Upconversion and Local Structure of Er^{3+} Doped Aluminate Glasses

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 Er^{3+} ドープアルミネートガラスのアップコンバージョンと局所構造

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Optical properties and structure of Er^{3+} doped $66.7\text{CaO} \cdot 33.3\text{Al}_2\text{O}_3$ glasses were investigated. Among three Judd-Ofelt intensity parameters Ω_2 and Ω_4 showed large values compared with those of Er^{3+} ions in other oxide glasses, indicating a large transition probability of 650 nm absorption. From the Mössbauer measurement, the coordination number of rare earth ions in this glass was found to be about 7 with low symmetry. The phonon energy was about 800 cm^{-1} , which corresponds to the stretching vibration of AlO_4 groups coupled with the rare earth ion in the glass. The multiphonon decay rate and its energy gap dependence were obtained from the fluorescence lifetime and radiative transition probability calculated for $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ levels. The rate was lower than that in silicate glasses and almost corresponded to the value for the phonon energy of 800 cm^{-1} . The upconversion fluorescence at 550 nm was observed by 650 nm pumping and its excitation spectra were monitored by a tunable DCM dye laser. It was concluded that the observation of green upconversion was possible due to a large transition probability of $^4\text{F}_{9/2} \leftarrow ^4\text{I}_{15/2}$ and also to an excited state absorption mechanism from $^4\text{I}_{13/2}$ to $^4\text{F}_{5/2}$ level.

Key-words: Upconversion, Rare earth, Multiphonon decay, Excited state absorption, Judd-Ofelt theory, Radiative transition

1. Introduction

The upconversion phenomena of rare earth ions in crystals^{1)–3)} and glasses^{4)–6)} are attracting a great interest because of the possibility of short wavelength upconversion lasers pumped with near-infrared radiations from laser diodes of III–V semiconductors. In particular Er^{3+} fluorescence upconversion is widely investigated since the high power III–V group laser diodes (LD) with the infrared wavelengths of $1.48\text{ }\mu\text{m}$,³⁾ $0.98\text{ }\mu\text{m}$,^{1),4)} and $0.80\text{ }\mu\text{m}$,^{5),6)} can be used as exciting sources. These wavelengths correspond to the absorptions from the ground state $^4\text{I}_{15/2}$ to the first ($^4\text{I}_{13/2}$), second ($^4\text{I}_{11/2}$) and third ($^4\text{I}_{9/2}$) excited states of Er^{3+} ion, respectively. As a host of rare earth ions, the glasses are attractive materials because they can be fabricated as optical waveguide structures or optical fibers in which the pumping

light is efficiently confined to maintain a high intensity over a long interaction length, and also because a large amount of active ions can be incorporated as impurities unlike crystals. Although oxide glasses are stable and also suitable for drawing fibers, a disadvantage as a fluorescence host is the presence of high frequency stretching vibrations of glass network former polyhedra, since the highest frequency phonons can conserve the energy gap in the lowest order process and therefore play the most important role in the nonradiative relaxation.⁷⁾ We reported, however, that efficient green emission due to $\text{Er}^{3+}: ^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ can be observed by $0.80\text{ }\mu\text{m}$ pumping with a GaAlAs LD in some heavy metal oxide glasses such as gallate, lead bismuth oxide and tellurite systems.⁵⁾ These phenomena could be explained by their lower phonon energies than those of conventional glasses composed of network-forming oxides such as B_2O_3 , P_2O_5 and SiO_2 . In addition to the reduction of non-radiative loss, the gain of radiative transition probability can be a way leading to efficient upconversion. The excitation efficiency of Er^{3+} ion can be improved by adopting $0.65\text{ }\mu\text{m}$ pumping laser source, since the transition probability of ground state absorption is higher for $^4\text{F}_{9/2}$ than that for $^4\text{I}_{9/2}$, owing to larger reduced matrix elements of the $^4\text{F}_{9/2} - ^4\text{I}_{15/2}$ transition. However, there have been few reports on $0.65\text{ }\mu\text{m}$ pumped Er^{3+} upconversion⁸⁾ until now, since the AlGaInP LD of this wavelength range was not easily available.⁹⁾

