 0.005 mol of Gd(NO₃)₃·6H₂O and 0.00025 mol of EuCl₃·6H₂O were dissolved in 100 ml of deionized water in a beaker at room temperature. After mechanical stirring for about 20 min, an aqueous solution of 0.015 mol of NaBF₄ (sample A), 0.015 mol of NH₄F (sample B) and 0.015 mol of NaF (for sample C) was added dropwise. After constant stirring for 12 h at room temperature, a white precipitate was formed. Each precipitate was collected by three cycles of centrifugation and successive washing with water and ethanol. Subsequently, the final product was dried in an oven at 80 °C. The nominal Eu³⁺ concentration was fixed at 5 mol%. To study the change in the lattice parameter upon adding Eu³⁺ to GdF₃, Eu-free GdF₃ polytype samples were also prepared by the same method. The Eu-free samples A and B are denoted as A⁰ and B⁰, respectively.

XRD analysis was performed on a Philips X’pert system using Cu Kα radiation at a 45 kV voltage and a 40 mA current. The morphology, size and Eu³⁺ concentration of the products were examined by a scanning electron microscopy of HITACHI S-4500 microscope equipped with EDX (EMAX-7000). The structural characteristics of the samples were further examined with a transmission electron microscope (JEOL, JEM-4000FX) using an accelerating voltage of 400 kV. The excitation and PL spectra were obtained using a F-7000 fluorescence spectrophotometer (Hitachi Co.). The PL decay curves of ⁵D₀ → ⁷F₁,₂ transitions were recorded using a time-resolved fluorescence system (Oriel Instruments: InstaSpec™ V) under excitation with a 337.1 nm N₂ laser (Usho, KEC-200).
4.3 Results and discussion

4.3.1 XRD pattern of Polytype GdF$_3$:Eu$^{3+}$ nanoparticles

Figure 4-2 shows the X-ray powder diffraction patterns of samples A, B and C. The XRD pattern of sample B is similar to that of sample C, these two patterns can be readily identified orthorhombic GdF$_3$ (PDF No.12-0788). It can be found that a (020) peak of sample B is sharper than that of sample C so that sample B seems to have better crystalinity. On the other hand, the XRD pattern of sample A clearly differs from those of B and C. Since the XRD data for the hexagonal GdF$_3$ have not been
reported, this phase is compared with hexagonal SmF$_3$ (PDF No. 05-0563) and all the diffraction peaks in Figure 4-2 (A) can be indexed to the hexagonal structure.

![XRD pattern](image)

Figure 4-2 XRD patterns of the sample A, B and C synthesized with NaBF$_4$, NH$_4$F and NaF, respectively.

4.3.2 SEM and TEM images of polytype GdF$_3$:Eu$^{3+}$ particles

Figure 4-3 shows SEM, TEM images and Selected Area Electron Diffraction (SAED) pattern of sample A. SEM image (a) shows that the particles have "disc"-like morphology with size about 0.9-1.5 µm in diameter. TEM image (b) elucidates the unique morphology same as SEM image. From the magnified TEM image (inset), it can be seen that this round shape is brought by aggregate of "plate"-like clusters. The SAED pattern (c) indicates that there are two kinds of clusters in disc-like particles. The lattice constant of one kind of clusters was $a=b=0.5926$ nm, and that of the other kind of clusters was $a=b=0.6928$ nm. It should be noted in spite of the difference of lattice constant, both clusters were hexagonal and each other kept epitaxial relationship.
Images of SEM and TEM of sample B and C are obtained and shown in Figure 4-4. For sample B, SEM image (a) and TEM image (b) shows that the particles exhibited a round shape with a hole in it and the particle size was about 0.8-1.2 μm in diameter, estimated from the magnified TEM image (inset b). It can be clearly seen that this round shape is formed due to clustered “hair”-like nanoparticles. The SEM image (c) and TEM image (d) of sample C shows “spindle”-like morphology with dimensions of 300-400 nm in length and 60-100 nm in width. SAED pattern of sample C is shown in Figure 4-5, which indicates that spindle-like clusters were orthorhombic and almost aligned like a single crystal, but it contained slightly tilted ones toward [011].
Figure 4-4 SEM image (a), TEM image (b) and SAED pattern (c) of sample B (Inset shows the magnified TEM image (b). TEM image of sample C (d).

Figure 4-5 SAED pattern of sample C with orthorhombic structure.
4.3.3 Fluorite precursors effect on GdF$_3$ polytype structure

Crystal structure and morphology of GdF$_3$:Eu$^{3+}$ nanoparticles depended on the fluoride source, even though the synthetic conditions were identical except for the fluoride sources. Recent investigations also demonstrated the formation of hexagonal and orthorhombic GdF$_3$ nanocrystals, and however these nanocrystals were synthesized at higher temperatures (>300 °C)$^{19,20,21,22}$. Our method is very simple and employed at room temperature, where it is demonstrated that different fluoride sources have the strong impacts not only on morphologies but also on crystal structures of GdF$_3$ nanocrystals.

