Upconversion properties, multiphonon relaxation, and local environment of rare-earth ions in fluorophosphate glasses

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The upconversion properties of Er^{3+} ions were studied for the fluorophosphate glasses $(45-x)AlF_3 \cdot xAlPO_4 \cdot 5ErF_3 \cdot 30CaF_2 \cdot 20BaF_2$, with use of the infrared radiation from a (Ga,Al)As laser diode ($\lambda = 802$ nm) as an excitation source. Green upconversion fluorescence due to the ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition could be observed for the fluoride glass, while the fluorescence intensity for fluorophosphate glasses decreased drastically with increasing AlPO₄ content. It was found from the phonon sideband spectra of Eu^{3+} that the phonon with $\hbar\omega = 1060$ cm⁻¹, corresponding to P-O⁻ stretching vibrations, became coupled to the multiphonon relaxation of rare-earth ions, and its electron-phonon coupling strength increased greatly with increasing phosphate content. The temperature dependence of upconversion intensity was large for the fluoride system, while it was small for the fluorophosphate system. These tendencies could be well explained by considering the multiphonon decay rate of the Er^{3+} intermediate level and its temperature dependence, which are functions of the phonon energy of the host and the energy gap to the next-lower level of Er^{3+} . Combined with the results of ¹⁵¹Eu Mössbauer spectroscopy, it was concluded that the upconversion properties in these glasses were largely influenced by the local structure and the phonon mode coupled to the rare-earth ions.

I. INTRODUCTION

The conversion of infrared light to visible light, "frequency upconversion" phenomena of rare-earth ions in solids, is attracting much research interest. The device applications are potential short-wavelength upconversion lasers¹⁻⁴ pumped with the infrared radiation from III-V laser diodes (LD). The glasses are particularly attractive hosts because they can be fabricated as an optical fiber to confine the pumping light from the LD efficiently to maintain a high intensity over a long interaction length, and also because different kinds of ion can be incorporated in various proportions. However, the optical properties of fluorescent ions are largely influenced by their ligand field and the vibrational property of the host. Thus, it is important to investigate the coordination states and multiphonon relaxation mechanisms of the rare-earth ions in multicomponent glasses in order to design optical devices. One of the advantages of fluoride hosts is their lower phonon energy compared with those of the oxide hosts, which contribute to a reduction in the nonradiative loss due to multiphonon relaxation.^{5,6} In this study, fluoride and fluorophosphate glass systems, which have been used as Nd³⁺-laser hosts, were chosen as hosts of Er^{3+} ions and their upconversion properties were studied by exciting with a (Ga,Al)As laser diode emitting 0.80- μ m infrared radiation. It is well known that the rate of the multiphonon relaxation is dominated by lattice phonons. Therefore, the phonon sideband^{7,8} was measured for Eu³⁺-doped glasses in order to get information about the phonon mode coupled to the rare-earth

ions. Moreover, the ¹⁵¹Eu Mössbauer effect⁹ was measured to determine the local structure of rare-earth ions in the glass. The compositions of the glasses investigated are those of AlF_3 -based fluorides and fluorophosphates. The AlF_3 system was chosen since it is chemically stable and can incorporate a substantial amount of phosphate and rare-earth ions in vitreous states.

II. EXPERIMENTAL

Glasses with compositions $(45-x)AlF_3 \cdot xA1PO_4$ $\cdot 5ErF_3 \cdot 30CaF_2 \cdot 20BaF_2$ (x = 0, 5, 10, 20) were prepared by using reagent-grade powders. For the fluoride glasses, a small amount of NH₄F·HF was also added in the batch. The powders of batch composition were well mixed in an alumina mortar and melted in a platinum-rhodium crucible at suitable temperature of 900-1000 °C for 15 min. The melt was poured on a stainless steel and pressed with another steel plate. The glass obtained was annealed, cut, and polished with diamond paste into $3 \times 3 \times 1$ mm³ size.