In this study, an aluminate glass was chosen as a host of Er^{3+} ion and the upconversion characteristics were investigated by the $0.65\text{ }\mu\text{m}$ radiation. Furthermore, to investigate the phonon energy and the local structure coupled with rare earth ions, Eu^{3+} -doped glass with the same composition was also prepared and the phonon sideband and ^{151}Eu Mössbauer spectra were also measured. In addition, to design an efficient upconversion laser glass, it is desirable to clarify which one is a controlling mechanism for upconversion; the energy transfer (*Addition de Photon par Transfert d'Énergie*, APTE) between adjacent two ions or by the excited state absorption (ESA) in a single ion.⁸⁾ To distinguish ESA and APTE mechan-

ism, a tunable dye laser was used as a pumping source to verify the upconversion mechanism by tuning over the Er^{3+} absorption band.

The results were discussed combined with the multiphonon decay rate of Er^{3+} in the glass.

2. Experimental

2.1 Sample preparation

Glasses with the composition of $66.7\text{CaO} \cdot 33.3\text{Al}_2\text{O}_3 \cdot x\text{Er}_2\text{O}_3$ ($x=0.1, 0.25, 0.5, 1.0$) in mol% were prepared by using reagent grade CaCO_3 , Al_2O_3 and Er_2O_3 as starting materials. For the Eu^{3+} doped glasses, Eu_2O_3 was used instead. The batches were mixed well in an alumina mortar and melted in an alumina crucible at 1500°C for 1 h. The melt was poured on a stainless steel plate heated at 900°C and cooled to room temperature. The glass obtained was annealed at 790°C for 20 min and was cut and polished into a rectangular parallelepiped shape of $10 \times 10 \times 3$ mm.

2.2 Absorption spectra and Judd-Ofelt analysis

Absorption spectra were measured at room temperature with a Shimadzu UV-2200 Recording Spectrophotometer in the range of 190–900 nm. The values of integrated absorbance and the mean wavelength of six absorption bands¹⁰⁾ were calculated from the digital spectral data. The density of the samples were measured by Archimedes method using kerosene as the immersing liquid and a silica glass as a standard. The refractive index of the glasses were measured with an ERMA Abbe refractometer.

The line strength of an absorption band between an initial J manifold $|(S, L)J\rangle$ and final manifold $|(S', L')J'\rangle$, $S_{JJ'}$, was calculated with the experimental values of the integrated absorbance by,¹¹⁾

$$\int_{\text{band}} k(\lambda) d\lambda = \frac{8\pi^3 e^2 \bar{\lambda} \rho}{3hc(2J+1)} \frac{1}{n} \left[\frac{(n^2+2)^2}{9} \right] S_{JJ'} \quad (1)$$

where $k(\lambda)$ is the absorption coefficient at λ , $\bar{\lambda}$ is the mean wavelength of the absorption band, ρ is the Er^{3+} concentration, h is Planck's constant, c is the speed of light, e is the elementary charge and n is the refractive index. According to the Judd-Ofelt theory^{12),13)} the line strength of the electric dipole transition is obtained by,

$$S_{JJ'} = \sum_{t=2,4,6} \Omega_t |\langle (SL)J || U^{(t)} || (S'L')J' \rangle|^2 \quad (2)$$

where three terms $\langle ||U^{(t)}|| \rangle$ are the reduced matrix elements of the unit tensor operators calculated in the intermediate-coupling approximation, and coefficients Ω_t ($t=2, 4, 6$) are the intensity parameters which contain the effects of the crystal field terms, radial integrals of electron, and so on.¹⁴⁾ Since the $\langle ||U^{(t)}|| \rangle$ is a constant characteristic to each transition, three intensity parameters Ω_t ($t=2, 4, 6$)

were obtained by the method of least squares fitting by using Eqs. (1) and (2).

