Energy transfer processes and Ho³⁺: ⁵I₅ level population dynamics in chalcohalide glasses

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Population dynamics of Ho³⁺: ⁵I₅ levels doped in chalcohalide glasses were investigated through the analysis of energy transfer processes. Excitation migration (${}^{5}I_{5}, {}^{5}I_{8} \rightarrow {}^{5}I_{8}, {}^{5}I_{5}$) predicted from the Dexter model dominated over the cross relaxation (${}^{5}I_{5}, {}^{5}I_{8} \rightarrow {}^{5}I_{7}, {}^{5}I_{7}$). Depopulation of the ${}^{5}I_{5}$ level due to upconversion was suppressed when the 890 nm excitation source was used since this pump wavelength significantly depressed the excited-state absorption transition from the ${}^{5}I_{5}$ level. The dominant energy transfer channel leading to the depopulation of the ${}^{5}I_{5}$ level is the energy transfer upconversion process between Ho³⁺ ions.

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I. INTRODUCTION

Energy transfer (ET) processes among rare-earth (RE) ions in various crystal and glass hosts have generated great research interest.^{1–3} The analysis of energy transfer provides information essential to the characterization and optimization of RE-doped laser materials. The representative ET processes frequently encountered in RE-doped materials include cross relaxation (CR), energy migration (EM), and energy transfer upconversion (ETU).⁴ Excited-state absorption (ESA) also contributes to upconversion although it is not considered an energy transfer process.

These energy transfer processes often act as quenching routes for the lasing level and result in degradation of laser performance.^{5,6} In this case, a materials system has to be carefully designed to minimize the interactions among RE ions.^{7,8} Proper selection of the host composition is important for glasses with low RE solubility to suppress the formation of RE clustering.⁷ Co-doping of elements such as Al³⁺ or Ga³⁺ to silica or sulfide glasses is effective in reducing the inhomogeneous distribution of RE ions.^{7,8} On the other hand, the CR, ETU, and ESA processes play important roles during upconversion.⁹ The EM process also accelerates energy transfer by migrating the excited energy to the point where the energy transfer is effective.¹⁰ Therefore, it is important to analyze the nature of these processes since they directly influence the transition probability and the population dynamics of the energy levels in RE ions.

Trivalent holmium ions exhibit several near infrared (NIR)¹¹ and visible (Vis)^{12,13} fluorescence, providing broad potential applications toward NIR/Vis solid-state lasers and *U*-band fiber-optic amplifiers.¹⁴ Several fluorescence and energy transfer channels have been reported for Ho³⁺-doped materials.¹⁵ However, these processes were focused on a limited number of energy levels such as the (${}^{5}S_{2}, {}^{5}F_{4}$) and ${}^{5}I_{7}$ levels. Recently, it has been reported that the ${}^{5}I_{5} \rightarrow {}^{5}I_{7}$ transition in Ho³⁺ provided the crucial 1.6 μ m emission for the *U*-band fiber-optic amplification.¹⁴ However, population dynamics of the ${}^{5}I_{5}$ level have not been investigated since this level is strongly quenched by the multiphonon relaxation (MPR) process in many glasses. Therefore, a detailed analysis on the population dynamics of the ${}^{5}I_{5}$ level is necessary to

provide crucial information for the realization of the practical amplifier materials.

From the materials point of view, it is critical to use host materials with low phonon energy if one were to realize the emission from the ${}^{5}I_{5}$ and ${}^{5}F_{3}$ levels in Ho³⁺. Although chalcogenide glasses are considered to be promising, they have limited transmittance in the visible spectrum that makes the upconversion luminescence difficult to observe.¹⁶ In this respect, chalcohalide glasses appear to be attractive since they have an extended transmission window in the visible region in addition to their low vibrational phonon energies.^{17,18}

In this work, we present spectroscopic properties and energy transfer mechanisms in Ho³⁺-doped chalcohalide glasses. In particular, we have focused on several depopulation processes associated with the ⁵I₅ level which is the upper emission level of the 1.6 μ m fluorescence. First, cross relaxation and energy migration processes from the ⁵I₅ level were evaluated using the microscopic parameters and critical distances of these two processes. Then, two other processes involved during the upconversion process, i.e., energy transfer upconversion and excited-state absorption, were analyzed as a function of temperature and excitation wavelength. A comprehensive analysis on the population dynamics of the ⁵I₅ level can provide a clue to the potential *U*-band fiber-optic amplifier and lasers.