The fluorescence and excitation spectra were measured with a Hitachi-850 Fluorescence Spectrophotometer. A Xe lamp and a GaAs/(Ga,Al)As laser diode (SONY SLD301-XT, $\lambda = 802$ nm, P < 100 mW) were used as the excitation source of the normal and upconversion fluorescence, respectively. Since the phonon sideband cannot be observed for an Er^{3+} ion in glasses, owing to the complex Stark splittings of its levels, Eu^{3+} -doped glasses were prepared instead. In the excitation spectra of $Eu^{3+}:^{5}D_{0} \rightarrow ^{7}F_{2}$ emission at 612 nm, the phonon sideband associated with the pure electronic ${}^{5}D_{2} \leftarrow ^{7}F_{0}$ transi-

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tion⁸ was increased by a factor of 100 to study the phonon mode coupled to the rare-earth ions.

The ¹⁵¹Eu-Mössbauer effect measurement was also carried out at room temperature using ¹⁵¹Sm₂O₃ (50 mCi) as a 21.6-keV γ -ray source. The velocity calibration was done with the spectrum of magnetic splitting of α -Fe by a ⁵⁷Co(Rh) source and the isomer shift was determined with respect to EuF₃. All the spectra were analyzed with a least-squares fitting program of Lorentzian curves.⁹

III. EXPERIMENTAL RESULTS

A. Upconversion intensity of Er^{3+} in fluoride and fluorophosphate glasses

Figure 1 shows the compositional variation of upconversion fluorescence spectra for $(45-x)AlF_3 \cdot xAlPO_4 \cdot 5ErF_3 \cdot 30CaF_2 \cdot 20BaF_2$ glasses (x=0,5,10,20). A homogeneous glass was not obtained for the composition of $x \ge 25$. It is clear that the fluorescence intensity of glasses decreased drastically with increasing AlPO₄ content. At 20 mole % AlPO₄, the green emission was hardly observable with the human eye at 30-mW excitation. The 410-nm emission peak due to the ${}^2H_{9/2} \rightarrow {}^4I_{15/2}$ transition, which appeared by excitation of the ${}^4G_{11/2} \leftarrow {}^4I_{15/2}$ transition at 378 nm, was barely observed for all the samples with the present laser apparatus, indicating that an excitation process of more than two steps may be necessary to reach the ${}^2H_{9/2}$ level.

B. Temperature dependence of Er³⁺ -upconversion intensity

The temperature variation of the upconversion fluorescences of $45AlF_3 \cdot 5ErF_3 \cdot 30CaF_2 \cdot 20BaF_2$ glass (x = 0) is shown in Fig. 2. The fluorescence intensity decreases with increasing temperature in the range from room temperature, 299 to 644 K. In Fig. 3 the integrated area of the ${}^{4}S_{3/2} + {}^{2}H_{9/2} \rightarrow {}^{4}I_{15/2}$ green fluorescence around 550 nm is plotted as a function of temperature for both (a) the fluoride glass (with x = 0) and the fluorophosphate glass (with x = 5). It was found that the intensity decreased by



FIG. 1. Compositional variation of upconversion fluorescence spectra in the fluorophosphate glasses $(45-x)AlF_3$ $\cdot xAlPO_4 \cdot 5ErF_3 \cdot 30CaF_2 \cdot 20BaF_2$.



FIG. 2. Temperature variation of upconversion fluorescence spectra in fluoride glass (x = 0).



FIG. 3. Temperature dependence of upconversion intensity of (a) the fluoride glass (x = 0) and (b) the fluorophosphate glass (x = 5).



FIG. 4. Phonon sideband spectra of fluorophosphate glasses having different $AIPO_4$ content.

less than 1/10 from room temperature to 350 °C for the fluoride glass, while it decreased by about $\frac{1}{2}$ for the fluorophosphate glass.