Here, we emphasized the crucial effect of NaBF$_4$ on the crystalline phases of the products in our current synthesis. In the case of NH$_4$F and NaF, a white precipitate appeared immediately after the gadolinium nitrate solution was mixed with sodium or ammonium fluoride, which indicated that the nucleation had taken place rapidly. On the other hand, the initial solution was kept clear and transparent when NaBF$_4$ was added as a fluoride source, suggesting that no fluoride precipitation was formed. The white precipitate was formed after stirring for 20 min. The probable reaction processes for the formation of GdF$_3$ can be summarized as follows:

\[
\begin{align*}
\text{BF}_4^- + 3\text{H}_2\text{O} & \rightleftharpoons 3\text{HF} + \text{F}^- + \text{H}_3\text{BO}_3 \quad \text{Eq.}(4-1) \\
2\text{H}_3\text{BO}_3 + 2\text{Na}^+ & \rightarrow \text{Na}_2\text{B}_2\text{O}_4 + 2\text{H}_2\text{O} + 2\text{H}^+ \quad \text{Eq.}(4-2) \\
\text{Gd}^{3+} + 3\text{F}^- & \rightarrow \text{GdF}_3 \quad \text{Eq.}(4-3)
\end{align*}
\]

In an aqueous solution, NaBF$_4$ was slowly hydrolyzed to produce BO$_3^{3-}$ and F$^-$ anions, as shown in Eq.(4-1) as the equilibrium constant of the hydrolysis reaction was very small ($K_\theta = 6.41 \times 10^{-12}$ at 25 °C)$^{23}$, the concentration of F$^-$ anions in the reaction solution was kept at a low level$^{24,25}$, from the view of the reaction equilibrium, and so the low F$^-$ concentration is brought in an acidic environment. Furthermore, the composition analysis of the clear solution after centrifugation demonstrated the formation of H$_3$BO$_3$ and Na$_2$B$_2$O$_4$ (Eq.(4-2)). The pH value of the aqueous solution was approximately equal to 6.0 at the beginning of the reaction, and when the reaction was complete the pH value decreased to 1.5. Finally, Gd$^{3+}$ ions were reacted with F$^-$ anions produced during the slow hydrolysis of NaBF$_4$, so as to form GdF$_3$ nuclei, as presented in Eq.(4-3). Because of the very low production rate of F$^-$ anions in solution, the particle growth of the precipitated GdF$_3$ solid was very slow. Additionally, the
hexagonal-structure could be stabilized if the fluorine anions were deficient, so the deficiency of F\(^-\) anions due to the low F\(^-\) concentration in solution might help synthesize hexagonal structure.

4.3.4 PLE spectra of polytype GdF\(_3\):Eu\(^{3+}\)

PLE spectra of 592 nm light emission from polytype GdF\(_3\):Eu\(^{3+}\) samples are shown in Figure 4-6. The excitation spectra of the \(^5\)D\(_0\) red emission indicate that the sharp peak located at 274 nm corresponds to excitation into \(^6\)I\(_{7/2}\) (\(J' = 7/2\) - \(17/2\)) \(\left(^8\text{S}_{7/2} \rightarrow ^6\text{I}_{7/2}\right)\) levels of Gd\(^{3+}\), and the peak located at 396 nm corresponds to the \(^7\)F\(_0\) - \(^5\)L\(_6\) direct excitation of Eu\(^{3+}\). The short wavelength excitation confirms the occurrence of energy transfers from \(^6\)I\(_{7/2}\), (\(J' = 7/2\) - \(17/2\)) level of Gd\(^{3+}\) to Eu\(^{3+}\). The 4f energy level overlap between the \(^6\)P\(_J\) states of Gd\(^{3+}\) and the \(^5\)H\(_J\) states of Eu\(^{3+}\) allows energy transfer from Gd\(^{3+}\) to Eu\(^{3+}\) and thus energy transfer route from Gd\(^{3+}\) to Eu\(^{3+}\) can be explained as follows: Gd\(^{3+}\) ions are first excited to \(^6\)I\(_{J}\), (\(J' = 7/2\) - \(17/2\)) energy level and through nonradiative relaxation decay to \(^6\)P\(_J\) states, and then from this level transfer its excitation energy to Eu\(^{3+}\) ion, resulting in the emission of visible photons due to the Eu\(^{3+}\): \(^5\)D\(_0\) - \(^7\)F\(_J\) transition.