II. EXPERIMENTAL PROCEDURES

The composition of chalcohalide glass used in this study was $0.95(\text{Ge}_{0.29}\text{Ga}_{0.05}\text{S}_{0.66})+0.05\text{CsBr}$ in atomic fraction. Ho³⁺ was added in the elemental form with concentrations of 0.02, 0.05, 0.1, and 0.2 mol %. Purities of all starting materials were 99.9% or better. Batches containing approximately 7 g of the starting elements were prepared inside an argonatmosphere glovebox. Silica ampoules containing the starting powders were sealed while being continuously evacuated. Powders in ampoules were then heated to 950 °C in a rocking furnace. At this temperature, for the homogenization of glass melts, the furnace was rocked for 12 h and the melts were subsequently quenched by immersing silica ampoules into water. After annealing at their respective glass transition temperatures for several hours, specimens were cut into disks of 10 mm in diameter and 2 mm in thickness and were polished for optical measurements. Sulfide $(Ge_{30}Ga_2As_8S_{60})$ and selenide $(Ge_{30}Ga_2As_8Se_{60})$ glasses were also prepared following similar procedures. Ho³⁺ concentrations in these glasses were 0.4 and 0.3 mol %, respectively.

Absorption spectra were recorded using an UV/Vis/NIR spectrophotometer. For the measurement of fluorescence spectra, specimens were placed in a cryostat cooled by compressed He gas. Specimen temperatures were then controlled between 20 and 293 K. An excitation beam with 860–940 nm in wavelength was supplied from a continuouswave (CW) Ti-sapphire laser pumped by an Ar⁺ laser. The fluorescence spectra were recorded using a photomultiplier tube (for Vis) or an InSb (for NIR) detector combined with a monochromator and a lock-in amplifier. Excitation spectra of the 491 nm emission from Ho³⁺ were recorded by measuring the changes in the emission intensity as the wavelength of the pumping beam increased from 860 to 940 nm. Time evolution of the fluorescence was monitored through a digital oscilloscope while modulating the excitation beam by a mechanical chopper. Laser power was kept at $\sim 150 \text{ W/cm}^2$ during all measurements.

III. RESULTS

A. NIR and Vis fluorescence

Excitation to the ${}^{5}I_{5}$ level of Ho³⁺ using the 910 nm beam revealed several Stokes (NIR) and anti-Stokes (Vis) fluorescence. The most dominant NIR fluorescence is located at 2.00 μ m corresponding to the electronic transition of ${}^{5}I_{7}$ $\rightarrow {}^{5}I_{8}$. Two additional bands centered at 1.66 and 1.18 μ m were found as shown in Fig. 1(a). With an increase in Ho³⁺ concentration, the intensity ratios between two NIR emissions (I_{1.66 μ m/I_{2.00 μ m}) showed a considerable decrease probably due to the cross relaxation (${}^{5}I_{5}$, ${}^{5}I_{8}$, ${}^{5}F_{1}$, ${}^{5}I_{7}$).¹⁴ Energy transfer upconversion (${}^{5}I_{5}$, ${}^{5}I_{8}$, ${}^{5}F_{1}$) followed by an another cross relaxation process (${}^{5}F_{3}$, ${}^{5}I_{8}$, ${}^{5}F_{5}$, ${}^{5}I_{7}$), also affected the emission intensity.¹⁹}

In case of the visible fluorescence, blue $({}^{5}F_{3} \rightarrow {}^{5}I_{8})$, green $({}^{5}S_{2}, {}^{5}F_{4} \rightarrow {}^{5}I_{8})$, and red $({}^{5}F_{5} \rightarrow {}^{5}I_{8})$ emission bands were evident as shown in Fig. 1(b). Among them, we will focus on the blue emission only since it is most important for the current energy transfer analysis. There are several aspects of this blue emission worth mentioning. First, the intensity of the blue emission decreased as temperature increased due to the activated multiphonon relaxation (MPR) between the ${}^{5}F_{3}$ and the next lower level. Second, the intensity ratio between the blue and red emission $(I_{0.49 \ \mu m}/I_{0.66 \ \mu m})$ decreased by increasing the Ho³⁺ concentration. This is most probably due to the cross relaxation process of ${}^{5}F_{3}$, ${}^{5}I_{8} \rightarrow {}^{5}F_{5}$, ${}^{5}I_{7}$.¹⁹ Third, intensity of the blue emission showed a quadratic dependence on the power of the excitation beam for all excitation wavelengths within the ${}^{5}I_{8} \rightarrow {}^{5}I_{5}$ absorption band. This indicates that the upconversion process leading to the blue emission is a two-photon excitation process.²⁰

B. Fluorescence decay from the ⁵I₅ level

Figure 2 shows the decay curves of the ${}^{5}I_{5} \rightarrow {}^{5}I_{7}$ transition for glasses doped with 0.02, 0.1, and 0.2 mol % Ho³⁺. A



FIG. 1. Emission spectra at (a) near infrared (NIR) and (b) visible (Vis) wavelengths from chalcohalide glasses doped with 0.02 and 0.2 mol % of Ho³⁺. The excitation wavelength was 910 nm. Emission intensities were normalized to the intensities of the 2.00 and 0.66 μ m emission bands for NIR and visible spectra, respectively.

