

Excited-state absorption spectra for optically forbidden f – f transitions in an $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ crystal and Eu^{3+} aqueous solution

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Extremely small transmission change spectra due to $4f$ – $4f$ transitions in a rare-earth ion Eu^{3+} in a crystal and in an aqueous solution were measured, to the best of our knowledge, for the first time. By multichannel double-lock-in pump-probe spectroscopy, photoluminescence (PL) and difference transmission spectra were simultaneously recorded for an $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ crystal with broadband lamp light sources for both the pump and the probe. A very weak transmission change signal hidden behind a 1–2 orders of magnitude more intense PL background signal was readily extracted. By comparing the transmission decrease due to the excited-state absorption (ESA) and the transmission increase due to the ground-state depletion it was found in the crystal that the oscillator strengths for the f – f transitions to the same final states are of the same order of magnitude for both the spin-allowed transitions from 5D_0 in the ESA and the spin-forbidden transitions from 7F_0 in the ground-state absorption (GSA). In addition, crystal-field split f – f transitions that have been hidden by the intense charge-transfer band in the GSA were revealed. © 2008 Optical Society of America

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1. INTRODUCTION

Excited-state absorption (ESA) due to $4f$ – $4f$ transitions in rare-earth (RE) ion doped crystals has been measured by resonant laser excitation for various REs, such as Nd^{3+} , Er^{3+} , Pr^{3+} , and Ho^{3+} [1–4]. The main interest of the ESA measurement resides in the exploitation of laser materials as well as of upconversion materials. Among RE doped solids, Eu^{3+} doped crystals, which have been important luminescent materials, have recently drawn much attention from potential applications to optical memories and quantum information devices [5–8]; $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ is especially promising because of its ultraslow optical dephasing time [9,10]. Knowledge of ESA is also useful for these applications because there is, what we believe to be, a new possibility to control quantum states through optical transitions to the higher excited states. From a theoretical point of view, Eu^{3+} is suitable for testing applicability of the Judd–Ofelt (JO) theory [11,12] by comparing ESA and ground-state absorption (GSA) since $4f$ electrons in Eu^{3+} have the same $J=0$ states for both ground (7F_0) and metastable excited (5D_0) states. In addition, Eu^{3+} doped crystals have an intense charge-transfer (CT) band above $35\,000\text{ cm}^{-1}$. It is difficult to obtain the CT absorption profile by a direct absorption measurement and weak absorption peaks because higher f – f transitions tend to be bur-

ied in the intense CT band. ESA could be a solution for these problems.

ESA cross sections for Eu^{3+} in LaF_3 and in CaF_2 were previously obtained from photoluminescence (PL) excitation spectra by double excitation with two tunable lasers [13,14], where the measurable wavelength regions are limited by the tunable ranges of available tunable lasers. From this reason, a direct pump-probe measurement is desirable with broadband white light sources as a probe, where the “direct” measurement means that the probe transmission change spectra are measured to simultaneously obtain positive ESA and negative GSA in the absorbance change spectra as described herein. There has been no pump-probe measurement for Eu^{3+} because its GSA (7F_J – $^5D_{J'}$) is spin-forbidden to have low excitation efficiency. In addition, the oscillator strength for RE in an aqueous solution is generally weaker than that in a crystal because the crystal field is nearly centrosymmetric to have a little odd parity component. In fact, there has been no report for direct pump-probe measurement of REs in an aqueous solution. Therefore the pump-probe measurement for Eu^{3+} in an aqueous solution is more difficult than for Eu^{3+} in a crystal.

In this paper, we employed highly sensitive multichannel double-lock-in spectroscopy for the pump-probe mea-

surement of ESA in Eu^{3+} . In this method, intense sharp-line lasers are not needed but broadband light sources are sufficient not only for probing but also for exciting Eu^{3+} in a crystal. ESA for an Eu^{3+} aqueous solution was also measured by resonant laser excitation for comparison with ESA in a crystal. ESA was obtained in the wide energy region of $13\,000\text{--}28\,000\text{ cm}^{-1}$, which corresponds to GSA in $30\,250\text{--}45\,250\text{ cm}^{-1}$.