![Figure 4-6 Photoluminescence excitation spectra of the Eu\(^{3+}\) doped in polytype GdF\(_3\) nanocrystals ((A) hexagonal, (B) and (C) orthorhombic).](image-url)
4.3.5 PL spectra of polytype GdF$_3$:Eu$^{3+}$

Room-temperature PL spectra of sample A, B and C excited at 274 nm and the spectra of sample A (hexagonal) and sample B (orthorhombic) excited at 396 nm and 274 nm are presented in Figure 4-7 and Figure 4-8, respectively. The luminescence bands are assigned according to Carnalls' paper 28. In both emission spectra has shown two intense bands associated with $^5$D$_0 \rightarrow ^7$F$_1$ and $^5$D$_0 \rightarrow ^7$F$_2$ transitions for Eu$^{3+}$. The peak centered at 592 nm corresponds to the $^5$D$_0 \rightarrow ^7$F$_1$ magnetic dipole transition, and the peak centered at 619 nm corresponds to the $^5$D$_0 \rightarrow ^7$F$_2$ electric dipole transition. The little peaks located at 525 nm, 530 nm and 554 nm were corresponding to the $^5$D$_1 \rightarrow ^7$F$_1$ transitions 15. The intensity of the 592 nm PL from hexagonal sample A was much larger than that of orthorhombic samples of B and C. As the excitation of 274 nm corresponds to the transition $^8$S$_{7/2} \rightarrow ^6$I$_1$ of Gd$^{3+}$, and 396 nm excitation corresponds to the transition $^7$F$_0 \rightarrow ^5$L$_6$ of Eu$^{3+}$ ions (see in Figure 4-8), it can be concluded that both the energy transfer from Gd$^{3+}$ to Eu$^{3+}$ and the intratransition in Eu$^{3+}$ can excite PL (592 nm and 619 nm). Hexagonal GdF$_3$:Eu$^{3+}$ emitted a stronger luminescence than orthorhombic GdF$_3$:Eu$^{3+}$ under both excitation wavelengths. More remarkably, the luminescence intensity of the nanocrystals excited at 274 nm is in both cases stronger than that of the nanocrystals excited at 396 nm. The intensity ratio of the 592 nm emission peaks under different excitation at 274 nm and 396 nm was estimated to be 5.5 for the hexagonal structure. Similarly, the ratio of the 592 nm emission intensity at 274 nm and 396 nm excitation was estimated to be 2.6 for the orthorhombic structure. Therefore, the energy transfer probability from the Gd$^{3+}$ ion to the Eu$^{3+}$ ion in the hexagonal structure is higher than that in the orthorhombic structure if we assume that the absorption cross sections of the transition $^7$F$_0 \rightarrow ^5$L$_6$ in Eu$^{3+}$ ions are the same.
Figure 4-7 Photoluminescence spectra of Eu$^{3+}$ ions doped in polytype GdF$_3$ nanocrystals ((A) hexagonal, (B) and (C) orthorhombic).

![Photoluminescence spectra](image)

Figure 4-8 Emission spectra of hexagonal (upper) and orthorhombic (lower) GdF$_3$:Eu$^{3+}$ nanophosphors excited at 274 nm and 396 nm.
4.3.6 Eu concentration analysis by EDX spectra

EDX spectra of the samples studied were shown in Figure 4-9. Peaks located at about 5.845 keV and 6.056 keV were assigned to the Eu L\textsubscript{α1} and Gd L\textsubscript{α1}, respectively. The spectra indicated that Eu concentrations in GdF\textsubscript{3}:Eu\textsuperscript{3+} were independent on the fluoride sources and a bit decreased from the nominal value (5 mol\%) to 4.2-4.4 mol\%. In was found that the obtained GdF\textsubscript{3}:Eu\textsuperscript{3+} nanophosphors had the almost same Eu\textsuperscript{3+} concentration. Therefore it can be concluded that the stronger PL intensity of hexagonal sample A than these of orthorhombic sample B and C would be caused by the polytype host GdF\textsubscript{3}. In EDX spectra (not shown here), no peaks from Na and N elements can be found so that Na and N elements concentration in particles are too low to be detected. Thus, NaGdF\textsubscript{4} and NH\textsubscript{4}GdF\textsubscript{4} have not be produced during the synthesis, and even if they exist, they are so little and can be ignored. It can also be found that hexagonal GdF\textsubscript{3} nanocrystals have higher O-to-Gd (O/Gd) elemental ratio than orthorhombic GdF\textsubscript{3} nanocrystals does. As a result, O concentration is higher in hexagonal crystals than in orthorhombic crystals. So, although hexagonal GdF\textsubscript{3}:Eu\textsuperscript{3+} nanocrystals have relatively higher amount of impurities related with OH groups, they exhibited stronger luminescence intensity than orthorhombic GdF\textsubscript{3}:Eu\textsuperscript{3+} nanocrystals.

![EDX spectra](image)

Figure 4-9 EDX spectra of different samples (A, B and without Eu\textsuperscript{3+})
In order to study the polytype GdF₃:Eu³⁺ nanoparticles structure with Rietveld refinement method, fine XRD patterns of sample A (hexagonal) and B (orthorhombic) as well as the non-doped Eu samples A⁰ and B⁰ (prepared with the method with sample A and B, respectively) were detected and shown in Figure 4-10. On the basis of the XRD patterns, the crystal structures of the prepared samples were refined by the Rietveld refinement using the software program RIETAN-FP (Izumi and Ikeda, 2000). For fitting, space groups of LnF₃ Pnma (D16h, No. 62) and P3̅c1 (D43, No. 165) were used for samples A (A⁰) and B (B⁰), respectively.

