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OPTICAL PROPERTIES AND PERSISTENT SPECTRAL HOLE BURNING OF Eu^{3+} IN Ge-Ga-S GLASS WITH ALKALI HALIDES

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Optical properties of Eu^{3+} in glassy Ge-Ga-S-MX (MX = alkali halide) materials were investigated. An efficient persistent spectral hole burning (PSHB) was also observed suggesting the potentials of these materials for high-density optical storage media. Several hole properties such as hole growth rates, burning power dependency, relaxation process and multi-hole formation were investigated to understand the hole burning mechanism. Reduction of Eu^{3+} to Eu^{2+} following the absorption of the pumping light was the most probable mechanism for the hole burning. Dependence of the spectroscopic properties on composition and temperature was related to the local phonon modes effectively coupled to the Eu^{3+} ion. Local structure surrounding rare-earth ions was investigated using the phonon side bands and site-dependent spectroscopy.

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1. Introduction

Glassy semiconductors in the Ge-Ga-S system have been widely investigated as hosts for rare-earth ions [1,2]. The glasses possess low phonon vibration energy and this property has been a crucial advantage toward the development of several important fiber-optic amplifiers in the optical communication system [2]. Modification of the glass composition with the addition of alkali halides further decreased the phonon energy and thereby increased the excited-state lifetimes as well as quantum efficiency of of emissions from rare-earth ions [3]. Addition of alkali halide also enhanced the visible transmittance of the host matrix and provided opportunities for other noble photonic applications including persistent spectral hole burning (PSHB) devices.

PSHB phenomenon is based on the formation of a hole-like feature inside the absorption spectrum of rare-earth ions [4]. First, rare-earth ion is excited by absorbing the pumping light of a specific frequency (ω_L). If this ion cannot return to its original state due to the physical or chemical changes, it will result in a decrease in the intensity of the absorption profile at the specific frequency and thus make a hole-like feature at ω_L. This hole burning becomes persistent if this artificial state induced by the external field lasts longer than its intrinsic fluorescence lifetime. PSHB process can be applied to the high-density optical memory devices with a recording density in excess of 10^{12} bits/cm^2 [4,5]. Frequency domain optical storage using multi-holes on the absorption spectrum, time domain storage with stimulated photon-echo phenomena and holographic recordings are only a few examples of the potential application areas [4-6]. However, most PSHB has been possible only at temperatures below 20 K except for the recent reports on the room temperature PSHB phenomenon using glasses doped with Sm^{2+} or Eu^{3+} [7-13]. However, host materials were mainly based on the oxide glasses and normally required long burning time of > 5 min with less than 10 % change in the depth profile [8-13].

This low hole-burning efficiency hindered the realization of high density optical storage using the PSHB process.

On the other hand, sulfide glasses generally provide high quantum efficiency and long excited-state lifetimes of rare-earth ions and therefore can become promising host materials. However, there has been no report on the PSHB in sulfides except for the low temperature (<10K) observation in Eu^{2+}-doped CaS and MgS crystals [14,15]. Formation of Eu^{3+} in sulfide glass was not known before the recent report by Chung and Heo [16] from Ge-Ga-S-KBr glasses. They also showed that a hole in Eu^{3+} experienced approximately 30 % intensity change with burning time of 1 min, considerable increase in the efficiency of the hole-burning process compared to its oxide counterpart.

Formation of Eu^{3+} and the accompanying changes in the spectroscopic properties of rare-earth ions in Ge-Ga-S-alkali halide glasses [3,17] are related to the changes in local structure surrounding rare-earth ions. Since Eu^{3+} ion has a simple electronic structure and non-degenerating excited state of $^5D_0$, it has been widely used as a probe ion for the investigation of the local structure of the glass matrix using fluorescence line narrowing (FLN) or phonon side-band (PSB) spectra [18-21]. Therefore, formation of Eu^{3+} in these sulfide glasses provides a good opportunity to elucidate the local structure of rare-earth ions.

This paper reports the spectroscopic and hole-burning properties of Eu^{3+} in Ge-Ga-S-MX (MX=alkali halide) glasses. Mechanism of the hole burning is proposed based on the various hole properties. Local structure surrounding Eu^{3+} is proposed from the phonon side band (PSB) and fluorescence line narrowing (FLN) spectra of these chalcohalide glasses.

