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Temperature dependent lifetime of Dy^{3+} : 1.3 μm emission in Ge–As–S glass containing very small amount of Ga and CsBr

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ABSTRACT

The lifetime of 1.3 μm emission from Dy^{3+} -doped Ge–As–S glass containing very small amount of Ga and CsBr reveals interesting temperature dependence; with the addition of Ga/CsBr up to ~ 0.2 mol% the lifetime decreases with increasing temperature. When the concentration of Ga/CsBr reaches ~ 0.3 mol%, however, the lifetime remains relatively constant regardless of temperature change. For further addition up to ~ 0.5 mol%, the lifetime increases as temperature rises. This uncommon behavior is explained through our understanding of the different temperature dependences of multiphonon relaxation and spontaneous emission rates associated with the thermally coupled Dy^{3+} : (${}^6\text{H}_{9/2}$, ${}^6\text{F}_{11/2}$) manifolds in our modified chalcogenide glass.

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1. Introduction

The intra-4f-configurational transitions of rare earth (RE) ions embedded in an amorphous dielectric solid are commonly known to be less sensitive to changes in their local structural environment than the $3d \leftrightarrow 3d$ transitions of doped transition metal ions [1]. There are some $4f \leftrightarrow 4f$ transitions of RE ions, however, that when doped into certain chalcogenide glasses are exceptionally sensitive to any structural change in their local environments that is induced by a very small amount of compositional modification [2,3]. For example, the measured lifetime of the 1.3 μm emission from Dy^{3+} ions embedded in sulfur-based chalcogenide glass is dramatically modified upon compositional adjustment of the host matrix via a combination of Ga and CsBr [2,4]. In this case, a greater than tenfold increase in the measured lifetime is typically observed when less than 1 mol% of Ga/CsBr is introduced to Ge–As–S (GAS) glass [5]. This novel observation is explained in terms of spontaneous atomic rearrangement in the immediate vicinity of Dy^{3+} ions which takes place as a result of the compositional modification as well as the hypersensitivity involved in the (${}^6\text{H}_{9/2}$, ${}^6\text{F}_{11/2}$) $\rightarrow$ ${}^6\text{H}_{15/2}$ transition. Specifically, multiphonon relaxation acting on the Dy^{3+} : 1.3 μm emission is efficient in an amorphous chalcogenide host such as GAS glass, thus reducing the measured lifetime to ~ 30 μs [6,7]. Gallium is known to form tetrahedral units in chalcogenide glass, thus violating the 8–N rule [8]. The ‘less covalent’ chemical bonds formed by Ga are responsible for the enhanced solubility of rare earths in Ga-containing GAS glass, even though the

addition of Ga itself hardly seems to alter the multiphonon relaxation. Bromine further introduced in the form of CsBr to this glass is then chemically bonded to Ga rather than Ge or As. Upon the addition of Ga and CsBr, i.e., typically less than 1 mol%, Dy^{3+} ions become preferentially located next to the $[\text{GaS}_3\text{Br}]$ units due to electrostatic interactions, and thereby their nearest neighbors are switched from S to Br. In this case, the multiphonon relaxation is governed by the phonon energy associated with the Ga–Br vibration modes, which then contributes in part to the increase of the measured lifetime [2]. In addition to this, the crystal fields perturbation to the intra-4f-configurational transitions of Dy^{3+} is reduced leading to a subsequent reduction in the spontaneous emission rate.

These previous experimental demonstrations indicate that, in the case of an amorphous chalcogenide solid doped with rare earths, it is possible to adjust spontaneous emission rate through compositional modification tantamount to a low doping level. The nonradiative multiphonon relaxation rate can be lowered at the same time whilst the thermal stability of the parent host material remains unaltered. This implies that the local structural modification made only in the nearest or next-nearest coordination shell improves the optical properties of doped rare earth ions. As such this compositional modification exemplifies the significant roles of the chemical environment of rare earth ions in controlling their radiative and nonradiative processes.