By using these parameters, the spontaneous emission probabilities $A_{J'J}$ for some electric-dipole transitions from an initial manifold $|(S', L')J'\rangle$ to a final manifold $|(S, L)J\rangle$ were calculated by,¹⁴⁾

$$A[(S'L')J'; (\bar{S}\bar{L})\bar{J}] = \frac{64\pi^4 e^2}{3h(2J'+1)\bar{\lambda}^3} n \left[\frac{(n^2+2)^2}{9} \right] S_{J'J} \quad (3)$$

2.3 Fluorescence measurement

The fluorescence and excitation spectra were measured with a Hitachi-850 Fluorescence Spectrophotometer. A Xe-lamp and a dye-laser (Spectra Physics Model 375 Dye Laser) excited by a cw Ar^+ -laser (Coherent innova 70) were used. A propylene carbonate solution of DCM dye (Dicyanomethylene-2-methyl-6-*p*-dimethylaminostyryl-4*H*-pyran) was used to obtain tunable range from 620 to 700 nm.

The fluorescence decay curves were measured upon excitation with 488 nm radiation of Coumarine 481 dye laser pumped with a pulsed N_2 laser (Ushio UKN-500). The exciting pulse duration was about 5 ns. The output was recorded using a storage oscilloscope (Tektronics 2432), a monochromator (Spex 1402) with a single grating and a photomultiplier (Hamamatsu Photonics R928). The fluorescence lifetime, τ_f was determined by a least square fitting of exponential functions. With the measured lifetime and $A_{J'J}$ calculated from Eq. (3), the nonradiative decay rate ($=\tau_{\text{NR}}^{-1}$) was obtained by,

$$\tau_{\text{NR}}^{-1} = \tau_f^{-1} - \sum_J A_{J'J} \quad (4)$$

where the summation is taken for all lower terminal J states.

2.4 Other spectroscopic measurement

Since the phonon sideband cannot be observed for Er^{3+} ion in glasses owing to the complex Stark splittings of its levels as well as inhomogeneous broadening of pure electronic lines, the measurement was done for the Eu^{3+} -doped glasses instead. In the excitation spectra of Eu^{3+} : $^5D_0 \rightarrow ^7F_2$ emission at 612 nm, the phonon sideband associated with the pure electronic $^5D_2 \leftarrow ^7F_0$ transition¹⁵⁾⁻¹⁸⁾ was multiplied by 50 times to study the phonon mode coupled with the rare earth ions.

The ^{151}Eu Mössbauer spectra were also measured at room temperature using $^{151}\text{Sm}_2\text{O}_3$ (50mCi) as 21.6 keV γ -ray source. The velocity calibration was done with the spectrum of magnetic splitting of $\alpha\text{-Fe}$ by a ^{57}Co (Rh) source of 14.4 keV γ -ray. The isomer shift was determined with respect to EuF_3 . All the spectra were analyzed with a least-square fitting program of Lorentzian curves.

The Al $K\alpha$ emission spectra was measured with an X-ray probe microanalyzer (Shimadzu Model ARL EMX-SM). The chemical shift was calculated in wavelength with respect to the peak for Al metal.

3. Results and discussion

3.1 Intensity parameters and local structure of rare earth ions in aluminate glasses

The refractive index, the concentration of Er³⁺ ions per a unit volume from the measured density, the Judd-Ofelt intensity parameters, Ω_t obtained by the least square fitting and the root mean square deviation, δ_{rms} are listed in Table 1. The values of δ_{rms} were less than 2 % for all the samples, indicating a good fit. Among three Ω_t values, Ω_2 and Ω_4 show relatively large values compared with those of Er³⁺ ions in other oxide glasses, such as silicate and germanate.¹⁹⁾ Especially Ω_2 is closely related to the hypersensitive transition²⁰⁾ and takes a large value in a field of lower symmetry.²¹⁾ According to Jørgensen and Judd,²¹⁾ the hypersensitivity appears most strikingly for the rare earth ions in highly polarized and asymmetric environment.

The ¹⁵¹Eu Mössbauer spectrum of 66.7CaO·33.3Al₂O₃·1Eu₂O₃ glass is shown in Fig. 1. An absorption peak is placed around +1 mm/s and one due to Eu²⁺ ions, which should appear around -10 mm/s,²²⁾ was not observed in any samples in this study. Thus all the europium ions in these glasses exist in trivalent state. Since the mass and ionic radius of Eu³⁺ ion are similar to those of Er³⁺, the estimation for the local environment of Eu³⁺ can hold also for that of Er³⁺. As shown in Table 2, the IS of Eu³⁺ in these glasses were around 0.9 mm/s independent of Eu³⁺ concentration. In the previous study on the Eu³⁺ ions in oxide crystals and glasses, the IS can be a measure of the coordination number (CN) ranging

Table 1. Refractive index, concentration of Er³⁺ ions per unit volume, Ω_t values and root mean square deviation of the glasses.