2. EXPERIMENTAL

The ESA spectra were measured with the pump-probe setup shown in Fig. 1. The samples were a $5\text{ mm} \times 5\text{ mm} \times 11\text{ mm}$ Y_2SiO_5 crystal doped with 1.0 at % europium and EuCl_3 aqueous solution (1.0 M). The intensity I_p of a probe, 150 W Xe lamp (Hamamatsu, L2274), was 2.5 W/cm^2 (420–700 nm) at the sample. A 200 W Hg–Xe lamp (Hamamatsu, L2570 in L8333) and an InGaN laser diode of 395 nm (20 mW, Nichia) were used as a pump for the $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ and for the EuCl_3 aqueous solution, respectively. The intensities of the pump at the sample were 9.9 W/cm^2 (Hg–Xe, 250–450 nm) and 1.9 W/cm^2 (LD, 395 nm). The UV to violet component of the Hg–Xe lamp was filtered out to efficiently excite the higher excited states of Eu^{3+} through the intense CT band in the UV ($\sim 240\text{ nm}$) for $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$. In the case of the Eu^{3+} aqueous solution, there is no CT band below vacuum UV so that the Hg–Xe lamp excitation was not effective. Therefore a laser diode (LD) was needed that could resonantly excite the ${}^7F_0\text{--}{}^5L_6$ transition for the Eu^{3+} aquo ions. The intensity I_{PL} of PL and modified transmitted probe light intensity ($I_p\Delta T$) due to difference transmittance (ΔT) were simultaneously detected through a 25 cm monochromator (JASCO, M25-TP) with a multichannel double-lock-in amplifier. A detailed description of the multilock-in amplifier is given in [15,16]. Since it has 128 detection channels connected to 128 avalanche photodiodes (APDs), all wavelength regions of interest were simultaneously detected. Here, in addition, we employed double-lock-in detection [17]. The pump and the probe beams were modulated at 210 Hz by a chopper as the first reference signal and at 0.05 Hz by a shutter as the second reference signal, respectively. Time constants were 3 s for the first lock-in and $1 \times 10^3\text{ s}$ for the second lock-in so that

the measurement times were 9 s and 50 min for the first and second lock-ins, respectively. Then, the first lock-in amplifier detected both I_{PL} and $I_p\Delta T$, which were modulated at the pump modulation frequency of 210 Hz. Finally the second lock-in extracted the signal due to the modulated component with the probe frequency (0.05 Hz) from them, i.e., $I_p\Delta T$. It was normalized by the probe transmission, I_pT , to obtain $\Delta T/T$, which is proportional to the absorbance change (ΔA) with and without excitation. In this experiment we used a 1200 grooves/500 nm blaze wavelength grating in the monochromator. The energy resolution was $\sim 10\text{ cm}^{-1}$. All the measurements were performed at room temperature.

If the probe light excites a substantial fraction of ions compared with those excited by the pump, the PL intensity is disturbed by the probe leading to a nonlinear photoluminescence (NPL) effect. This signal component cannot be separated from the ΔT component even with double-lock-in detection. A low-pass filter was hence used for the probe to remove the higher energy component than the measurement region to minimize the intensity I_{NPL} of the NPL signal. Since the NPL signal is negative in ΔT and appears at the same wavelength as the PL signal, one can discriminate it from the ΔT signal.

3. RESULTS

In Figs. 2(a)–2(c), the GSA spectrum in the top, the first lock-in signal in the middle, and the second lock-in signal in the bottom, respectively, are displayed for the $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ crystal. The first lock-in signals ($I_p\Delta T + I_{\text{PL}}$) are typically 10^{-10} A (APD photocurrent) while the second lock-in signals ($I_p\Delta T + I_{\text{NPL}}$) are typically 10^{-12} to 10^{-11} A . The latter are by 1–2 orders of magnitude smaller than the former. From the known PL spectra of $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$, the former are concluded to mainly reflect PL spectra. By double-lock-in detection we can extract very small ΔT signals buried in the background of 10 to 100 times larger PL signals.