In an effort to deepen our knowledge on the compositional effects, in this Letter, we have analyzed temperature dependence of the measured transition rate of the 1.3 μm emission of Dy^{3+} in modified GAS glass. Specifically, the corresponding decay profile was measured at various temperatures for GAS glass unmodified

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or modified with less than 0.5 mol% of Ga/CsBr. Absorption spectra for the ${}^6\text{H}_{15/2} \rightarrow ({}^6\text{H}_{9/2}, {}^6\text{F}_{11/2})$ transition were also recorded as a function of temperature. We observe that the measured lifetime reveals a very interesting behavior, which is detailed below. This novel behavior is then discussed in terms of the characteristic temperature dependences of multiphonon relaxation rate and spontaneous emission rate.

2. Experimental

Dy-doped GAS glasses unmodified or modified with Ga and CsBr were prepared, of which nominal compositions were $1.98\text{Ge}-(37-2x)\text{As}-61\text{S}-0.02\text{Dy}-x(\text{Ga}-\text{CsBr})$ for $0 \leq x \leq 0.5$ in mol%. Here, Ga and CsBr were set to be equal in concentration, and all starting materials were used in their elemental forms apart from CsBr. A rocking furnace was used for 12-h-long melting of batches sealed inside silica ampoules, which were subsequently quenched in air. All the samples were then annealed at around 490 K. Note that our samples were prepared following the conventional processing route for chalcogenide glasses, and all the samples thus prepared turned out to be amorphous, as verified by X-ray diffraction. In order to optically excite Dy^{3+} ions in our glass samples and thereby to get the 1.3 μm emission, we used a Ti: sapphire laser operating at 802 nm. The pump beam was chopped with an acousto-optic modulator, and temperature of the samples was controlled by using a thermo-electric cooler. The fluorescence intensity decay was recorded by using a digital oscilloscope. More detailed information for the sample preparation and the decay profile acquisition is available elsewhere [2,4,9].

3. Results and discussion

Figure 1 shows representative decay profiles measured at 300 and 133 K for GAS samples doped with 0.5 mol% Ga/CsBr along with the system response. From such profiles, the measured lifetime, i.e., the first e -folding time, was determined as a function of doping concentration. Figure 2a shows the measured lifetime plotted as a function of temperature from which two interesting find-

Figure 1. Representative decay profiles for the Dy^{3+} : 1.3 μm emission of a glass sample containing 0.5 mol% Ga/CsBr measured at different temperatures. Note that the inset shows a schematic energy level diagram of Dy^{3+} ions.

Figure 2. Temperature dependences of (a) lifetime and (b) transition rate of the thermally coupled (${}^6\text{H}_{9/2}$, ${}^6\text{F}_{11/2}$) levels of Dy^{3+} ions embedded in the Ge–As–S glass compositionally engineered with a small amount of Ga and CsBr. Note that the uncertainty involved in the lifetime determination is less than the size of each symbol.

ings are revealed; firstly, comparison of the lifetimes measured at an identical temperature, e.g., at room temperature, shows an increase as the size of compositional modification increases in good agreement with previously reported results [4]. Secondly, but more interestingly, the measured lifetimes for each sample exhibit clearly distinguishable temperature dependency. Specifically, for a Ga/CsBr concentration below 0.3 mol% the lifetime decreases with increasing temperature, as typically found from the multiphonon relaxation dominated transitions. However, as the concentration is further increased the lifetime becomes temperature independent (at 0.3 mol%) before displaying a more unusual increase in lifetime with temperature at 0.5 mol%.

The measured transition rate W_m , that is reciprocal of the measured lifetime, can be expressed as sum of spontaneous emission

rate (which refers to the intrinsic radiative transition probability) W_{SER} and multiphonon relaxation rate W_{MPR} assuming other radiationless ion-ion interactions such as energy transfer between Dy^{3+} ions are insignificant. We notice that some decay traces are non-exponential to some extent for a long elapsed time. The deviation from the single-exponential decay presumably results from the energy transfers among Dy^{3+} ions [10]. A prolonged population feeding to the (${}^6\text{H}_{9/2}$, ${}^6\text{F}_{11/2}$) level can happen after the ceasing of the optical excitation by the cooperative upconversion energy transfers associated with the lower-lying levels with longer population duration time. As such it is reasonably assumed that the measured lifetime here indicating the first e -folding time is mainly dominated by W_{SER} and W_{MPR} rather than the radiationless energy transfer rate.