2. Experimental procedures

Host composition of $Ge_{18}Ga_{18}S_{64}$ (at.%) has been selected since it shows good glass-forming ability and high transmittance to the visible light [3,17]. Alkali halides (MX = KBr, CsBr, CsI or CsCl) were added in the form of (1-x) ($Ge_{18}Ga_{18}S_{64}$) + x MX where x=0.08, 0.12, 0.14, 0.15 and 0.18 in mole fraction. 0.1 mol% of Eu was doped to each sample. High purity elemental starting materials (Ge, Ga, S, MX, Eu) were batched into the silica ampoule in a dry box filled with high purity argon gas. The ampoules were sealed and the melting was done at 950 °C for 10 hours in a 3-zone rocking furnace. After melting, the ampoules were quenched into water and annealed for 1 hour at 310 °C. The glass was recovered by breaking the ampoule and was cut into the disks followed by the optical polishing.

UV/VIS/NIR absorption spectra were recorded to find the absorption edge of the glasses as well as to identify the absorption lines due to the 4f transitions in Eu^{3+} ion. For the measurement of the spectroscopic properties, a dye laser (rhodamine 6G) driven by an argon-ion laser was used to pump the Eu^{3+} ion to the $^5D_0$ level. Linewidth of the laser was less than 0.7 cm^{-1}. A glass specimen was placed inside the cryostat (Oxford CCC1104) cooled by compressed helium gas to control the temperature of the sample. Fluorescence from the sample was collected at an angle perpendicular to the excitation source and detected with a photo-multiplier tube (PMT) via a 1/4 m monochromator. Lock-in amplifier with mechanical chopper and a digital oscilloscope were used to record the signal. To obtain the excitation spectrum of the Eu^{3+}:$^5D_0$ level, Eu^{3+}:$^5D_0$□$^7F_2$ fluorescence was monitored while continuously increasing the wavelength of a dye laser with a computer-driven stepping motor (Coherent Wave-scan^{TM}). For the hole burning experiment, laser beam with 50 mW in power was illuminated on the sample. The excitation spectrum was recorded and compared to the one obtained before the burning. When measuring the hole-burning spectrum, a neutral density (ND) filter of 1/40 was placed in front of the excitation source to reduce the interference of the probe beam on the hole spectrum.

3. Results and discussion

3.1. Spectroscopic properties of Eu^{3+} in Ge-Ga-S-MX glasses

No absorption or fluorescence from Eu^{3+} was observed when the measurement was done at room temperature. However, as temperature decreased, characteristic fluorescence lines from the

Eu^{3+}:$^5D_0$ level to lower-lying $^7F_1$ (~ 593 nm) and $^7F_2$ (~ 612 nm) levels clearly appeared from all glasses except for one containing CsI. (Fig. 1) No evidence of Eu^{3+} formation was found in glasses without addition of alkali halides even at temperatures as low as 10 K. A strong emission line of $^5D_0 \rightarrow {}^7F_2$ transition was monitored to investigate the temperature dependence of the Eu^{3+} formation as shown in Fig. 2. Emission from Eu^{3+} ions decreased as temperature increased and eventually disappeared above ~ 130 K. This decrease in the emission at high temperature can be due to the interaction between the excited-state ion and the phonon modes of the host glass, resulting in strong multiphonon relaxation. However, the active phonon mode in the glasses has energy smaller than 350 cm^{-1} [2,3,17] while the energy gap between the $^5D_0$ and the next lower-lying energy level is larger than 12,000 cm^{-1}. Furthermore, the lifetimes of the excited energy level showed no change with the temperature. Therefore, it is hard to believe that the multiphonon relaxation is an important factor for disappearance of the Eu^{3+} emission at high temperature.

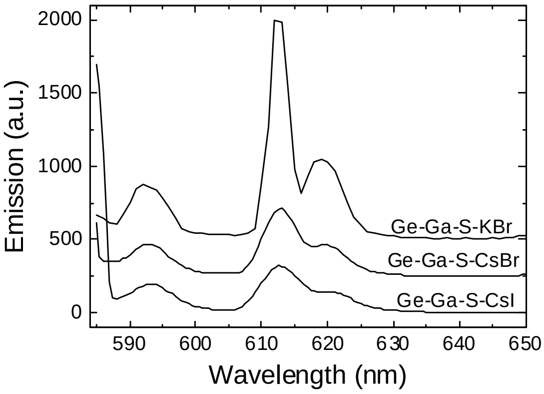


Fig. 1. Fluorescence from the Eu^{3+}:$^5D_0$ level in 0.85 ($Ge_{18}Ga_{18}S_{64}$) + 0.15 MX (MX = CsCl, CsBr or KBr) glasses at 10 K. Excitation wavelength was 579.7 nm. Baselines of the spectra were shifted for clarity.