C. Phonon sideband spectra of Eu³⁺

The phonon sideband spectra associated with $\operatorname{Eu}^{3+}: {}^{5}D_{2} \leftarrow {}^{7}F_{0}$ transition the are shown for (45-x)AlF₃·xAlPO₄·5EuF₃·30CaF₂·20BaF₂ glasses (x=0,5,10,20) in Fig. 4. The intense band due to the pure electronic transition is located around 464 nm, while the phonon sideband coupled to the rare-earth ions is observed in the higher-energy range. The band around 442 nm appears above x = 5 and its intensity increases with increasing x. The intensity of the shoulder around 451 nm decreases with increasing x. The phonon energy $\hbar\omega$ can be obtained as

$$\hbar\omega(\mathrm{cm}^{-1}) = 10^7 / \lambda_{\mathrm{PSB}}(\mathrm{nm}) - 10^7 / \lambda_{\mathrm{PET}}(\mathrm{nm})$$
,

where λ_{PSB} and λ_{PET} are the wavelength (nm) of the phonon sideband and that of the pure electronic transition, respectively. Thus the energies of two bands are found to be about 1060 and 600 cm⁻¹.

D. ¹⁵¹Eu Mössbauer spectroscopy

The ¹⁵¹Eu Mössbauer spectrum of $25AlF_3 \cdot 20AlPO_4$ $\cdot 5EuF_3 \cdot 30CaF_2 \cdot 20BaF_2$ glass (x = 20) is shown in Fig. 5.



FIG. 5. 151 Eu Mössbauer spectrum of the $25A1F_3 \cdot 20A1PO_4 \cdot 5EuF_3 \cdot 30CaF_2 \cdot 20BaF_2$ fluorophosphate glass.



FIG. 6. Compositional dependence of the isomer shift of $^{151}Eu^{3+}$ in fluorophosphate glasses.

An absorption peak is located around 0 mm/sec and the one due to Eu^{2+} ions, which should appear around -14 mm/sec,¹⁰ has not been observed in any samples in this study. Therefore, all the europium ions in these glasses exist in the trivalent state as Eu^{3+} . In Fig. 6 the compositional dependence of the isomer shift (IS) is plotted as a function of the AlPO₄ content. The IS of the fluoride glass (x = 0) was lower than that of EuF_3 (0 mm/sec), while that of fluorophosphate glasses increases with increasing AlPO₄ content, and becomes positive above 10 mole % AlPO₄.

IV. DISCUSSION

A. Local structure and multiphonon relaxation mechanisms of rare earths in fluoride and fluorophosphate glasses

From the Mössbauer results, all the europium ions in the present glasses were found to exist in the trivalent state, as Eu^{3+} . Since the mass and ionic radius of the Eu^{3+} ion are similar to those of Er^{3+} , their chemical environments should also be similar. The isomer shift (IS) of a Mössbauer nucleus of an absorber with respect to a source can be expressed as^{11,12}

$$IS = C\{|\Psi_a(0)|^2 - |\Psi_s(0)|^2\}, \qquad (1)$$

where C is a constant related to the radius ratio of excited to ground states and is positive for ¹⁵¹Eu nuclei.⁹ Thus, the lower IS can be attributed to a lower electron density at the ¹⁵¹Eu nucleus, $|\Psi(0)|^{2.9}$ As the electronegativity of F ($x_{\rm E}$ = 3.98) is larger than that of O ($x_{\rm O}$ = 3.44),¹³ the covalency of the Eu-O bond is larger than that of the Eu-F bond. Therefore, the increasing tendency of the IS of Eu^{3+} ion in the fluorophosphate glass shown in Fig. 6 indicates the increased s-electron density of Eu^{3+} , i.e., covalency of the Eu ligand by the oxygen coordination. Since the IS of Eu^{3+} in a phosphate glass $(70P_2O_5 \cdot 30Na_2O \cdot 1Eu_2O_3)$, where no F^- ions exist, is 0.23 mm/sec, the increasing slope of IS against x in Fig. 6 indicates a preferential coordination of divalent O²⁻ to a rare-earth ion rather than monovalent F⁻ ions in a mixed-anion host. On the other hand, the negative IS in the fluoride glass suggests that the local basicity of Eu³⁺