The Eu^{3+} ion excited by the pump through the CT transition rapidly relaxes to the 5D_0 state by a nonradiative process [5]. Then, transitions from 5D_0 to higher excited states should be observed as positive peaks in ΔA . If the NPL effect could not be suppressed without the filter, an

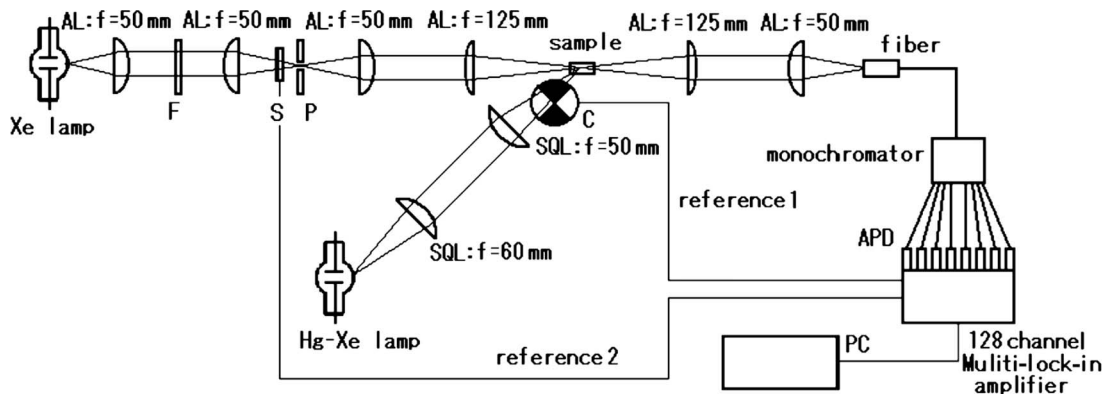


Fig. 1. Experimental setup. A Hg–Xe lamp and a Xe lamp were used for the pump and probe lights, respectively. The probe beam was focused through a $400\text{ }\mu\text{m}$ pinhole on the fiber. AL, achromatic lens; SQL, synthetic quartz lens; F, filter; S, shutter; P, pinhole; C, chopper; APD, avalanche photodiode. For the EuCl_3 aqueous solution, an InGaN laser diode was used for the pump instead of the Hg–Xe lamp.