Changes in the electronic state of Eu ions from Eu^{3+} to Eu^{2+} with temperature has been observed from the metallic compounds of Eu_3S_4 [22], $EuCu_2Si_2$ and $Eu(Pd_{1-x}Fe_x)_2Si_2$ [23,24]. Here, electronic interaction of 4f electron with the conduction band at high temperature was responsible for the Eu^{3+}→ Eu^{2+} transition. Thermal agitation can also change the coordination of rare-earth ions in the glass and it in turn, can change the electronic state of the ion [25]. In any case, the change in the electronic state of Eu ions at high temperature appears to provide more plausible explanation than the multiphonon relaxation mechanism.

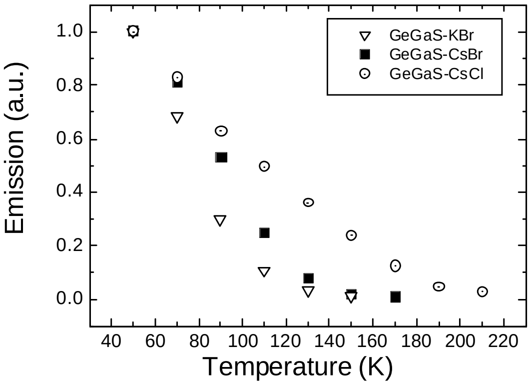


Fig. 2. Changes in the emission intensity from the Eu^{3+}: $^5D_0 \rightarrow {}^7F_2$ transitions in 0.85 ($Ge_{18}Ga_{18}S_{64}$) + 0.15 MX (MX = CsCl, CsBr, KBr) glasses at different temperature.

Formation of Eu^{3+} in the Ge-Ga-S-MX glasses also showed the compositional dependency. Specifically, fluorescence from the Eu^{3+} ion appeared only when the concentration ratio of MX:Ga in glass was equal to or greater than unity. The same compositional dependency was also observed previously from the lifetime increase of Dy^{3+} in Ge-Ga-S-CsBr glasses [3]. Changes in the local structure around rare-earth ions were considered to be responsible. Furthermore, formation of Eu^{3+} ions strongly depended on the relative concentration between Ga and Ge regardless of the alkali halide concentration. From these observation, it became clear that amount of Ga and alkali halide in glasses were crucial for the formation of Eu^{3+}. This further indicated the importance of local structure surrounding Eu ions and it will be discussed later.

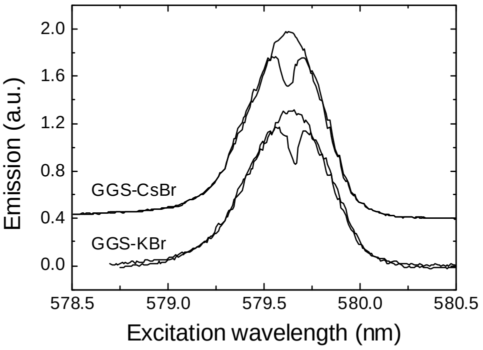


Fig. 3. Excitation spectra of the Eu^{3+}:$^5D_0$ level in 0.85 ($Ge_{18}Ga_{18}S_{64}$) + 0.15 MX (MX = CsBr or KBr) glasses before and after the hole burning at 77 K. Hole was burnt at 579.7 nm with 50 mW power for 1 min. Baselines of the spectra were shifted for clarity.

3.2. Persistent spectral hole burning in Eu^{3+} - doped Ge-Ga-S-Mx glasses

Hole burning was performed on the inhomogeneously broadened absorption spectrum of Eu^{3+} by irradiating 578.5 nm laser beam for 1 min at 77 K. A clear hole was found from the $Ge_{18}Ga_{18}S_{64}$ glass containing CsBr or KBr (Fig. 3). Depth of the hole was ~ 30 % of the original intensity. Depth of the hole increased significantly compared to those in oxide glasses which were only ~10% even after 5 min of hole burning [8-13]. This large hole depth represents the high hole burning efficiency in the present glasses. Precise analysis on the evolution of the hole depth with time provided quantitative figures on the quantum efficiency of hole burning process. Hole burning quantum efficiency is normally represented as [26,27]

$$\eta = \frac{\left[{d\phi(t)}/{dt} \right]_{t=0}}{4(I/\hbar\omega_L)(1/\pi\gamma_{hole})\phi_0(1-\phi_0-R)\sigma_{tot}} \tag{1}$$

where $\phi(t)$ is the time-dependent transmittance function at the burning frequency of ω_L and I is the laser intensity. ϕ_0 is the initial sample transmittance at ω_L and R represents the reflectance. σ_{tot} is the absorption cross section of rare-earth ions within the total inhomogeneous band width. γ_{hole} is the hole width at the half maximum intensity. Time-dependent transmittance $\phi(t)$ is the decrease in transmittance, i.e., increase in the depth of the hole with time and can be expressed as [26,28]

$$\phi(t) = \phi_0\left[1-\exp(-Kt)\right] \tag{2}$$

where K accounts for the rate constant of the process, [$d\phi(t)$/dt] at t=0.