specimen with 0.02 mol % Ho³⁺ showed a near-exponential decay with the measured lifetime of 9.38 ms. This value is comparable to the radiative lifetime (9.44 ms) calculated from the Judd-Ofelt analysis.^{21,22} This led to the high quantum efficiency of ~99%, clearly due to the small phonon energy of chalcohalide glasses (~245 cm⁻¹).^{17,22} As Ho³⁺ concentration increased, the lifetime of the ⁵I₅ level started to decrease and decay curves deviated from the exponential behavior. One of the energy transfer processes responsible for this decrease is cross relaxation (${}^{5}I_{5}$, ${}^{5}I_{8} \rightarrow {}^{5}I_{7}$, ${}^{5}I_{7}$) as evidenced from the decrease in the emission intensity ratio (I_{1.66 µm}/I_{2.00 µm}). Further analysis described in the follow-



FIG. 2. Decay curves of the 1.66 μm emission (5I_5 level) from chalcohalide glasses doped with (a) 0.02, (b) 0.1, and (c) 0.2 mol % of Ho^{3+} ions.

TABLE I. Measured lifetimes (τ_m) of the Ho³⁺: ⁵I₅ level at 293 K for chalcohalide glasses doped with different concentrations of Ho³⁺. The radiative lifetime (τ_r) of the ⁵I₅ level was 9.44 ms as calculated from the Judd-Ofelt analysis. The overall energy transfer rate (W_{ET}) was obtained using the relation of $W_{ET}=1/\tau_m-1/\tau_r$ [see Eq. (5)].

Ho ³⁺ Concentration (mol %)	$ au_m$ (ms)	$\frac{W_{ET}}{(s^{-1})}$
0.02	9.38	1
0.05	8.41	13
0.1	6.18	56
0.2	4.16	134

ing sections showed that the energy transfer upconversion (${}^{5}I_{5}, {}^{5}I_{5} \rightarrow {}^{5}I_{8}, {}^{5}F_{1}$) also affected lifetimes of the ${}^{5}I_{5}$ level. Values of the ${}^{5}I_{5}$ level lifetime for several Ho³⁺ concentrations are summarized in Table I and important depopulation channels can be found from Fig. 3.

C. Decay and excitation spectra from the ${}^{5}F_{3}$ level

The calculated radiative lifetime of the ${}^{5}F_{3}$ level was \sim 430 μ s and is comparable to the lifetime measured at 20 K from the glass containing 0.02 mol % Ho³⁺ (Table II). On the other hand, lifetime measured at 293 K was \sim 320 μ s, was considerably shorter than the value obtained at 20 K due to increased multiphonon relaxation with temperature. In addition, when the Ho³⁺ concentration was 0.2 mol %, the measured lifetime was further reduced to \sim 240 μ s. This de-



FIG. 3. Schematic energy level diagram of Ho^{3+} ion together with several depopulation channels that affect the population and lifetimes of the Ho^{3+} : ⁵I₅ level. EM, CR, ETU, and ESA are energy migration, cross relaxation, energy transfer upconversion, and excited state absorption, respectively.

TABLE II. Measured lifetimes of the Ho³⁺: ${}^{5}F_{3}$ level for 0.02 and 0.2 mol % Ho³⁺-doped chalcohalide glasses. Lifetimes for 0.2 mol % Ho³⁺ specimens under 890 nm excitation were obtained by fitting the latter part of the decay curve (see text for details).

Ho ³⁺ Concentration (mol %)	Excitation (nm)	$ au_m$ (ms)	Temperature (K)
0.02	910	0.44	20
		0.32	293
0.2	910	0.24	20
		0.18 (fast), 1.6 (slow)	293
	890	2.7 (slow)	20
		1.7 (slow)	293

crease in measured lifetimes of the ${}^{5}F_{3}$ level with Ho³⁺ concentration is attributed to the cross relaxation process (${}^{5}F_{3}, {}^{5}I_{8} \rightarrow {}^{5}F_{5}, {}^{5}I_{7}$) as explained previously.¹⁹ Presence of this energy transfer is also supported by the decrease in the emission intensity ratio ($I_{0.49 \ \mu m}/I_{0.66 \ \mu m}$) with increasing Ho³⁺ concentration as shown in Fig. 1(b).