![XRD patterns](image)

Figure 4-10 XRD patterns of hexagonal (upper panel) and orthorhombic (lower panel) GdF₃ nanophosphors. Upper and lower patterns in the panels are Eu doped and Eu free, respectively.

In Table 4-1, the reported and fitted lattice parameters of LnF₃ materials are listed. The lattice parameters of LnF₃ linearly decreased in the sequence of SmF₃, EuF₃, GdF₃, and TbF₃, depending on the rare-earth ion radius in the orthorhombic structure. The lattice parameters \( a, b, \) and \( c \) of orthorhombic GdF₃ in this work \( (a=0.6563 \text{ nm}, b=0.6971 \text{ nm}, \text{ and } c=0.4387 \text{ nm}) \) were slightly smaller than the reported data \( (a=0.6571 \text{ nm}, b=0.6984 \text{ nm}, \text{ and } c=0.439 \text{ nm}) \). Only the lattice parameters of hexagonal SmF₃ and EuF₃ are listed in Table 4-1, owing to the lack of data for hexagonal GdF₃ and
TbF₃ in the JCPDS (Joint Committee for Powder Diffraction Standards) database. In hexagonal LnF₃, a linear decrease in the lattice parameters with the rare-earth ion radius was also confirmed. The fitting results of samples A and B are shown in Figure 4-11. The solid line and dots are the Rietveld fitting and observed XRD patterns, respectively. Comparing the Rietveld refinement results of Eu⁺⁺⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻--;
The measured values indicated that the increases in the lattice parameters upon 4% Eu doping in hexagonal GdF$_3$ were approximately $\Delta a_0=0.16$ pm and $\Delta c_0=0.18$ pm; and those in orthorhombic GdF$_3$ were approximately $\Delta a_0=0.23$ pm, $\Delta b_0=0.26$ pm and $\Delta c_0=0.56$ pm. The good consistency of the calculated increases in the lattice parameters with the measured values indicates that most Eu ions in GdF$_3$ can substitutionally be positioned at the Gd site.

On the basis of the Reitveld refinement results, crystal structures were drawn using VEST software and are shown in Figure 4-12. In both the hexagonal and orthorhombic structures, the numbers of Gd$^{3+}$ ions around the center Gd$^{3+}$ ion are the same but the distances between Gd$^{3+}$ ions are different as listed in Table 4-2. In the hexagonal structure, there are four equivalent nearest-neighbor Gd ion sites from the center Gd ion and the distance was calculated to be 0.38553 nm. On the other hand, there are two equivalent nearest-neighbor Gd ion sites from the center Gd site in the orthorhombic structure and the distance was 0.39307 nm. According to the Förster resonance energy transfer theory, the energy transfer probability $P_{AB}$ is expressed as follows$^{31,32}$:

$$P_{AB} = 1.4 \times 10^{24} f_A f_B S / [\Delta E^2 R^6]$$

**Table 4-1 Lattice parameters of LnF$_3$**

<table>
<thead>
<tr>
<th>Lattice Parameter (nm)</th>
<th>Hexagonal</th>
<th>Orthorhombic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SmF$_3$</td>
<td>EuF$_3$</td>
</tr>
<tr>
<td></td>
<td>($P6_3/mmc$)</td>
<td>($P321$)</td>
</tr>
<tr>
<td>c=0.6952</td>
<td>0.6920</td>
<td>0.687823</td>
</tr>
<tr>
<td>c</td>
<td>0.7122</td>
<td>0.706216</td>
</tr>
</tbody>
</table>

$^*$JCPDS number
$f_A$, $f_B$: oscillator strengths of the donor and acceptor, respectively,

$S$: overlap of donor emission and acceptor absorption,

$\Delta E$: transition energy,

$R$: distance between the donor and acceptor.

The probability of energy transfer depends inversely on the sixth power of the distance between the donor and the acceptor. Therefore, the shorter distance between Gd$^{3+}$ and substituted Eu$^{3+}$ ions in the hexagonal structure can induce a higher energy transfer probability from Gd$^{3+}$ ions to Eu$^{3+}$ ions than that in the orthorhombic structure.

![Hexagonal and Orthorhombic Structures](image)

**Figure 4-12** Configuration of Gd$^{3+}$ ions in hexagonal and orthorhombic GdF$_3$:Eu$^{3+}$ structure according the Rietveld refinement results.
Table 4-2 Gdₓ→Gd₀ distance in polytype GdF₃:Eu³⁺. X denotes the ion site in Figure 4-12.