Changes in depth of the hole with time in the Ge-Ga-S-KBr glass were monitored and were compared with the oxide glasses doped with Eu^{3+} [10,28,29]. As shown in Fig. 4, the initial growth rate of the hole was approximately 3.9×10^{-2} s^{-1} and it is about 50 times higher than the number found from Eu^{3+}-doped silicate glasses [28]. It clearly proved the high hole burning quantum efficiency in the present chalcohalide glasses.

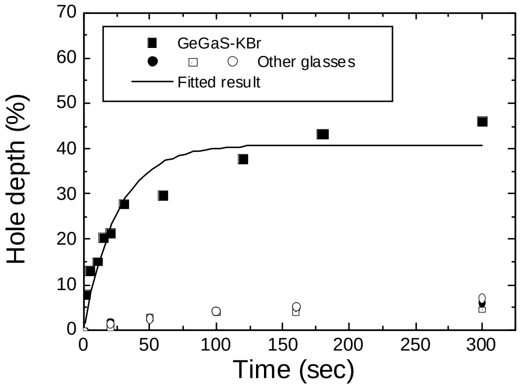


Fig. 4. Changes in the intensity of the hole at a center wavelength as a function of the burning time in Ge-Ga-S-KBr glass. Holes were burnt with a burning power of 50 mW at 77 K. Solid line is a result of fitting using eq. (2).

Erasure of the existing holes with the second light source is an another important procedure for the realization of read-write optical storage media. PSHB phenomenon in most glasses suffered from the poor erasing abilities. An argon laser of 488 or 514 nm in wavelength was used to erase the hole in oxide glasses with only a partial success [8]. On the other hand, the hole was completely erased in Ge-Ga-S-KBr glass by irradiating Ar^{+} laser for 10 min as shown in Fig. 5. This result again clearly shows the advantage of using the present glasses. Since the energy of an argon laser corresponds to the ionization energy of the Eu^{2+}, erasure of the hole with an argon laser strongly indicated the presence of Eu^{3+}→Eu^{2+} transition during the initial hole burning process [8]. Thus, the complete recovery of the hole in the glass supported the possible hole burning mechanism (Eu^{3+}→Eu^{2+}) and this will be discussed in detail later.

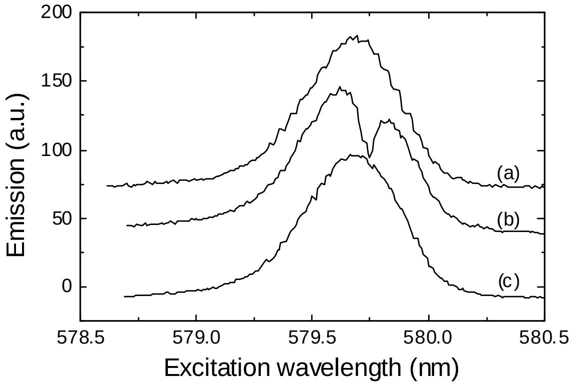


Fig. 5. Formation and erasure of the holes with the Argon laser irradiation. (a) before the hole burning, (b) after the hole burning and (c) after the Argon laser irradiation.

Recording multi-holes without contamination of the previously burnt one is also highly important but has not been observed in glass systems. Burning of the second hole near the first one usually resulted in the refilling of the previously burnt holes [7,8,30]. This refilling has been attributed to the redistribution of the elements participating the hole burning process during the irradiation of the second burning light. Therefore, it was necessary to make a compromise between the burning time and the depth of the previously burned holes [31] to achieve multi-hole formation. However, successive burning on the Ge-Ga-S-KBr glass under the identical condition showed less influence on the previous hole as illustrated in Fig. 6, suggesting another advantage of using chalcohalide glasses.

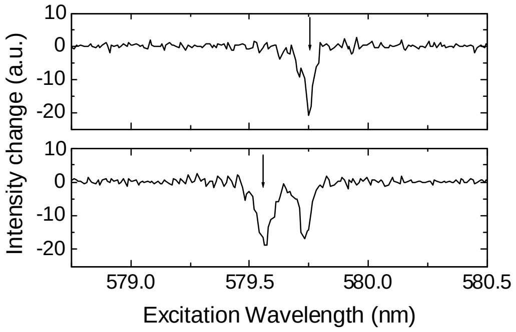


Fig. 6. Changes in the intensity of the holes in Ge-Ga-S-KBr glass during the two successive hole formation with 579.73 nm (top) and 579.57 nm (bottom), irradiation. Hole burning condition was kept same as that in Fig. 4.