Sample	n_D^{20}	ρ (10 ²⁰ cm ⁻³)	Ω_2 (10 ⁻²⁰ cm ²)	Ω_4 (10 ⁻²⁰ cm ²)	Ω_6	δ_{rms} (%)
x=0.1	1.685	0.427	7.67	1.86	0.40	1.40
x=0.25	1.685	1.061	7.33	1.78	0.47	1.78
x=0.5	1.685	2.118	7.46	1.79	0.50	1.00
x=1.0	1.685	4.181	6.87	1.50	0.70	1.90

Fig. 1. ¹⁵¹Eu Mössbauer spectrum of 66.7CaO·33.3Al₂O₃·1Eu₂O₃ glass.

Table 2. Isomer shift of ¹⁵¹Eu in the glasses.

x	Isomer shift (mm/sec)
0.1	0.91
0.25	0.87
0.5	0.90
1.0	0.88

from 6 to 12.²³⁾ This value is lower than that of C-Eu₂O₃ (1.06 mm/s) and higher than that of Eu₃Ga₅O₁₂ garnet (0.85 mm/s), where the CN of Eu³⁺ are 6 and 8, respectively.²³⁾ Thus the average CN of rare earth ions in this glass is estimated to be around 7, which is lower than those in aluminosilicate glasses where the CN of Eu³⁺ is 12.²⁴⁾ This result indicates a relatively decreased Eu-O bond length and CN of Eu³⁺ in the host with a large basicity. It is plausible that the large Ω_2 value was attained in a distorted ligand field with small coordinating number of polarizing oxygen atoms.

In the excitation spectra of Eu³⁺: ⁵D₀→⁷F₂ emission for 66.7CaO·33.3Al₂O₃·1Eu₂O₃ glass, the phonon sideband coupled with the rare earth ions was observed in the higher energy range (~22300 cm⁻¹) of the pure electronic ⁵D₂←⁷F₀ transition at 21500 cm⁻¹. Therefore the phonon energy, $\hbar\omega$ can be obtained to be about 800 cm⁻¹. From the chemical shift of Al K α emission in Table 3, the CN of Al³⁺ ions²⁵⁾ are considered to be 4 in this glass. According to the infrared absorption study on aluminate glasses,²⁶⁾ the band at 800 cm⁻¹ is due to the stretching vibration of AlO₄⁻ group, while the band at 600 cm⁻¹ is to AlO₆²⁻ group. Therefore, the phonon sideband at 800 cm⁻¹ can be ascribed to the stretching vibration of AlO₄⁻ groups coordinating the rare earth ion to neutralize its positive charge. Accordingly, the local vibration due to ⁴Al-O bond with the 800 cm⁻¹ are considered to contribute to the multiphonon relaxation of rare earth ions.

3.2 Upconversion in aluminate glass

The upconversion fluorescence spectra by 650 nm excitation for the 66.7CaO·33.3Al₂O₃·1Er₂O₃ glass

Table 3. Chemical shift of Al K α emission.

sample	Coordination Number	Chemical shift (10 ⁻⁵ nm)
α -Al ₂ O ₃	6	20
Al(PO ₃) ₄	6	29
α -AlPO ₄	4	16
K-feldspar	4	8
Ca-Al-O glass	(4)	9

showed emission bands around 550 nm, 660 nm, and 800 nm. The 410 nm emission peak due to ${}^2H_{9/2} \rightarrow {}^4I_{15/2}$ transition, which appeared by UV excitation of ${}^4G_{11/2} \leftarrow {}^4I_{15/2}$ at 380 nm, was scarcely observed for all the samples with the present laser apparatus, indicating that more than two-step excitation is necessary to reach the ${}^2H_{9/2}$ level. The excitation power dependences of emission intensities are plotted in Fig. 2 in log-log scale. The ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ and ${}^4I_{9/2} \rightarrow {}^4I_{15/2}$ emissions have a slope of almost unity, while the ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ upconversion emission a slope of two, which indicates a two-step excitation by ESA or APTE.