Figure 4 shows the decay curves of blue emission from the ${}^{5}F_{3}$ level for the glass with 0.2 mol % Ho³⁺. Both curves were recorded at 20 K, each at excitation wavelengths of 890 and 910 nm, respectively. When Ho³⁺ ions were excited by the 890 nm pump source, the blue emission at 491 nm decayed fast at the beginning followed by a slow decay as shown in Fig. 4(a). The lifetime estimated from the latter (slower) part of the decay curve was 2.7 ms. On the other hand, only a fast decay with a lifetime of 240 μ s was observed from the 910 nm excitation. This large dependence of the measured lifetime on the pump wavelength is a clear indication of the different upconversion mechanism operating for each different excitation wavelength. Lifetimes of the



FIG. 4. Decay curves of blue (491 nm) emissions for 0.2 mol % Ho³⁺-doped chalcohalide glass obtained by exciting at (a) 890 nm and (b) 910 nm in wavelength. The inset shows the excitation spectra of the blue emission where the excitation wavelength for each decay curve is shown by an arrow. All spectra were recorded at 20 K.



FIG. 5. Excitation spectra of the blue emission (491 nm) for 0.2 mol % Ho³⁺-doped chalcohalide glass measured at (a) 20 K, (b) 100 K, (c) 293 K, and (d) the absorption spectrum corresponding to the ${}^{5}I_{8} \rightarrow {}^{5}I_{5}$ transition. The excitation spectrum for glass with 0.02 mol % Ho³⁺ was also included in (a) for a comparison. The excitation spectrum at 293 K was enlarged by a factor of two.

 ${}^{5}F_{3}$ level under different conditions (Ho³⁺ concentration, excitation wavelength, and measurement temperature) are summarized in Table II.

The excitation spectra were recorded using a glass doped with 0.2 mol % Ho³⁺ at several different temperatures (Fig. 5) by monitoring the ${}^{5}F_{3} \rightarrow {}^{5}I_{8}$ emission located at 491 nm. The excitation spectra were composed of two bands, each centered at 890 and 910 nm in wavelength, respectively. The 890 nm band was more intense than the other in the spectrum recorded at 20 K. However, as temperature increased to 100 and 293 K, the excitation spectra were dominated by the 910 nm band. Furthermore, relative intensity of the excitation bands changed significantly with the Ho³⁺ concentration in glasses as shown in Fig. 5(a). These results again suggest that the upconversion mechanism depends on the Ho³⁺ concentration, measurement temperature, and excitation wavelength. However, the excitation spectra recorded at temperatures of 100 and 293 K did not show any noticeable concentration dependence.

IV. DISCUSSION

As mentioned previously, one of the main purposes of the current research is to develop the materials for the U-band fiber-optic amplifier and lasers operating in the

1625–1675 nm region. In this respect, population densities of the upper emission level of 1.66 μ s fluorescence, that is the Ho³⁺: ⁵I₅ level, are important. The population of this level is, however, affected by several depopulation processes in addition to the ground-state absorption by the pump source. They are energy migration (EM), cross relaxation (CR), energy transfer upconversion (ETU), and excited-state absorption (ESA) as shown in Fig. 3. This section will provide a detailed analysis on the population dynamics of the ⁵I₅ level in Ho³⁺.

A. Cross relaxation and excitation migration

This section is focused on the CR (${}^{5}I_{5}, {}^{5}I_{8} \rightarrow {}^{5}I_{7}, {}^{5}I_{7}$) and EM (${}^{5}I_{5}, {}^{5}I_{8} \rightarrow {}^{5}I_{8}, {}^{5}I_{5}$) processes among donor ions that affect the population of the ${}^{5}I_{5}$ level. The EM process enhances the probabilities of CR and ETU processes by transferring the excitation energy to the site where the energy transfer to the acceptor is efficient. Therefore, the migration of energy among Ho³⁺ ions can significantly influence the population dynamics of the ${}^{5}I_{5}$ level.

1. Microscopic parameters

To get a precise description on the Ho³⁺-Ho³⁺ energy transfer, the microscopic parameters of the energy migration (C_{EM}) and cross relaxation (C_{CR}) need to be calculated. Dexter's model for dipole-dipole interaction was employed to obtain C_{EM} and C_{CR} defined as follows²³

$$C_{EM} = \frac{R_{EM}^{\rm o}}{\tau_r},\tag{1}$$

$$C_{CR} = \frac{R_{CR}^6}{\tau_r}.$$
 (2)

Here, R_{EM} (or R_{CR}) is the critical distance of the energy migration (or cross relaxation) process. This is defined as the distance between two interacting ions at which the energy transfer rate becomes equal to the radiative transition rate of the specific energy level. τ_r is a radiative lifetime of the ⁵I₅ level.

Critical distance for the energy migration is then expressed as¹

$$R_{EM}^{6} = \frac{3hc^{2}Q_{A}Q_{D}\tau_{r}}{8\pi^{4}n^{2}}\int \frac{f_{D}(E)f_{A}(E)}{E^{2}}dE,$$
 (3)

where *h*, *c*, and *n* are Planck's constant, speed of light, and refractive index, respectively. Q_D (or Q_A) and f_D (or f_A) are the area and normalized line-shape function of the 900 nm emission (or 900 nm absorption) cross-section, respectively. The cross section of the 900 nm emission was calculated from the 900 nm absorption cross-section using McCumber relation.²⁴ From values of the cross sections in Fig. 6(a), R_{EM} was calculated using Eq. (3) and then, C_{EM} was estimated from Eq. (1). All values thus obtained are listed in Table III.