Holes on the inhomogeneously broadened spectrum are regarded as metastable states since the strong external field drove them. Thus, they are likely to return to their original states and refill the holes. Relaxation of the burnt holes is described by the two-level system comprised of the burnt (Eu^{2+}) and un-burnt state (Eu^{3+}) with the energy barrier in-between [4,27,32,33]. Relaxation of the hole is achieved either by overcoming the energy barrier or by tunneling through the barrier. Stability of the burnt hole, therefore, is determined by the relaxation rate of the burnt hole as a function of temperature and/or time.

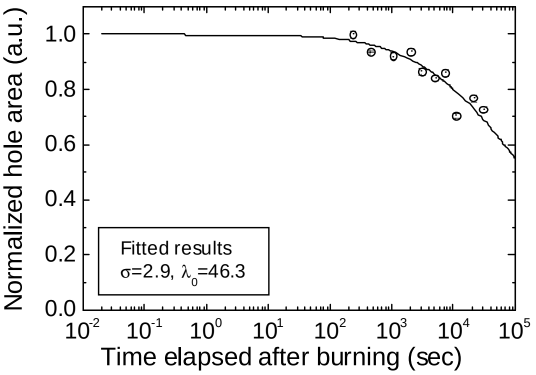


Fig. 7. Hole area change with time in Eu^{3+}-doped Ge-Ga-S-KBr glass. After the hole burning at 77 K, hole burning spectra were monitored. Hole areas were normalized to that immediately after the burning. Solid line is the result of fitting using eq. (3).

Holes start to relax as soon as the burning light stopped. Area of the hole after the time *t* was examined to investigate the stability of the hole with time in Ge-Ga-S-KBr glasses. The number of burnt centers [*N(t)*] remaining after time *t* can be expressed as follows [27,33].

$$\frac{N(t)}{N(0)} = \int_0^{\infty} g(\lambda) exp[-\Gamma_0 t\, exp(-\lambda)] d\lambda \tag{3}$$

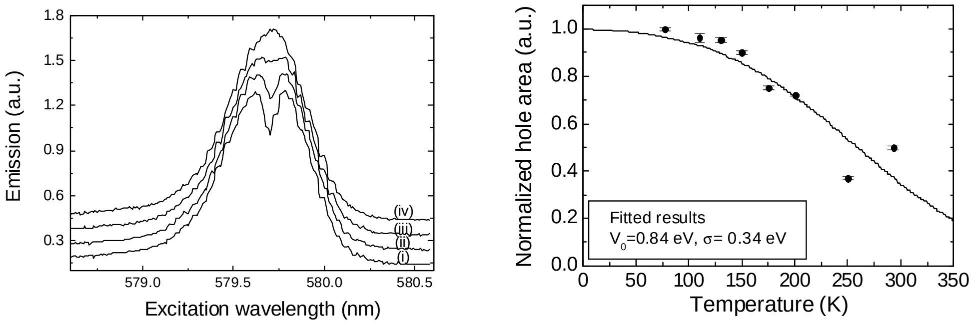
N(0) indicates the number of burnt states at *t*=0. *g(λ)* is the distribution of the tunneling parameter

λ and usually assumed to have Gaussian distribution in the following form [27,33]:

$$g(\lambda)=\frac{1}{\sqrt{2\pi\sigma^2}}exp\left[-\frac{(\lambda-\lambda_0)^2}{2\sigma^2}\right] \tag{4}$$

where σ represents the full width at half maximum intensity of the Gaussian distribution and λ_0 is the center value of λ in $g(\lambda)$. Γ_0 is the attempt frequency and λ is a tunneling parameter equal to $(2mV)^{1/2}d/\hbar$ where m and d are the mass of tunneling entity and the width of the barrier, respectively. V is the energy barrier height.

The hole remained for up to 10^5 seconds after the burning for one min at 77K. Burning light was 579.7 nm in wavelength with power of 50 mW. The experimental results in Fig. 7 were fitted using eq. (3) by assuming the pure electronic nature of the hole relaxation with the attempt frequency (Γ_0) of $5\times10^{14}s^{-1}$ [33]. From the result of fitting, the center value of the tunneling parameter (λ_0) and the width of the Gaussian distribution function (σ) were calculated to be 46.3 and 2.9, respectively. From these values the dominant relaxation rate [$\Gamma_0 exp(-\lambda_0)$] of 3.9×10^{-6} s^{-1} was obtained This is smaller than those calculated from other Eu^{3+}-doped systems (> 10^{-5} s^{-1}) [8,34]. It implies that the relaxation of the holes proceeds slowly in our chalcohalide glasses compared to the relaxation in other Eu^{3+}-doped materials.



a b

Fig. 8. (a) Hole burning spectra after the thermal annealing at (i) 77 K, (ii) 150 K, (iii) 293 K, and (iv) before the hole burning. (b) Change in the normalized hole area with the annealing temperature. The original hole was burnt at 77 K and kept at each temperature for one minute. All hole spectra measured at 77 K. Result of the fitting using eq. (5) was shown as a solid line.