ions is lower than that in the single europium (III) fluoride. That is, the second nearest neighbors of Eu^{3+} , which forms a chemical bond with the nearest F^- ions, can be acidic cations, such as Al^{3+} ions with higher electron polarizing ability, rather than Ca^{2+} and Ba^{2+} ions. From the peak assignment of the phonon sideband spectra in Fig. 4, it is clear that the band around 1060 cm^{-1} is due to the P-O⁻ stretching vibrations of the phosphate end member,^{14,15} and the band around 600 cm⁻¹, to the Al-F stretching mode.¹⁶ Therefore, in fluoride glasses the Al-F bond is coordinated to the Eu^{3+} ion, while in fluorophosphate glasses the oxygen ions of P-O⁻ bonds are coordinated to the rare-earth ion. In addition, as plotted in Fig. 8, the electron-phonon coupling strength g of the P-O⁻ stretching mode, which is given as the intensity ratio of the phonon sideband to that of the pure electronic line, 1,7 increases with increasing x and almost saturates around x = 30. Accordingly, phonons due to the P-O⁻ bond with the highest frequency are considered to contribute to the multiphonon relaxation of rare-earth ions.

B. Upconversion of Er^{3+} in glass

The energy-level diagram and a possible upconversion mechanism of Er^{3+} by 0.80- μ m excitation are shown in Fig. 7. The efficiency of upconversion fluorescence depends on the probability of multistep excitation by the excited-state absorption or the energy transfer between adjacent excited ions, as well as the quantum efficiency of the emitting level. By either process, the probability becomes proportional to the lifetime of the intermediate excited states. The lifetime of an excited state, τ is dominated by the radiative and nonradiative decay rates and given by

$$1/\tau = W_{\rm RD} + W_{\rm p} + \cdots, \qquad (2)$$

where $W_{\rm RD}$ is the radiative decay rate and W_p is the nonradiative decay rate due to the multiphonon relaxation. To minimize the nonradiative loss, it is advantageous to suppress W_p , which is given, at T=0 K, by¹⁷

$$W_{p}(0) = W_{0}(0) \exp[-\alpha \Delta E / \hbar \omega], \qquad (3)$$

$$\alpha = \ln(p/g) - 1 , \qquad (4)$$

$$p \simeq \Delta E / \hbar \omega$$
, (5)

where ΔE is the energy gap to the next lower level, g is the electron-phonon coupling strength, p is the number of phonons consumed during multiphonon relaxation, and $W_0(0)$ is the decay rate at $\Delta E = 0$ and T = 0. Accordingly, W_p increases with increasing $\hbar \omega$ and g. The presence of high-energy stretching vibrations of network polyhedra⁵ in most oxide glasses lowers the efficiency of upconversion. However, in some heavy-metal oxide glasses, the cutoff frequency is still low and comparable to those of fluoride glasses,¹⁸ which results in the observation of the upconversion fluorescence in oxide glasses such as tellurite and gallate systems.¹⁹ In fluorophosphate glasses, the cutoff frequency was 1060 cm⁻¹, which is higher than those of germanate and tellurite glasses. Furthermore, as



FIG. 7. Energy-level diagram and a possible mechanism of two-step excitation for the Er^{3+} ion under 800-nm excitation.

shown in Fig. 8, the rapid increase of the electronphonon coupling strength g with phosphate addition also contributes to W_p .

Therefore, the compositional dependence of fluorescence intensity in Fig. 1 can be attributed to the coupling of the high-energy phonon to rare-earth ions in fluorophosphate glasses, since the multiphonon decay rate increases with increasing $\hbar\omega$ and g, as expected from Eqs. (3)-(5).

C. Temperature dependence of upconversion fluorescence

The rate of multiphonon relaxation at a temperatrue T is influenced by the population of the phonon mode, which is given by the Planck distribution function²⁰ n(T), where $n(T) = [\exp(\hbar\omega/kT) - 1]^{-1}$. In the relaxation process of creating p Stokes phonons, the probability becomes proportional to $[n(T)+1]^p$. The multiphonon relaxation rate is then given by^{1,5,21}

$$W_{p}(T) = W_{p}(0)[n(T)+1]^{p}$$

= $W_{p}(0)[1-\exp(-\hbar\omega/kT)]^{-p}$, (6)

where $W_p(0)$ is the multiphonon decay rate at 0 K given



FIG. 8. Compositional dependence of the electron-phonon coupling strength of the P-O stretching mode.