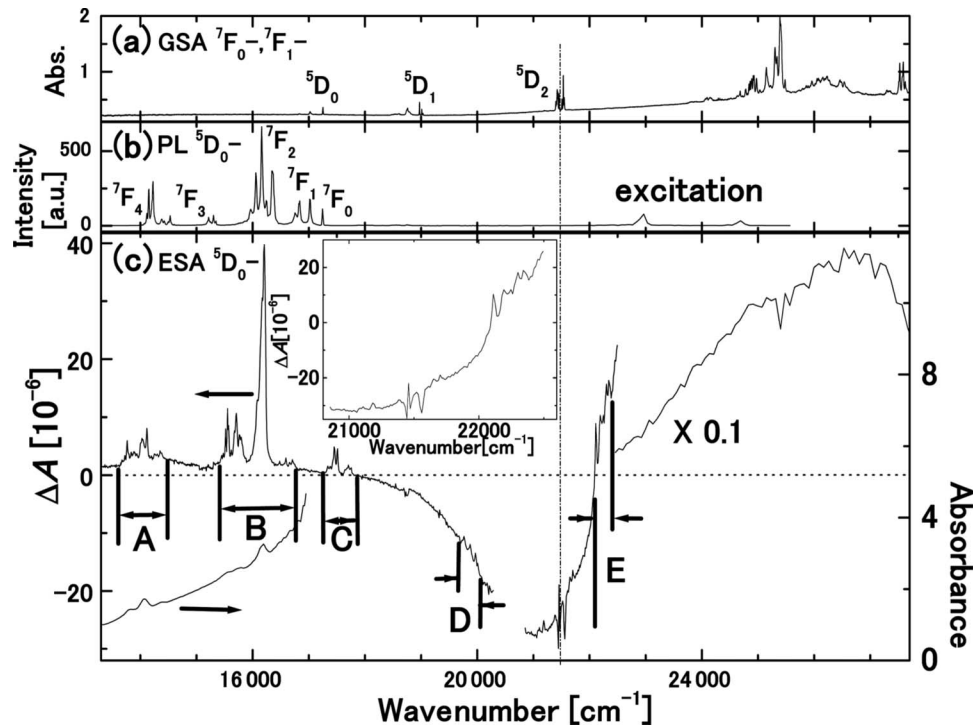


Fig. 2. (a) Absorbance (GSA), (b) PL, and (c) absorbance change ΔA (ESA) spectra of the $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ crystal. The peaks labeled “excitation” are a part of the scattered pump spectrum (Hg 435.84 and 404.66 nm lines). The PL spectrum is not corrected for spectral sensitivity of the instruments. In (c), the GSA spectrum shifted by the ${}^7F_0-{}^5D_0$ transition energy of 17 250 cm^{-1} along the horizontal axis is also shown for comparison with the ESA. Five characteristic regions are indexed by A, B, C, D, and E. The vertical dashed-dotted line highlights negative-peak absorption-saturation signals. Inset: ESA spectrum in 21 000–22 500 cm^{-1} is magnified.

inverted PL replica in ΔT is expected to appear in the second lock-in signal. All the ΔA peaks in Fig. 2(c), however,

Table 1. Oscillator Strength of Main Peaks in ESA and GSA for $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$

ESA ^a Label	OS ^b [10 ⁻⁷]	Wavenumber ^c [cm ⁻¹](exp)	Assigned Transition ^d
A	8.0	13 600–14 500	${}^5D_0-{}^5H_4$, ${}^5D_0-{}^5H_6$
B	38.8	15 400–16 800	${}^5D_0-{}^5F_2$, ${}^5D_0-{}^5F_4$
C	3.8	17 280–17 830	${}^5D_0-({}^5I, {}^5H)_6$
D	3.2	19 700–20 050	${}^5D_0-{}^5K_6$
E	9.2	22 060–22 380	${}^5D_0-{}^5G_4$
GSA ^e Label	OS [10 ⁻⁷]	Wavenumber [cm ⁻¹](exp)	Assigned Transition
	0.215	17 210–17 290	${}^7F_0-{}^5D_0$
	2.61	18 330–19 130	${}^5F_0-{}^5D_1$, ${}^5F_1-{}^5D_1$
	3.22	21 350–21 600	${}^7F_0-{}^5D_2$, ${}^7F_1-{}^5D_2$
A	15.2	30 850–31 750	${}^7F_0-{}^5H_4$, ${}^7F_0-{}^5H_6$ ${}^7F_1-{}^5H_4$, ${}^7F_1-{}^5H_6$
B	12.8	33 130–33 560	${}^7F_0-{}^5F_2$, ${}^7F_0-{}^5F_4$ ${}^7F_1-{}^5F_2$, ${}^7F_1-{}^5F_4$

^aTop main positive peaks in the ΔA spectrum are labeled A, B, C, D, and E in Fig. 2(c).

^bThe summed OS for each set of the labeled peaks is listed in the “OS” column.

^cThe “wavenumber” column indicates experimental peaks in each region.

^dThe assignment of the transitions listed in the rightmost column is due to Ofelt [18] and Carnall *et al.* [19].

^eThe OSs of GSA for comparison with ESA.

differ from the PL peaks in Fig. 2(c). Therefore, these peaks are not caused by the NPL effect but by ESA. In Fig. 2(c) the positive peaks indicating ESA are dominant in the ΔA spectrum. This is further verified by good agreement of peak positions between the ΔA and the energy-shifted GSA spectra in Fig. 2(c). We assigned these peaks to transitions from 5D_0 in Table 1 on the calculations by Ofelt [18] for the free Eu^{3+} ion with EuCl_3 parameters and the results by Carnall *et al.* [19] for Eu^{3+} in a dilute acid solution. In Fig. 3 the ESA spectrum for the Eu^{3+} aqueous solution is displayed and compared with the energy-shifted GSA spectrum. Here the correspondence of the absorption peaks between the ESA and GSA spectra is more clearly confirmed.