Thermal stability of the holes in Ge-Ga-S-KBr glass was examined by annealing for 1 min at various temperatures (T) and the result is shown in Fig. 8. Hole centers with barrier energies less than the given thermal energy were relaxed back to the unburned state during the annealing process. All specimens were cooled down to 77 K for measurements after annealing. Hole has clearly survived even after annealing at room temperature. The fraction of hole centers survived after annealing at temperature T_{max} during time τ_{hold} is given by equation (5), assuming the Gaussian distribution of the barrier energy V [27,35].

$$f=1-\int_0^{kT_{max}ln(\Gamma_0\tau_{hold})} g(V)dV \tag{5}$$

$g(V)$ is the Gaussian distribution function of a barrier height as equation (4). k is the Boltzmann constant. The hole areas after annealing at each temperature were plotted in Fig. 8(b) after correction for the time relaxation during the measurement [27]. They fitted well to eq. (5) as shown with a solid line in Fig. 8(b). Estimated values of V_0 and σ were 0.84 eV and 0.34 eV, respectively. Values of V_0 obtained from other Eu^{3+}-doped glasses were ~0.3 eV even after 5 min of burning time [10,32,36,37].

Therefore, Ge-Ga-S-KBr glass showed the highest energy barrier and it again supported the high stability of burnt holes in these chalcohalide glasses.

3.3. Hole burning mechanism in Eu^{3+}-doped Ge-Ga-S-MBr glasses

Unlike the glasses containing alkali bromides, the glass with CsCl showed no evidence of hole burning even though there is clear fluorescence from Eu^{3+}. In addition, glasses with CsBr or KBr showed similar hole burning properties. This suggested that the hole formation is mostly dependent on the type of halide ions rather than alkali ions. Based on the partial hole-filling with Ar^{+}-laser irradiation in addition to the absence of anti-hole in the hole burning spectra, Fujita et al.[8,9,29] proposed that the photo-reduction of Eu^{3+} to Eu^{2+} is a main mechanism of hole burning in oxide glasses. As shown in Fig. 3, no anti-hole was found in our glasses and a complete erasure of the hole was achieved by the argon laser irradiation. Therefore, reduction of Eu^{3+} to Eu^{2+} during the hole burning is the most plausible mechanism. Photo-induced process normally requires the absorption of several photons and the precise number is dependent on its mechanism. Changes in the hole area, i.e., changes in the amount of burnt holes were measured while varying burning power at 77 K. Log-log plot of this result in Fig. 9 gave a slope of ~ 0.82. This result implied that the hole formation in Ge-Ga-S-MX glass is an one-photon process.

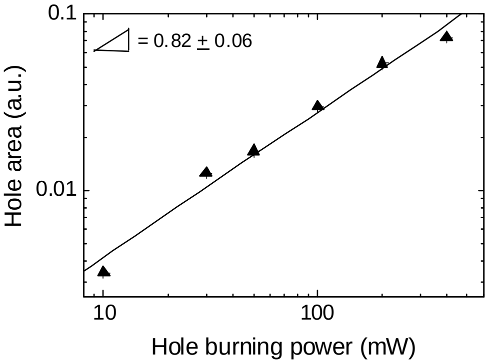


Fig. 9. Dependency of the hole area on the pumping power. Linear fit to the data was shown as a solid line.

It has been reported that the glass should be prepared under the reducing atmosphere or it needs to be irradiated by x-ray to realize the hole burning in oxide glasses [7-13]. Oxygen-related defects are formed during these special treatments and these defects are crucial for the photo-reduction of Eu^{3+} to Eu^{2+} [11-13]. However, no such treatment was necessary for our chalcohalide glasses to achieve an efficient hole burning in our glasses. This suggests that the photo-reduction path in chalcohalide glasses is different from other oxide glasses and the hole formation became possible due to the inherent properties of the host glass.