<table>
<thead>
<tr>
<th>x</th>
<th>Hexagonal Interatomic distance Gdₓ→Gd₀(nm)</th>
<th>Orthorhombic Interatomic distance Gdₓ→Gd₀(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.385532</td>
<td>0.393070</td>
</tr>
<tr>
<td>2</td>
<td>0.385532</td>
<td>0.393070</td>
</tr>
<tr>
<td>3</td>
<td>0.385532</td>
<td>0.394006</td>
</tr>
<tr>
<td>4</td>
<td>0.385532</td>
<td>0.394006</td>
</tr>
<tr>
<td>5</td>
<td>0.406382</td>
<td>0.394006</td>
</tr>
<tr>
<td>6</td>
<td>0.406382</td>
<td>0.394006</td>
</tr>
<tr>
<td>7</td>
<td>0.421907</td>
<td>0.437152</td>
</tr>
<tr>
<td>8</td>
<td>0.421907</td>
<td>0.437152</td>
</tr>
<tr>
<td>9</td>
<td>0.429091</td>
<td>0.437152</td>
</tr>
<tr>
<td>10</td>
<td>0.429091</td>
<td>0.437152</td>
</tr>
<tr>
<td>11</td>
<td>0.429091</td>
<td>0.439695</td>
</tr>
<tr>
<td>12</td>
<td>0.429091</td>
<td>0.439695</td>
</tr>
<tr>
<td>Average</td>
<td>0.40959</td>
<td>0.41585</td>
</tr>
</tbody>
</table>

4.3.8 Decay curves analysis of polytype GdF₃:Eu³⁺

Figure 4-13 shows the decay curves of ⁵D₀ → ⁷F₁,₂ emissions for polytype GdF₃:Eu³⁺ nanophosphors. Luminescence decay curves can be well fitted with a double-exponential function using the least-squares fitting method:

\[ I(t)/I₀ = α \exp(-t / τ_f) + β \exp(-t / τ_s), \]  

where \( τ_f \) is the decay time of the fast component, \( τ_s \) is the decay time of the slow component, and \( α \) and \( β \) are the amplitude ratios of the fast and slow components, respectively (\( α + β = 1 \)). The results fitted to the decay curves are summarized in Table 4-3 and Table 4-4 for hexagonal and orthorhombic GdF₃:Eu³⁺, respectively. For clarity, the average lifetimes of ⁵D₀ → ⁷F₁,₂ emissions were also calculated with Eq.(4-7) using the fitted results and are given in Table 4-5.
\[ \tau = \frac{\alpha \tau_f^2 + \beta \tau_s^2}{\alpha \tau_f + \beta \tau_s} \]

Eq.(4-8)

It is very clear that hexagonal GdF$_3$:Eu$^{3+}$ exhibits a longer lifetime than orthorhombic GdF$_3$:Eu$^{3+}$, supporting the notion that Eu$^{3+}$ ions are positioned in hexagonal systems with a higher symmetric structure.

Figure 4-13 Decay curves of $^5D_0 \rightarrow ^7F_{1,2}$ emissions (592 and 619nm) are shown by open triangles and open circles, respectively. The solid curves are fitting result to two exponential functions by a least-square fitting method. Right and left panels indicate hexagonal and orthorhombic GdF$_3$:Eu$^{3+}$ nanophosphors, respectively.
Table 4-3 Lifetimes and amplitude ratio obtained by fitting the decay curves of $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ emission for hexagonal GdF$_3$:Eu$^{3+}$ nanocrystals.

<table>
<thead>
<tr>
<th></th>
<th>$^5D_0-^7F_1$ emission</th>
<th>$^5D_0-^7F_2$ emission</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fast decay</td>
<td>slow decay</td>
</tr>
<tr>
<td>Decay time / ms</td>
<td>4.6</td>
<td>14.97</td>
</tr>
<tr>
<td>Amplitude, $\alpha, \beta$</td>
<td>0.57</td>
<td>0.43</td>
</tr>
<tr>
<td>Luminescence Intensity</td>
<td>2.62</td>
<td>6.45</td>
</tr>
<tr>
<td>Relative Contribution</td>
<td>29%</td>
<td>71%</td>
</tr>
<tr>
<td></td>
<td>0.29</td>
<td>0.71</td>
</tr>
<tr>
<td>Intensity Ratio</td>
<td>(=\eta_f)</td>
<td>(=\eta_s)</td>
</tr>
<tr>
<td></td>
<td>1.00 (=\eta_f + \eta_s)</td>
<td>0.59 *1) (=\xi_f + \xi_s)</td>
</tr>
</tbody>
</table>

Microscopic

$A_{fast} = 0.75$ *2) $\quad A_{slow} = 0.21$ *3)

$W_{0.2} \quad W_{0.2}^{dis} = 0.75W_{0.1} \quad W_{0.2}^{he} = 0.21W_{0.1}$

*1) corresponding to the apparent asymmetric ratio $A$ of 0.59 obtained from the luminescence spectrum in Figure 4-7.

*2) $A_{fast} = \xi_f / \eta_f$ ,

*3) $A_{slow} = \xi_s / \eta_s$
Table 4-4 Lifetimes and amplitude ratio obtained by fitting the decay curves of $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ emission for orthorhombic GdF$_3$:Eu$^{3+}$ nanocrystals.