A different approach is necessary to calculate the value of R_{CR} , since there is no spectral overlap between the 1.6 μ m emission and 2.0 μ m absorption [Fig. 6(b)]. In this case, the



FIG. 6. Spectral superposition between the emission and absorption cross-sections used to calculate the microscopic parameters of the (a) energy migration and (b) cross relaxation. An emission sideband assisted by the four phonons was also included (see the text for the explanation).

overlap integral between phonon sidebands of the emission and absorption cross-sections needs to be considered.³ Phonon sidebands can be simulated from the measured cross sections by considering appropriate phonon modes as well as the probability of phonon creation and annihilation.²⁵ Figure 6(b) shows one example of the phonon side band of 1.66 μ m emission with the assistance of four phonons. Then, the critical distance of the nonresonant cross relaxation can be expressed²⁵

$$R_{CR}^{6} = \frac{6c \tau_r g_{low}}{(2\pi)^4 n^2 g_{up}} \sum_{N=0}^{\infty} \int \sigma_{emis}(\lambda_N^+) \sigma_{abs}(\lambda) d\lambda$$
$$\times \left(\sum_{k=0}^{N} P_{(N-k)}^+ P_k^- P_k^+\right). \tag{4}$$

Here, g_{low} and g_{up} are the degeneracy of the ${}^{5}I_{7}$ and ${}^{5}I_{5}$ levels, respectively. *N* is the total number of the phonons

involved in the cross relaxation process. $\sigma_{emis}(\lambda_N^+)$ is the measured cross section of the 1.66 μ m emission translated to the 2.00 μ m absorption cross-section $[\sigma_{abs}(\lambda)]$ by the amount of $E = N\hbar\omega$. $P_{(N-k)}^+$ is the probability of multiphonon emission with *N*-*k* the number of phonons while P_k^- means the probability of multiphonon absorption with *k* the number of phonons. This method has been successfully applied to calculate microscopic parameters of the nonresonant energy transfers in LiYF₄ crystal doped with Tm³⁺ and Ho³⁺ (Ref. 25). The Huang-Rhys factor used during the calculation was 0.1, a typical value for rare-earth ions. The coupled phonon energy was assumed to be 245 cm⁻¹ (Refs. 17 and 26). Values of R_{CR} and C_{CR} calculated in our study are also given in Table III.

2. Energy transfer processes activities

As is evident from Table III, the value of C_{EM} for chalcohalide glass is approximately an order of magnitude larger than C_{CR} . Since microscopic parameters are proportional to the energy transfer rates, one can easily accept the presence of active energy migration among Ho³⁺ ions. In fact, this result was anticipated since the EM process is quasiresonant while CR is a nonresonant process that requires the assistance of several phonons. A similar trend in the C_{EM}/C_{CR} ratio was observed in Tm³⁺-doped fluorozirconate glasses where cross relaxation is also a phonon-assisted process.²⁷ The number of phonons involved in the cross relaxation process was either 2, 3, or 4 and each contributed approximately 22, 62, and 16% of the overall CR process, respectively (Table III). This relative contribution was calculated from the relative magnitude of CR due to a specific number of phonons involved compared to the total CR rates.²⁵

To have insight into the general properties of the cross relaxation and excitation migration, microscopic parameters of sulfide, and selenide glasses doped with Ho³⁺ were also calculated. The phonon energies of 375 cm⁻¹ and 200 cm⁻¹ were used for sulfide and selenide glasses, respectively.^{28,29} As also shown in Table III, the values of C_{EM} are larger than C_{CR} for both glasses, similar to the case of chalcohalide glass. These results again indicate that the excitation migration among Ho³⁺ ions plays an important role in the Ho-Ho energy transfer. The value of C_{EM} for chalcohalide glass, however, is smaller due to small cross sections in chalcoha-

TABLE III. Calculated microscopic parameters (*C*) and critical distances (*R*) for the excitation migration (EM) and cross relaxation (CR) processes. The number of phonons involved in the cross relaxation process is also indicated with their contribution (in %) for several Ho³⁺-doped glasses.