4. DISCUSSION

The pump light generates the excited-state ions at the expense of the ground-state ions. The resultant depletion of the ground state must be accompanied by the decrease in the ground-state absorbance. This is observed as the sign-reversed replica of the linear absorption spectrum. For the $4f-4f$ transitions, the two sharp negative peaks are found in Fig. 2(c) corresponding to the ${}^7F_{0,1}-{}^5D_2$ transitions from the ground state. In addition, as shown in Fig. 4, there are three negative peaks corresponding to the ${}^7F_{0,1}-{}^5D_0$ transitions whose amplitudes are as small as $|\Delta A| \sim 2 \times 10^{-7}$, which is close to the detection limit of the measurement system. From the known oscillator strength (2×10^{-8} , averaged value for the two sites) [9,10] of the ${}^7F_0-{}^5D_0$ transition for $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ and the relative ar-

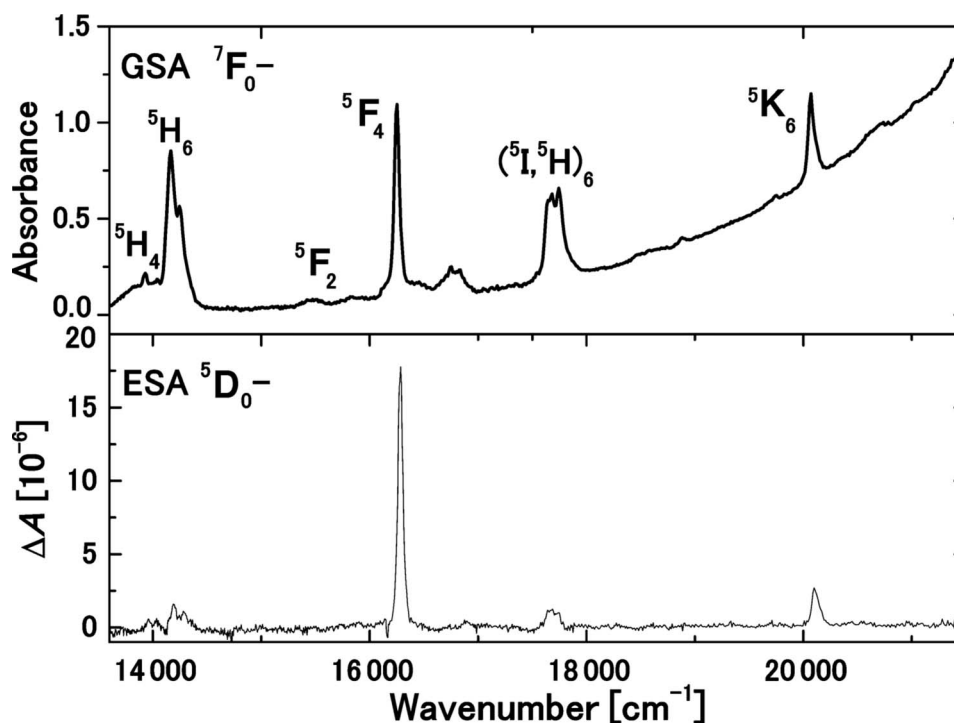


Fig. 3. GSA and ESA spectra of the EuCl_3 aqueous solution. The GSA spectrum is shifted by $17\,250\text{ cm}^{-1}$ on the horizontal axis.

eas of the peaks in the GSA and ESA spectra, the oscillator strengths (OSs) for ESA (5D_0 – 5L_J transitions) are estimated in Table 1. For comparison, the OSs for the main peaks of GSA ($^7F_{0,1}$ – 5L_J transitions) are also listed in Table 1.

Surprisingly, except for the extremely weak 7F_0 – 5D_0 transitions, the OSs for the spin-allowed ESA are of the same order of magnitude as those for the spin-forbidden GSA. In REs the spin-orbit interaction is large but it is not so large as to completely break the spin selection rule. One of the possible reasons for the small difference in OS is as follows: for Eu^{3+} doped crystals the CT state is considered to be coupled with the initial- or final- $4f$ state by the odd-parity crystal field to make the f – f transition enabled [11,12]. Since the crystal field does not affect the spin state, the ground 7F_0 state is coupled with the septet

CT state to which the excited 5D_0 state cannot be coupled. The quintet CT state to which the 5D_0 can be coupled is considered to be much higher (by $30\,000\text{ cm}^{-1}$) than the septet CT state [20]. As a result, the 5D_0 – 5L_J transitions are less allowed in parity than the 7F_0 – 5L_J transitions.