As explained previously, formation of Eu^{3+} was highly sensitive to the composition of the host glasses. This has been attributed to the possible formation of local chemical complex of Eu-Ga-S-MX. Fluorescence of Eu^{3+} also showed strong temperature dependence and the change in the oxidation states $Eu^{3+} \rightarrow Eu^{2+}$ due to the fluctuation of electrons between the localized 4f level and conduction band in Eu^{3+} was proposed [16,23,24]. However, electron spin resonance (ESR) signals revealed that a large portion of Eu ions is still in Eu^{2+} state at 77 K [16].

Taking those spectroscopic behaviors of Eu^{3+} into account, it is possible to propose the process of $Eu^{3+} \rightarrow Eu^{2+}$ photo-reduction upon the absorption of one-photon. Since the formation of Eu^{3+} ions is sensitive to the host glass composition, the process must be closely related to the local structure around Eu^{3+}. The formation of $[GaS_{3/2}X]^{-}:M^{+}$ (X = Br or Cl and M = Cs or K) complex has been suggested upon the addition of alkali halides into Ge-Ga-S glasses [3,17,38,39]. Formation of the complex became possible only when CsBr/Ga ratio in glass was larger than unity. Since the formation of Eu^{3+} became evident only on glasses with CsBr/Ga ≤ 1 [3,17], it is possible to assume that the presence of $[GaS_{3/2}X]^-$ complex (X = Br or Cl) near Eu ions is crucial to the formation of Eu^{3+}. Interaction of Eu^{3+} ions with nearby ligands containing halogen ions can provide an electron necessary for the treatment of Eu^{3+} to Eu^{2+} [40].

The mechanism of the hole burning in Eu^{3+} can be summarized as follows. First, the burning light excites Eu^{3+} ions to the $^5D_0$ level. Since this level is located near the local conduction band or a charge transfer level of its local neighbor, 4f electrons of the excited Eu^{3+} ions can interact with the conduction band resulting in the transformation of the Eu^{3+} ion into Eu^{2+}. Other Eu^{2+} ions or free electrons in glass act as hole-trapping centers necessary to complete the reaction. Since this process involves only electronic interaction, the hole formation is efficient and provides the high quantum efficiency. Since Cl^- has higher electro-negativity than Br^-, it is difficult for electrons to be released from Cl^- to Eu^{3+} to form Eu^{2+}. Therefore, the hole burning was not possible from the glass containing CsCl.

3.4. Local structure around Eu^{3+} ion

As noted before, formation of Eu^{3+} as well as its hole burning requires well-coordinated local structure surrounding Eu^{3+} ions. A similar compositional dependence on the lifetimes of the excited-state energy levels in Dy^{3+} was also reported [3,17]. Thus, it is important to investigate the local structure of Eu^{3+} in Ge-Ga-S-CsBr (or KBr) glasses to fully understand the nature of Eu^{3+} formation in these glasses. Changes in the molecular structure of Ge-Ga-S glasses with CsBr addition was investigated by Shin *et al.* [3,17] using Raman scattering spectroscopy. Tverjanovich *et al.* [38,39]proposed the structural model of Ge-Ga-S-CsCl glass. Both groups suggested the formation of $[GaS_{3/2}Br]^-$ or $[GaS_{3/2}Cl]^-$ subunits with the addition of CsBr or CsCl into GeS_2-Ga_2S_3.

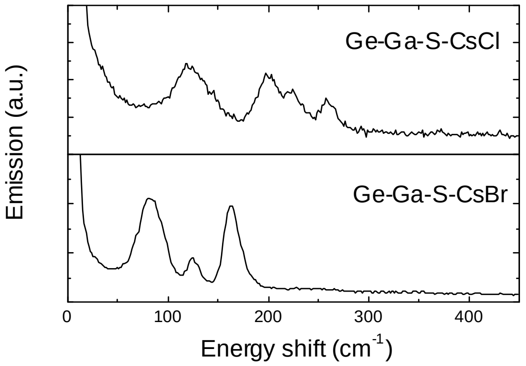


Fig. 10. Phonon side band spectra obtained by monitoring the fluorescence from Eu^{3+}:$^5D_0$ in 0.85 $(Ge_{18}Ga_{18}S_{64})$ + 0.15 MX (MX = CsBr, KBr) glasses at 10 K.