Glass	$\frac{C_{EM}}{(10^{-41} \text{ cm}^6/\text{s})}$	$\frac{C_{CR}}{(10^{-41} \text{ cm}^6/\text{s})}$	R _{EM} (Å)	R _{CR} (Å)	N (# of phonon) (% contribution)
Chalcohalide	0.20	0.02	5.2	3.5	2-3-4 (22-62-16)
Sulfide	5.44	3.17	7.1	6.5	1-2-3 (3-94-3)
Selenide	3.18	0.03	6.2	2.9	2-3-4-5 (14-45-37-4)

lide compared to those for other glasses. In addition, the CR parameter in sulfide glass is high since this process needs only two phonons to bridge the energy difference. On the other hand, it was necessary to incorporate three or four phonons in other glasses. Since the probability of the energy transfer process assisted by phonon generation is inversely proportional to the phonon numbers involved, sulfide glass showed the largest C_{CR} value among three glasses compared. These microscopic parameters will be used later to calculate the macroscopic parameters of a cross relaxation assisted by an energy migration.

B. Energy transfer upconversion and excited-state absorption

The blue upconversion fluorescence at 491 nm due to the ${}^{5}F_{3} \rightarrow {}^{5}I_{8}$ transition is directly related to the population density of the ${}^{5}I_{5}$ level as shown in Fig. 3. Therefore, spectroscopic analysis of the blue emission can provide insight into the population dynamics of this level. Careful investigation of the population dynamics at several different temperatures showed that the upconversion mechanism depends not only on temperature but also on the Ho³⁺ concentration and excitation wavelengths.

1. Upconversion at 20 K

Upon excitation to the ${}^{5}I_{5}$ level, there are two possible routes to populate the ${}^{5}F_{3}$ level. First, Ho³⁺ ions in the ground state are excited to the (${}^{5}F_{1}$, ${}^{5}G_{6}$) levels (hereafter, denoted as ${}^{5}F_{1}$) by a successive absorption of two pump photons (${}^{5}I_{8} \rightarrow {}^{5}I_{5} \rightarrow {}^{5}F_{1}$). Then they relax to the final ${}^{5}F_{3}$ level through the multiphonon relaxation. This is a typical excitedstate absorption (ESA) process involving only one Ho³⁺ ion. On the other hand, two Ho³⁺ ions, both excited to the ${}^{5}I_{5}$ level, can interact to excite one ion further to the ${}^{5}F_{1}$ level while the other loses energy and decays to the ground state. The ion promoted to the ${}^{5}F_{1}$ level subsequently relaxes nonradiatively to the ${}^{5}F_{3}$ level and this process is known as the energy transfer upconversion (ETU).

Investigation on time evolution of the upconverted fluorescence can help to distinguish between these two possible routes. For the pulsed excitation, fluorescence intensity will rise first followed by a gradual decay if the ETU process is a dominant process for the upconversion.³⁰ This is due to the time delay needed for the energy transfer to take place and also due to the dependence of the ETU process on the lifetime of the intermediate excited level. On the other hand, during the ESA process the fluorescence simply decays following its own lifetime since the ESA process takes place fast within the duration of the pulsed excitation (<10 ns).³⁰ In case of excitation by a continuous-wave source, different decaying behavior appears. When the ETU process is dominant, the measured lifetime of the upper emission level becomes considerably longer than its intrinsic value (τ_r) since the population feeding from the intermediate level continues for the lifetime of the intermediate level (τ_i) even after the cease of the excitation. This is especially true when τ_i is much longer than the intrinsic lifetime of the upper emission level. However, when the ESA upconversion mechanism is



FIG. 7. Rise curves of the 1.66 μ m (⁵I₅) and 491 nm (⁵F₃) emissions recorded at 20 K for 0.2 mol % Ho³⁺-doped chalcohalide glasses. Rise time for the 491 nm emission was different for different excitation wavelengths of 890 and 910 nm.

dominant, decay behavior remains similar to that of the pulsed excitation.

The decay curves in Fig. 4 recorded under the CW excitation can be used to interpret the upconversion mechanisms in our glass systems. When Ho³⁺ was excited by the 890 nm pump source at 20 K, the measured lifetime of the luminescence at $t > \tau_r$ is 2.7 ms. It is considerably longer than the intrinsic lifetime (430 μ s) of the upper-emission (⁵F₃) level as shown in Fig. 4(a). Therefore, one can propose that the mechanism for the blue upconversion fluorescence is the ETU process. On the other hand, when the 910 nm excitation source was used, the upconversion fluorescence appeared to be governed by the ESA process because the measured lifetime of the ${}^{5}F_{3}$ level was only 240 μ s, close to its intrinsic value [Fig. 4(b)]. Therefore, at a temperature of 20 K, the dominant upconversion mechanism from the ${}^{5}I_{5}$ level is the ETU process when the 890 nm excitation source was used while the ESA process is responsible for the upconversion under the 910 nm excitation. A similar change in the upconversion mechanisms with the pump wavelength was also reported from CsCdBr₃ crystal doped with Ho³⁺ (Ref. 13).