<table>
<thead>
<tr>
<th></th>
<th>$^5D_0 \rightarrow ^7F_1$ emission</th>
<th>$^5D_0 \rightarrow ^7F_2$ emission</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fast decay</td>
<td>slow decay</td>
</tr>
<tr>
<td>Decay time / ms</td>
<td>1.28</td>
<td>7.06</td>
</tr>
<tr>
<td>Amplitude, $\alpha, \beta$</td>
<td>0.25</td>
<td>0.75</td>
</tr>
<tr>
<td>Luminescence Intensity</td>
<td>0.32</td>
<td>5.3</td>
</tr>
<tr>
<td>Relative Contribution</td>
<td>5.7%</td>
<td>94.3%</td>
</tr>
<tr>
<td>Intensity Ratio</td>
<td>$\eta_f$</td>
<td>$\eta_s$</td>
</tr>
<tr>
<td>1.00 ($=\eta_f + \eta_s$)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Microscopic

$A$

$W_{0.2}$

$A_{fast} = 0.53^2$ $A_{slow} = 0.48^3$

$W'_{0.2, dis} = 0.53W_{0.2}$ $W'_{0.2, ls} = 0.48W_{0.2}$

$^1$) corresponding to the apparent asymmetric ratio $A$ of 0.48 obtained from the luminescence spectrum in Figure 4-7.

$^2$) $A_{fast} = \xi_f / \eta_f$

$^3$) $A_{slow} = \xi_s / \eta_s$

Table 4-5 Average lifetimes of Eu$^{3+}$ ions $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ emission and fractional number located in higher symmetry sites in polytype GdF$_3$ nanocrystals.

<table>
<thead>
<tr>
<th></th>
<th>Average luminescence lifetime (ms)</th>
<th>Fraction of Eu$^{3+}$ occupied in symmetric site</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^5D_0 \rightarrow ^7F_1$ (592 nm)</td>
<td>$^5D_0 \rightarrow ^7F_2$ (619 nm)</td>
</tr>
<tr>
<td>Hexagonal GdF$_3$:Eu$^{3+}$ (A)</td>
<td>11.8</td>
<td>7.5</td>
</tr>
<tr>
<td>Orthorhombic GdF$_3$:Eu$^{3+}$ (B)</td>
<td>6.7</td>
<td>4.8</td>
</tr>
</tbody>
</table>

As mentioned above, the $^5D_0 \rightarrow ^7F_1$ emission peak at 592 nm from Eu$^{3+}$ indicates a magnetic dipole transition in nature, which is insensitive to the atomic coordination around Eu$^{3+}$ ions, however, the...
electric dipole transition of the $^5D_0 \rightarrow ^7F_2$ peak at 619 nm from Eu$^{3+}$ is quite sensitive to the atomic coordination. Since the atomic coordination around Eu$^{3+}$ ions or the site symmetry of Eu$^{3+}$ ions is strongly dependent on the location of Eu$^{3+}$ in the GdF$_3$ matrix, that is, interstitial, surface-state, or substitutional Eu$^{3+}$ in GdF$_3$ nanocrystals, the decay behavior owing to electric-dipole and magnetic-dipole transitions includes information on the Eu location. The observed nonexponential decay curves (see Figure 4-13), expressed by Eq. (4-7), mean that at least two sites for Eu$^{3+}$ ions exist in GdF$_3$:Eu$^{3+}$ nanocrystals for both hexagonal and orthorhombic structures. As mentioned in Chapter 2, luminescence with a short lifetime can be observed from Eu$^{3+}$ ions positioned in very asymmetric sites (e.g., surface-state and interstitial sites), whereas luminescence with a long lifetime was observed from Eu$^{3+}$ ions in a highly-symmetric site (substitutional site). Considering the crystal structures of GdF$_3$, the latter site is considered to be a crystallographic position in the substitution site of GdF$_3$ nanocrystals. As the decay lifetime of the $^5D_0 \rightarrow ^7F_2$ emissions fast component were estimated as 1.84 ms and 0.59 ms for hexagonal and orthorhombic crystals, respectively, it is longer than that in the case of LaF$_3$:Eu$^{3+}$ particles which are about 1.12 ms and 0.2 ms (See Chapter 3). By reference to the result of Chapter 3, the Eu fraction in high symmetric site as the function of reciprocal crystalline size (1/D) was shown in Figure 4-14. According to the TEM image of Figure 4-3, particle size was estimated about 80 nm for hexagonal GdF$_3$:Eu$^{3+}$ sample and the value 1/D was about 0.013 nm$^{-1}$, so it can be confirmed that Eu fraction located on the particle surface is very small. In Table 4-3 and Table 4-4, the asymmetric ratios for hexagonal GdF$_3$:Eu$^{3+}$ nanocrystals were estimated as $A_{\text{slow}}=0.21$ and $A_{\text{fast}}=0.75$, for orthorhombic GdF$_3$:Eu$^{3+}$ nanocrystals asymmetric ratio were estimated as $A_{\text{slow}}=0.48$ and $A_{\text{fast}}=0.53$. The $A_{\text{slow}}$ values in both GdF$_3$:Eu$^{3+}$ polytype nanocrystals were according well with the data estimated in LaF$_3$:Eu$^{3+}$ nanocrystals ($A_{\text{slow}}=0.25$, see Chapter 2), it means that high symmetric site in both GdF$_3$:Eu$^{3+}$ polytype structures are substitutional site. On the other hand, the $A_{\text{fast}}$ values in both GdF$_3$:Eu$^{3+}$ polytype nanocrystals are smaller than that in LaF$_3$:Eu$^{3+}$ nanocrystals ($A_{\text{fast}}=12.0$), so it can be confirmed that the disordered site in GdF$_3$:Eu$^{3+}$ polytype nanocrystals are different with that in LaF$_3$:Eu$^{3+}$ nanocrystals (surface-state site), it must be substitutional site with small displacement from the ideal position in polytype GdF$_3$:Eu$^{3+}$ lattice matrix. Since $\alpha T$ and $\beta T$ are strongly correlated with the number of Eu$^{3+}$ ions in the above-mentioned sites, the fractional numbers of Eu$^{3+}$ ions positioned in the substitution site of GdF$_3$ nanocrystals in both crystal systems can be estimated using the theory of transition probability and data obtained by decay curve analysis. The results are listed in Table 4-5. The fractional numbers
were 71% for the hexagonal structure and 69% for the orthorhombic structure. This estimation is strongly supported by the fact that from the results of Rietveld refinement, most Eu$^{3+}$ ions could substitutionally be positioned at the Gd$^{3+}$ site in hexagonal and orthorhombic GdF$_3$:Eu$^{3+}$ nanocrystals. The similarity between the dispersibility of Eu$^{3+}$ ions in the cores of hexagonal and orthorhombic GdF$_3$:Eu$^{3+}$ nanocrystals indicates that the stronger Eu$^{3+}$ luminescence of hexagonal GdF$_3$:Eu$^{3+}$ nanocrystals is a consequence of the highly symmetric hexagonal structure and the shorter interatomic distance between Gd$^{3+}$ and Eu$^{3+}$ ions and, that the polytype structure is the main factor for determining the luminescence properties of these samples.