Phonon side band (PSB) spectra can give direct information on the phonon modes that are effectively coupled to the fluorescing energy level of rare-earth ions [21,41]. PSB spectra of Ge-Ga-S-CsCl and Ge-Ga-S-CsBr glasses doped with Eu^{3+} were recorded and were shown in Fig. 10. PSB spectra were measured at 10 K by monitoring the fluorescence of the $^5D_0 \rightarrow {}^7F_2$ while changing the laser energy near the ground-state absorption of the $^7F_0 \rightarrow {}^5D_0$ transition. Five distinct phonon modes located at ~120, 149, 199, 226, and 259 cm^{-1} were identified from Ge-Ga-S-CsCl glass. Most PSB modes matched well to the vibration modes of Ga_2Cl_6 dimer [42] and $CsGaS_{1.5}Cl$ [39]. It also matched fairly well to the modes of $EuCl_3$ compound [43]. Therefore, it seems that Eu^{3+} ions are located next to Cl^- ions in the structural units of $[GaS_{3/2}Cl]^-$ or Ga_2Cl_6 and coordination number of Cl^- around Eu^{3+} is 6~8 as in $EuCl_3$. PSB spectrum for Ge-Ga-S-CsBr glass also suggests that Br ions are also located in the vicinity of Eu^{3+}, possibly in the form of Ga_2Br_6 or $[GaS_{3/2}Br]^-$ units with the coordination number of 6~8 as Ge-Ga-S-CsCl glass.

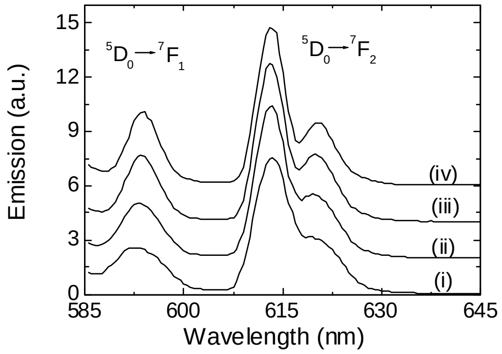


Fig. 11. Fluorescence measured from Eu^{3+}:$^5D_0$ in 0.85 ($Ge_{18}Ga_{18}S_{64}$) + 0.15 CsBr glass at the excitation wavelength of (i) 579.3, (ii) 579.5, (iii) 579.7, and (iv) 579.9 nm, respectively. All measurements were done at 10K.

If the proposed structural model is reasonable, Er^{3+} ion should be located next to the well-coordinated structure. This is supported by the narrow inhomogeneous linewidth of the excitation spectrum in Fig. 3. Full width at half maximum (FWHM) intensity is ~ 13 cm^{-1} and it is much narrower than those in other oxide glasses (~ 30 cm^{-1}) [8-13]. Fluorescence line narrowing (FLN) spectra measured from Ge-Ga-S-CsBr glass at 10K further supported the formation of the well-coordinated structure. As shown in Fig. 11, no remarkable change was found in the absorption profile of the $^5D_0$ level as the wavelength of the excitation beam increased. Moreover, (2J+1) number of the fluorescence peaks should be observed from the $^5D_0 \rightarrow {}^7F_{1,2}$ transition if the local site symmetry of Eu^{3+} is lower than C_{2v} [18-20]. No such (2J+1) splitting was resolved from the fluorescence of both $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions as shown in Fig. 11. This reflects the higher symmetry of the local structure surrounding Eu^{3+} ions in Ge-Ga-S-CsBr glass than that in conventional glasses.

4. Conclusions

Effects of alkali halide addition on the spectroscopic properties and persistent spectral hole burning of Eu^{3+} in Ge-Ga-S glasses were investigated. Temperature and host composition dependency of the Eu^{3+} fluorescence were also studied. The initial hole growth rate was 3.9×10^{-2} s^{-1} and it is approximately 50 times higher than the rates observed in oxide glasses. The relaxation rate was 3.9×10^{-6} s^{-1} with a thermal barrier height of 0.84 eV. These values also showed a considerable improvement over those for oxide glasses in terms of the stability of hole against time and temperature. Hole burning in chalcohalide glasses is a one-photon process. Interaction between the localized 4f electrons in the excited Eu^{3+} ions and a local conduction band of surrounding $[GaS_{3/2}Br]^-$ units is responsible for the reduction of Eu^{3+} into Eu^{2+}. The high efficiency of this hole burning is due to the electronic nature of the hole burning process.

Phonon side band (PSB) spectra recorded for Ge-Ga-S-CsBr and Ge-Ga-S-CsCl glasses showed several phonon modes (around 100 cm^{-1}) associated with halogen ions. For instance, in Ge-Ga-S-CsBr glasses, the local environment of Eu^{3+} ions is comprised of Br^- ions. These Br^- ions are a part of $EuBr_3$, tetrahedral $[GaS_{3/2}Br]^-$ subunits and/or Ga_2Br_6. Eu^{3+} is located next to Br^- ions. These new Eu-Br bonds exerted less electron-phonon coupling compared to Eu-S bonds in glasses without CsBr.

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