by Eq. (3). For the host of larger $\hbar\omega$, the temperature dependence becomes small, whereas $W_p(0)$ is large. Assuming that W_p is large enough compared with $W_{\rm RD}$, which holds for the levels with low quantum efficiency such as ${\rm Er}^{3+}$: ${}^4I_{9/2}$ and ${\rm Er}^{3+}$: ${}^4I_{11/2}$, one can calculate the relative lifetime of the intermediate excited state of the ${\rm Er}^{3+}$ ion by Eqs. (2) and (6). Since the probability of upconversion excitation is expected to be proportional to the lifetime of the intermediate excited state, it is interesting to investigate the temperature dependence of the intermediate levels of the ${\rm Er}^{3+}$ ion. In the case of 800-nm excitation of ${\rm Er}^{3+}$ in this study, the absorption occurs from the ground ${}^4I_{15/2}$ to the excited ${}^4I_{9/2}$ level. The energy gap of ${}^4I_{9/2}$ to the next ${}^4I_{11/2}$ level is about 2000 cm⁻¹, while that from ${}^4I_{11/2}$ to ${}^4I_{13/2}$ is about 3300 cm⁻¹. The estimated phonon-energy dependence of the relative lifetime of ${}^4I_{9/2}$ and ${}^4I_{11/2}$ are shown as a func-



FIG. 9. Temperature dependence of the calculated lifetime of Er^{3+} : (a) ${}^{4}I_{9/2}$ and (b) ${}^{4}I_{11/2}$ level for various $\hbar\omega$.



FIG. 10. Temperature dependence of the intensity of upconversion fluorescence for $\Box: y = 0$ and $\circ: y = 5$ glass. That of the $40AlF_3 \cdot 10ErF_3 \cdot 30CaF_2 \cdot 20BaF_2$ glass is also shown by \blacklozenge for comparison.

tion of the temperature in Figs. 9(a) and 9(b), respectively. Clearly, the temperature dependence of the fluoride host $(\hbar\omega = 600 \text{ cm}^{-1})$ is larger than that of the fluorophosphate glass ($\hbar\omega = 1100 \text{ cm}^{-1}$). The phonon energy of 800 cm⁻¹ corresponds to that of tellurite glasses,¹⁹ in which the lifetime is long compared with that of the fluorophosphate glass. Here, the ratio of the lifetime between different $\hbar\omega$ is also a function of the energy gap. The ratio of the lifetime of fluoride to that of fluorophosphate is larger for the energy gap of 3300 cm⁻¹ (${}^{4}I_{11/2}$) than for 2000 cm⁻¹ (${}^{4}I_{9/2}$). The relative ratio of the upconversion intensity of two glasses shown in Figs. 3(a) and 3(b) is plotted in Fig. 10 in addition to that of $40A1F_3 \cdot 10ErF_3 \cdot 30CaF_2 \cdot 20BaF_2$ glass. This tendency is similar to that shown in Fig. 9(b) rather than that in Fig. 9(a). Accordingly, the level crucial to the efficiency of upconversion process can be ${}^{4}I_{11/2}$ rather than ${}^{4}I_{9/2}$. This interpretation is supported by the fact that the emission due to the ${}^{2}H_{9/2} \rightarrow {}^{4}I_{15/2}$ transition is not efficiently observed in the upconversion spectra under 802-nm excitation, which indicates that the second-step excitation does not start from the $4I_{9/2}$ level and thus a three-step excitation is needed to reach the ${}^{2}H_{9/2}$ level. Therefore, we conclude that the ${}^{4}I_{9/2}$ level decays to the ${}^{4}I_{11/2}$ level by a rapid multiphonon relaxation and excitation process starting from this level.

V. CONCLUSIONS

The Er^{3+} -upconversion intensity of fluorophosphate glasses decreased drastically with increasing phosphate content. The temperature dependence of the intensity for the fluorophosphate glass, on the other hand, was much weaker than that for the fluoride, since the P-O stretching mode with a larger phonon energy is coupled to rareearth ions in the fluorophosphate glass. These differences in local structure and multiphonon mechanisms were confirmed by the ¹⁵¹Eu Mössbauer spectroscopy and pho-

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non sideband measurement. It is concluded that the efficiency of the upconversion process is dominated by the lifetime of the intermediate level, which is influenced by the phonon mode locally coupled to the rare-earth ion in the glass.

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