The assignment of the upconversion mechanisms is also supported by the rise curves of several emissions at 20 K (Fig. 7). When the ETU process is dominant, population of the ${}^{5}F_{3}$ level reaches the steady-state after its intermediate level (in this case, the ${}^{5}I_{5}$ level) due to the time necessary for the energy transfer. This is exactly true under the 890 nm pumping. In contrast, the rise time for the ${}^{5}F_{3}$ level population is similar to that of the ${}^{5}I_{5}$ level when the 910 nm pumping was used, supporting the presence of the strong ESA process.

To date, our discussion has focused on glass containing 0.2 mol % of Ho³⁺. However, Fig. 5(a) also shows the excitation spectrums from a glass with a low Ho³⁺ content of 0.02 mol %. One can easily find that intensity of the 890 nm band decreased sharply compared to the spectrum recorded from the glass with the 0.2 mol % Ho³⁺. The probability of the ETU process increases with Ho³⁺ concentration since the energy transfer rate depends on the ionic distance (*R*), e.g., R^{-6} for the dipole-dipole interaction. Therefore, it is reason-



FIG. 8. Decay curves of the blue (491 nm) emission under different excitation wavelengths and temperatures. The solid line in curve (b) corresponds to the result of fitting with a double exponential decay function.

able to expect an active ETU process from the glasses with a high rare-earth concentration. A decrease in the intensity of the 890 nm band with a decreasing Ho^{3+} concentration reaffirms the proposition that the excitation band at 890 nm is associated with the ETU process. On the other hand, the ESA process does not directly depend on the rare-earth concentration in glass and thereby, provides a relatively large contribution in the glass containing a small amount of Ho^{3+} .

2. Upconversion at high temperatures

At 20 K, the dominant upconversion mechanisms for 890 and 910 nm excitation were the ETU and ESA processes, respectively. However, as the temperature increased to 100 and 293 K, excitation spectra in Fig. 5 changed in shape most probably due to the changes in the main upconversion routes.

This behavior can be clearly visualized from the decay curves in Fig. 8. When a 910 nm excitation was used, the curve measured at 20 K decayed monotonically following the intrinsic decaying behavior of the ${}^{5}F_{3}$ level as shown in Fig. 8(a). However, the same curve showed a slow decay part as in Fig. 8(b), if measured at 293 K. According to our previous discussion, this long tail is a clear indication of the ETU process. Fitting of the decay curve in Fig. 8(b) was attempted by assuming a double exponential function with 20% of the decay due to ETU (lifetime of 1.6 ms) and 80% due to ESA (lifetime of 180 μ s) processes. As temperature increased, the ETU process also affected the upconversion in Ho³⁺ even when the 910 nm excitation source was used. However, its contribution to the total depopulation of the ${}^{5}I_{5}$ level was smaller than the ESA process. On the other hand, the temperature appeared to have a negligible effect on the upconversion process when the 890 nm beam was used for excitation as shown in Figs. 8(c) and 8(d) and the whole upconversion was dominated by the ETU process.

3. Upconversion mechanisms and their origins

The dominant upconversion mechanisms at different temperatures and excitation wavelengths are summarized as follows. At 20 K, upconversion is mainly supported by the ETU process when an 890 nm beam is used as a pump source. The dominant upconversion route, however, is changed to the ESA process when the wavelength of the excitation beam is 910 nm. On the other hand, blue upconversion at room temperature is evident only when a 910 nm pump is used and in this case, the dominant upconversion route is the ESA process. This means that the spectrum of the ESA transition is located at the longer wavelength side of the GSA spectrum.¹³

In terms of this spectral structure proposed, the origin of different upconversion mechanisms can be explained as follows. At low temperature, absorption cross-section due to the ${}^{5}I_{8} \rightarrow {}^{5}I_{5}$ transition should be small under the 910 nm excitation since only lower-lying Stark sublevels of the ⁵I₈ manifold were populated. Therefore, the overall population of the ⁵I₅ available for the ESA upconversion is small at low temperature. As temperature increases, however, the GSA cross sections at the 910 nm excitation band becomes strong since the upper Stark levels of the ${}^{5}I_{5}$ manifold are also populated. This results in the strong ESA upconversion at room temperature. On the other hand, the magnitude of the spectral overlap between the emission $({}^{5}I_{5} \rightarrow {}^{5}I_{8})$ and ESA spectra decreases with increasing temperature due to the blue (red) shift of the emission (ESA) spectra. Therefore, the dominant process for the 491 nm blue upconversion changes from an ETU to ESA process with increasing temperature.

It is worth mentioning that a detailed analysis of the upconversion mechanisms provided valuable information on the most suitable excitation wavelength for *U*-band amplification. Considering relatively strong upconversion with 910 nm excitation, it is desirable to use the 890 nm excitation band to maximize the population density of the ${}^{5}I_{5}$ level, that is, the starting level of the 1.66 μ m emission. In this case, the upconversion due to the ESA process becomes negligible and therefore, the population dynamics of the ${}^{5}I_{5}$ level can be analyzed by considering the rates of the EM, CR, and ETU processes quantitatively.