3.3 Upconversion mechanism

In the case of APTE mechanism, the incident light is absorbed only in the transition from the ground state, so the wavelength dependence of efficiency should depend only on the ${}^4F_{9/2} \leftarrow {}^4I_{15/2}$ transition. In ESA mechanism, however, the efficiency depends also on the excited state absorption cross section of the transition from a certain intermediate level. In general, the ESA cross section will not vary with wavelength in the same way as the ground state absorption. Since the 550 nm upconversion in the present glass occurs by two-step process, the energy transfer can occur between ${}^4I_{11/2}$ or between other levels. However, by the ESA mechanisms, a possible level from which the absorption of 650 nm photon can occur is uniquely the ${}^4I_{13/2}$, because the ${}^2H_{9/2}$ emission could not be observed at least by two-step process. Thus the ${}^4F_{5/2} \leftarrow {}^4I_{13/2}$ should be the possible transition, for which the peak should appear at 645 nm. The upconversion excitation spectra of $x=0.1$ and 1.0 samples are shown in Fig. 3. Also shown in Fig. 4 are the absorption profiles of ${}^4F_{9/2} \leftarrow {}^4I_{15/2}$ for the respective samples. Although the profiles of excitation and absorption spectra are similar for both samples, the peak of the excitation spectra (645 nm)

Fig. 3. Laser excitation spectra of 550 nm upconversion fluorescence with 100 mW power for the $x=0.1$ and 1.0 glasses.

Fig. 4. Absorption profile of ${}^4F_{9/2} \leftarrow {}^4I_{15/2}$ transition for the $x=0.1$ and 1.0 glasses.

Fig. 2. The pumping power dependence of emission intensities.

Fig. 5. Upconversion process by the ESA mechanism in the present glass.

are placed at higher energy side than that of the absorption spectra (652 nm). This is an evidence of the excited state absorption, the peak position of which becomes at 645 nm for the $^4F_{5/2} \leftarrow ^4I_{13/2}$ transition (Fig. 5). In this upconversion process, the ground state absorption also contributes to the upconversion efficiency, since the second excitation probability becomes proportional to the population of the intermediate level. That is why the profile of the excitation is also similar to that of the ground state absorption.

3.4 Multiphonon decay rate and quantum efficiency

For the $^4S_{3/2}$ and $^4F_{9/2}$ levels, the values of A , branching ratio β , radiative lifetime τ_R calculated with the Ω_i values, measured τ_f and quantum efficiency η are listed in Table 4 for the $x=0.1$ sample. The compositional dependence of τ_f and nonradiative decay rate ($=\tau_{NR}^{-1}$) is plotted as a function of Er³⁺ concentration in Fig. 6. Clearly, the τ_f decreases and τ_{NR}^{-1} increases quadratically with increasing Er³⁺ concentration, which indicates energy transfer due

Table 4. Spontaneous emission probability A , branching ratio β , lifetime, and quantum efficiency for $^4S_{3/2}$ and $^4F_{9/2}$ levels of Er³⁺ ions in the $x=0.1$ sample.

$ SLJ\rangle$	$ S'L'J'\rangle$	$A_{JJ'}$ (sec ⁻¹)	β	τ_R (msec)	τ_f (μ sec)	τ_{NR}^{-1} (sec ⁻¹)	η (%)
$^4S_{3/2}$	$\rightarrow ^4I_{15/2}$	461.0	0.64	1.39	12.03	8.24×10^4	0.87
	$\rightarrow ^4I_{13/2}$	197.1	0.27				
	$\rightarrow ^4I_{11/2}$	18.7	0.03				
	$\rightarrow ^4I_{9/2}$	43.7	0.06				
$^4F_{9/2}$	$\rightarrow ^4I_{15/2}$	1445.4	0.91	0.630	1.20	8.30×10^5	0.19
	$\rightarrow ^4I_{13/2}$	88.6	0.06				
	$\rightarrow ^4I_{11/2}$	48.3	0.03				
	$\rightarrow ^4I_{9/2}$	6.0	0.00

Fig. 6. Concentration dependence of the lifetime and nonradiative decay rate of $^4S_{3/2}$ level.