![Graph](image)

**Figure 4-14** Eu fraction in high symmetric site as the function of reciprocal crystalline size (1/D), proportional to surface/volume ratio of LaF$_3$:Eu$^{3+}$ samples synthesized with different CTAB concentration.
4.4 Conclusion

In this Chapter, we succeeded in effectively characterizing hexagonal and orthorhombic GdF$_3$:Eu$^{3+}$ nanophosphors synthesized by the precipitation method. It was estimated by the Rietveld fitting of XRD patterns and by PL dynamics analysis that most of the doped Eu replaced Gd in both polytypes. In addition, Rietveld analysis indicated that the interatomic distance between Gd and substituted Eu in the hexagonal structure was shorter than that in the orthorhombic structure. A higher PL intensity owing to more efficient PL excitation via energy transfer from Gd$^{3+}$ to Eu$^{5+}$ in hexagonal GdF$_3$:Eu$^{3+}$ nanophosphors was demonstrated. This was explained by the energy transfer probability, taking account of the interatomic distance. The polytype control (hexagonal to orthorhombic) of matrix LnF$_3$ enabled us to enhance the energy transfer probability from Gd$^{3+}$ to Eu$^{3+}$ by varying the interatomic distance.
4.5 References


28. W. T. Carnall, P. R. Fields, K. Rajnak, “Electronic energy levels in the trivalent lanthanide aquo


30. Handbook on the Physics and Chemistry of Rare Earths; Elsevier North-Holland: Amsterdam, The


Chapter 5. Summery

In this dissertation, size tuned LaF$_3$:Eu$^{3+}$ and polytype GdF$_3$:Eu$^{3+}$ nanoparticles were prepared. The effects of their crystal structure and particle size on Eu$^{3+}$ luminescence properties were discussed. By analyzing Eu$^{3+}$ ions position in host particles, luminescence properties in relation to the particles size and polytype structure were also discussed. The results of each chapter are summarized as follows.

In Chapter 2, the new method for estimating doped Eu$^{3+}$ ions position in host particles were introduced. This method was based on Eu$^{3+}$ ions typical luminescence properties. By analyzing Eu$^{3+}$ ions $^5D_0 - ^7F_{1,2}$ decay curves with double exponential function, Eu fractions located in each symmetric and distorted site in host particles can be estimated. This method as well as Rietveld refinement method should be the usefully tools in luminescence nanomaterials studies.