C. Energy transfer process rates

When the glasses are excited by a 890 nm pump source, the measured lifetime of the ${}^{5}I_{5}$ level is affected by the cross relaxation and energy transfer upconversion. Both are accelerated by the excitation migration process that moves energy to the site where the energy transfer is efficient. These processes are related to the total transition rate of the ${}^{5}I_{5}$ level (W_{total}) as follows:

$$W_{total} = \frac{1}{\tau_m} = \frac{1}{\tau_r} + W_{mpr} + W_{ET} = \frac{1}{\tau_r} + W_{mpr} + (W_{CR} + W_{ETU}).$$
(5)

Here τ_r (9.44 ms) is a radiative lifetime of the ${}^{5}I_{5}$ level. W_{mpr} is the multiphonon relaxation rate from the ${}^{5}I_{5}$ level which was assumed to be zero for the chalcohalide glasses. W_{ET} is the total energy transfer rate. W_{CR} and W_{ETU} are the rates of CR and ETU processes assisted by excitation migration, respectively. Values of W_{ET} were calculated from Eq. (5) using measured and radiative lifetimes as shown in Table I.

	W	W	n_{Ho}		
Glass	$(10^{-19} \text{ cm}^3 \text{ s}^{-1})$	(s^{-1})	(s^{-1})	(mol %)	$(10^{20} \text{ cm}^{-3})$
Chalcohalide	0.02(0.006)	0.1(0.04)	134 (134)	0.2	0.6
Sulfide	2.01(0.81)	30.3(12.30)	281 (299)	0.4	1.5
Selenide	0.29(0.04)	3.0(0.45)	250 (253)	0.3	0.7

TABLE IV. Calculated macroscopic parameters of cross relaxation and energy transfer rates from Eqs. (5) and (7) for the diffusion model. Values in parenthesis are obtained from the hopping model.

If we assume a random distribution of RE ions in glass matrix as well as rapid excitation migration among RE ions, rate equation formalism can be used to calculate the energy transfer rates.²³ Under the condition of weak excitation and small population feeding from the upper levels, the rate equation of the ${}^{5}I_{5}$ level can be expressed as

$$\frac{dn}{dt} = \sigma \phi n_{Ho} - \left(\frac{1}{\tau_r} + W_{mpr} + w_{CR} n_{Ho} + w_{ETU} n\right) n.$$
(6)

Here, *n* is the population density of the ${}^{5}I_{5}$ level. σ and ϕ are the cross section of the ${}^{5}I_{8} \rightarrow {}^{5}I_{5}$ absorption and pump photon flux, respectively. w_{CR} and w_{ETU} are defined as the macroscopic parameters of CR and ETU processes, respectively. n_{Ho} is the total Ho³⁺ concentration. Equations (5) and (6) can be combined to yield $W_{CR} = w_{CR}n_{Ho}^{31,32}$ and w_{CR} can be expressed as follows for the diffusion and hopping model.^{23,31}

Diffusion model:
$$w_{CR} = 28(C_{CR})^{1/4}(C_{EM})^{3/4}n_{Ho}$$
, (7)

Hopping model:
$$w_{CR} = 13(C_{CR})^{1/2}(C_{EM})^{1/2}n_{Ho}$$
, (8)

Now we can determine W_{CR} using w_{CR} obtained from Eqs. (7) and (8). The results are shown in Table IV. The calculation of W_{ETU} from Eq. (5) is straightforward. The ratio of W_{ETU}/W_{CR} is larger than 10³ for the chalcohalide glass, implying that most ions excited to the ⁵I₅ level were further excited to the ⁵F₁ level via the ETU process. Of the three glasses investigated, sulfide glass showed the largest CR rate (30.3 s⁻¹). This is mainly due to the small number of phonons involved in the CR process as shown in Table III which in turn considerably increases the probability of cross

relaxation. In addition, Table IV shows that W_{ETU} values are considerably larger than W_{CR} for all glasses. As explained previously, the CR process is a nonresonant energy transfer which requires the assistance of phonons while the ETU process is a resonant process. This difference makes the ETU process more favorable than the CR process.

V. CONCLUSIONS

The energy transfer processes controlling the population dynamics of the Ho³⁺: ⁵I₅ level doped in chalcohalide glasses were evaluated. The microscopic parameter of the energy migration (EM) process from the ⁵I₅ level is approximately 10 times higher than the cross relaxation (CR) process due to the nonresonant nature of the latter process. In addition, analysis of the upconversion mechanisms leading to the blue emission of 491 nm in wavelength indicated that the upconversion can be minimized by using the 890 nm excitation beam at room temperature. The calculation of energy transfer rates for cross relaxation (including energy migration) and energy transfer upconversion processes, however, showed that the ETU process is the most dominant depopulation route of the Ho³⁺: ⁵I₅ level.

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