The effect of the ground-state depletion is also recognized by the decrease in the absorbance in a broad spectral range above $18\,000\text{ cm}^{-1}$ in Fig. 2(c). This can be interpreted to be the low-energy tail of the absorption saturation of the intense CT band. The broad signal changes its sign to positive at $22\,100\text{ cm}^{-1}$ and extends to a peak $\sim 27\,000\text{ cm}^{-1}$. This positive signal is due to the transition from the 5D_0 to the CT state since its energy coincides with the CT band located $\sim 44\,000\text{ cm}^{-1}$ above the ground state. Note that fine structures labeled E (5D_0 – 5G_4) $\sim 22\,000$ – $22\,500\text{ cm}^{-1}$ are clearly observed in the ESA superimposed in the broad CT band. These fine structures, which are due to crystal-field splitting, have not previously been reported for $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ because they are buried in the intense CT band in the GSA. Similar structures were previously reported only for $\text{Eu}^{3+}:\text{LiYF}_4$ above $39\,500$ ($17\,250 + 22\,250$) cm^{-1} for which a strong CT band is absent in the GSA spectrum by using a synchrotron radiation source as a PL excitation spectrum [21]. The reason why weak f – f transitions can be observed in the ESA with the CT band overlapped is that the transition intensity from the 5D_0 to the CT state is relatively weak: the CT band in the GSA is due to a spin-allowed transition from the 7F_0 to the septet CT state, while the transition from the 5D_0 state to this CT state is spin-forbidden.

In the JO theory, the OS of the electric dipole transitions has a selection rule that the OS from $J=0$ to $J=\text{even}$ is larger than that from $J=0$ to $J=\text{odd}$. In Fig. 2, this feature can be noticed in the ESA spectra as well as

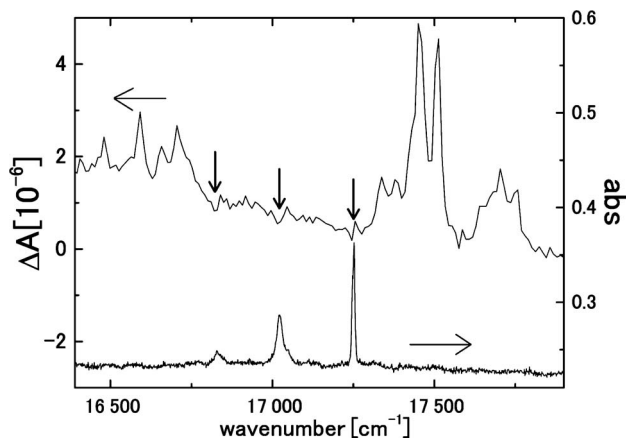


Fig. 4. Detailed ΔA spectrum in the selected region in Fig. 2(c). The three arrows indicate small negative peaks located at the same wavenumbers as the peaks in the GSA spectrum. These are induced by ground-state depletion.

in the GSA and PL spectra. This feature is even more evident in the GSA and ESA spectra for the Eu^{3+} aqueous solution in Fig. 3. Therefore it can be concluded that the JO theory is applicable even for ESA. There is, however, one remarkable difference between the GSA and ESA spectra both for the crystal and solution: in the ESA the peak at $16\,210\text{ cm}^{-1}$ (5D_0 – 5F_4) is much more intense than the other peaks while in the GSA it is not different from the other peaks in intensity. This feature should sensitively reflect the difference in the wave function between the 5F_4 state and the other states so that it cannot be simply explained without a more detailed analysis.

5. CONCLUSIONS

We have succeeded in the direct pump-probe measurement of the ESA (5D_0 – 5L_J) spectra for an $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ crystal and an Eu^{3+} aqueous solution. It was experimentally confirmed that the JO theory is applicable to ESA as well as to GSA for Eu^{3+} , but there was a large difference between ESA and GSA in the relative intensity of one of the transitions: for ESA the transition to the 5F_4 state is much more enhanced than that of the other final states. The OSs for the spin-allowed ESA were experimentally determined for the crystal, which were found to be in the same order of magnitude as those for the spin-forbidden GSA. The fine $4f$ – $4f$ structures buried in the intense CT band were also clearly observed, which is one of the major advantages in an ESA study.

It was demonstrated that multichannel double-lock-in pump-probe spectroscopy is useful for ESA measurements of REs because broadband lamp light sources are sufficient for both the pump and the probe if the samples have a strong CT or f – d band. No need for a suitable laser resonant with sharp absorption lines will enlarge a variety of measurable RE samples for an ESA study.

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