Fig. 7. The energy gap dependence of the multiphonon decay rate of rare earth levels in various oxide glasses.

to electric dipole interaction.²⁷⁾ The multiphonon decay rate at negligible energy transfer of $^4S_{3/2}$ level can be evaluated as the value of y -section in this figure to be 8.2×10^4 s⁻¹. In the same way, the rate for $^4F_{9/2}$ level was obtained to be 8.3×10^5 s⁻¹. Generally, the energy gap dependence of multiphonon decay rate of an excited level is given by,²⁸⁾

$$W_p = W_0 \cdot \exp[-\alpha \Delta E / \hbar \omega] \quad (5)$$

where ΔE is the energy gap to the next lower level, α is a function of the electron-phonon coupling strength and $W_0(0)$ is the decay rate at $\Delta E=0$ and $T=0$. Accordingly, the W_p increases rapidly with a decrease of the energy gap. The ΔE and $\hbar \omega$ dependences of the experimental value of W_p are plotted in Fig. 7 along with the data by Layne et al.⁷⁾ For the Er³⁺: $^4S_{3/2}$ and $^4F_{9/2}$ levels, the values of W_p in the aluminate glass is almost comparable to or a little lower than those in a germanate glass where $\hbar \omega$ is 850 cm⁻¹. In the aluminate glass, the $\hbar \omega$ from the phonon sideband measurement is 800 cm⁻¹, which is lower than that of a germanate glass. Both results are almost consistent.

3.5 Excitation efficiency of Er³⁺

In spite of the relatively large phonon energy in the aluminate glass, the upconversion could be observed by 650 nm pumping. This can be ascribed to the larger excitation probability of $^4F_{9/2} \leftarrow ^4I_{15/2}$ than that of $^4I_{9/2} \leftarrow ^4I_{15/2}$. Since the $\langle ||U^{(2)}|| \rangle^2$ values of both transitions are zero and the Ω_4 in this host is large, the 650 nm pumping becomes advantageous because of the much larger $\langle ^4F_{9/2} || U^{(4)} || ^4I_{15/2} \rangle^2$ value ($=0.5655$) than $\langle ^4I_{9/2} || U^{(4)} || ^4I_{15/2} \rangle^2$ ($=0.1452$).¹¹⁾ This large excitation efficiency should result in a large population of $^4I_{13/2}$ level, since the ΔE of this level is large enough to suppress the multiphonon loss, while the W_p of the upper 4I_J levels ($J=9/2, 11/2$) are large due to small ΔE and a sufficient $\hbar \omega$. Therefore, the excited state absorption efficiency depends on the population of the intermediate level which can be gained by the probability of the ground

state absorption. The practical opportunity of 650 nm pumping will be wider by the development of high power AlGaInP laser diodes.

4. Summary

The optical properties of Er^{3+} ions doped in aluminate glasses were investigated.

(1) Among three intensity parameters obtained from absorption spectra by Judd-Ofelt theory, Ω_2 and Ω_4 showed a large value compared with those in other oxide glasses.

(2) The multiphonon decay rates of the $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ levels were obtained from the radiative transition probabilities and concentration dependence of nonradiative decay rate. The values were nearly equal to those in a germanate glass. The energy gap dependence of the multiphonon decay rate was consistent with the phonon energy of this host, 800 cm^{-1} obtained from the phonon sideband measurement.

(3) The upconversion fluorescence at 550 nm was observed with excitation at 650 nm corresponding to the $^4\text{F}_{9/2} \leftarrow ^4\text{I}_{15/2}$ absorption, for which the Ω_4 value dominates the transition probability.

(4) The profile of the excitation spectra of upconversion fluorescence by a tunable dye laser showed a deviation from that of the ground state absorption. This result indicates that the excited state absorption from the $^4\text{I}_{13/2}$ level contributes the upconversion in the present glasses.

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