In Chapter 3 size tuned LaF$_3$:Eu$^{3+}$ nanocrystals were prepared via a hydrothermal route. A cationic surfactant CTAB was used to control particle size, particle growth mechanism was also discussed. The influences of post-annealing temperature and CTAB concentration on the size and morphology as well as on the photoluminescence (PL) properties were studied. It was found that the sample synthesized with 0.006 mol% CTAB and heated at 600°C with large particle size exhibited stronger luminescence intensity than others. By estimating Eu fraction in high symmetric site using the method introduced in Chapter 2, it was found that the most of Eu$^{3+}$ ions (94.6%) were successfully incorporated in a higher symmetric site, in a LaF$_3$ lattice structure and as a result engaged in the strong PL. XRD patterns refinement analysis also showed the same result. The fraction of Eu ions located in a high symmetric site in LaF$_3$ lattice matrix was increased as particle size increased. Thus large particles induce strong luminescence.

Chapter 4 illustrated the correlation between host structure and doped Eu ions luminescence properties in polytype GdF$_3$. Hexagonal and orthorhombic GdF$_3$:Eu$^{3+}$ nanophosphors were separately synthesized via a simple soft chemical route at room temperature. The structure and morphology of GdF$_3$:Eu$^{3+}$ nanophosphors were controlled by using different fluoride precursors. Hexagonal GdF$_3$:Eu$^{3+}$
nanocrystals were formed when NaBF$_4$ was used as a fluoride precursor, while orthorhombic GdF$_3$:Eu$^{3+}$ nanocrystals were obtained with NaF or NH$_4$F fluoride precursor. Hexagonal GdF$_3$:Eu$^{3+}$ nanophosphors intrinsically exhibited stronger Eu$^{3+}$ luminescence intensity under ultraviolet excitation. The Rietveld fitting of well-defined XRD data elucidated that the inter-atomic distances between Gd$^{3+}$ ions in the hexagonal structure were shorter than those in the orthorhombic structure and that most Eu ions in GdF$_3$:Eu$^{3+}$ occupied Gd sites. The stronger luminescence in the hexagonal structure was conclusively explained by the much more efficient energy transfer from Gd to Eu in the hexagonal structure than in the orthorhombic structure, as determined on the basis of the inter-atomic distance between Gd and Eu.

In this thesis, the analysis of the correlation relationship between particle size and RE luminescence properties indicated that doping of Eu ions in large particles (in nano-size range) provide strong luminescence intensity, because the high fraction Eu ions posited substitution site in LnF$_3$ host lattice matrix and defect density is low in large particle according to the low surface/volume ratio. The correlation studies between host structure and RE luminescence properties show that short distance between donor and accepter in LnF$_3$ hexagonal structure host induced high energy transfer probability and strong luminescence intensity.

For further future research work in LnF$_3$:RE photoluminescence material field, the study suggested that LnF$_3$:RE luminescence materials can be improved by choosing the host which is in large particles and easy for RE ions to be doped in and located in substitution site so as to minimize luminescence quenching, in the host there should be an acceptor matching with the RE donor and the distance between them must short so as to maximize the energy transfer probability.
Publications Including Studies in this Dissertation

1. Photoluminescence Properties and $^5$D$_0$ Decay Analysis of LaF$_3$:Eu$^{3+}$ Nanocrystals Prepared by Using Surfactant Assist
   
   Xiaoting Zhang, Tomokatsu Hayakawa and Masayuki Nogami,
   

2. Synthesis and luminescence properties of well-dispersed LaF$_3$:Eu$^{3+}$ nanocrystals.
   
   Xiaoting Zhang, Tomokatsu Hayakawa, Masayuki Nogami, Yukari Ishikawa
   
   Journal of Ceramic Processing Research (in press)

3. Selective Synthesis and Luminescence Properties of Nanocrystalline GdF$_3$:Eu$^{3+}$ with Hexagonal and Orthorhombic Structures
   
   Xiaoting Zhang, Tomokatsu Hayakawa, Masayuki Nogami, Yukari Ishikawa
   

4. Variation in Eu$^{3+}$ Luminescence Properties of GdF$_3$:Eu$^{3+}$ Nanophosphors Depending on Matrix GdF$_3$ Polytype
   
   Xiaoting Zhang, Tomokatsu Hayakawa, Masayuki Nogami, Yukari Ishikawa
   
   Journal of Alloys and Compounds Volume 509, issue 5, February 2011, 2076-2080

5. Size-Dependence of LaF$_3$:Eu$^{3+}$ Nanocrystals on Eu$^{3+}$ Photoluminescence Intensity
   
   Xiaoting Zhang, Tomokatsu Hayakawa and Masayuki Nogami
   

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Other Publications

1. Blue light emission from Eu$^{2+}$ ions in sol–gel-derived Al$_2$O$_3$–SiO$_2$ glasses
   Yukari Kishimoto, Xiaoting Zhang, Tomokatsu Hayakawa and Masayuki Nogami

2. Optical detection of near infrared femtosecond laser-heating of Er$^{3+}$ doped Zn-Nb$_2$O$_5$-TeO$_2$
   glass by green up-conversion fluorescence of Er$^{3+}$ ions.
   M.Hayakawa, T.Hayakawa, X.T.Zhang, M.Nogami,
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