The temperature dependence and the Ga/CsBr concentration dependence of W_m can thus be explained in terms of those of W_{MPR} and W_{SER} associated with the Dy^{3+} : (${}^6\text{H}_{9/2}$, ${}^6\text{F}_{11/2}$) $\rightarrow$ ${}^6\text{H}_{15/2}$ transition in our samples. The temperature dependence of multiphonon relaxation rate $W_{\text{MPR}}(T)$ is then expressed as follows [11];

$$W_{\text{MPR}}(T) = W_{\text{MPR}}(0) \left\{ 1 - \exp \left(-\frac{\hbar\omega}{kT} \right) \right\}^{\frac{-\Delta E_{21}}{\hbar\omega}}, \quad (1)$$

where $\hbar\omega$ and ΔE_{21} indicate the representative phonon energy participating in the multiphonon relaxation process and energy gap between the fluorescing (${}^6\text{H}_{9/2}$, ${}^6\text{F}_{11/2}$) level and the ${}^6\text{H}_{11/2}$ level located immediately below, respectively. As displayed in the inset of Figure 1, ΔE_{21} is quite small, i.e., approximately 1870 cm^{-1} , whereas $\hbar\omega$ is $\sim 350 \text{ cm}^{-1}$ for unmodified glass with Ga/CsBr [2]. As discussed above, the Dy^{3+} : (${}^6\text{H}_{9/2}$, ${}^6\text{F}_{11/2}$) $\rightarrow$ ${}^6\text{H}_{15/2}$ transition is dominated by W_{MPR} even in the present low-phonon-energy host, i.e., Ge–As–S glass. However, as a result of the incorporation of Ga and CsBr, W_{MPR} decreases because both the phonon energy and electron–phonon coupling coefficients decrease [12]. The measured transition rate over temperature observed from samples with very small amount of Ga/CsBr, i.e., less than 0.3 mol% in the present case,

is thus explainable in terms of the typical temperature dependence of multiphonon relaxation as appears in Eq. (1).

Since energy difference between the centers of gravity of the ${}^6\text{H}_{9/2}$ and ${}^6\text{F}_{11/2}$ levels ΔE_{32} (see the inset of Figure 1) is just $\sim 100 \text{ cm}^{-1}$ [13], this pair of levels is thermally coupled. As such, when assessing the temperature dependent spontaneous emission rate $W_{\text{SER}}(T)$, we need to consider the population distribution statistics, which would then be expressed as follows [13];

$$W_{\text{SER}}(T) = \frac{g_2 W_{20}(T) + g_3 W_{30}(T) \exp \left(-\frac{\Delta E_{32}}{kT} \right)}{g_2 + g_3 \exp \left(-\frac{\Delta E_{32}}{kT} \right)}, \quad (2)$$

where g_2 and g_3 , implying degeneracy of levels #2 and #3, are 6 and 5, respectively. Here, W_{20} and W_{30} indicate the radiative transition probability for #2 $\rightarrow$ #0 and #3 $\rightarrow$ #0 transitions, respectively. Since the branching ratio for (${}^6\text{H}_{9/2}$, ${}^6\text{F}_{11/2}$) $\rightarrow$ ${}^6\text{H}_{15/2}$ transition is notably larger (>0.9 in general) compared with that of other transitions sharing the (${}^6\text{H}_{9/2}$, ${}^6\text{F}_{11/2}$) as a fluorescing level [6,7,14], we can reasonably assume that a good combination of W_{20} and W_{30} determines the spontaneous emission rate of the (${}^6\text{H}_{9/2}$, ${}^6\text{F}_{11/2}$) levels. On the other hand, the ${}^6\text{F}_{11/2} \rightarrow {}^6\text{H}_{15/2}$ transition that satisfies the selection rules for the electric quadrupole transition is more sensitive to the structural modifications around Dy^{3+} ions than the ordinary ${}^6\text{H}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ transition [1]. It is known that in usual cases $W_{20} > W_{30}$ [4,6,7], so that W_{30} influences W_{SER} more significantly with increasing temperature. More specifically, this implies that W_{SER} tends to decrease as temperature rises. In fact, this phenomenon is also observed from other thermally coupled levels with lower-lying one possessing greater radiative transition rate such as Pr^{3+} : (${}^3\text{P}_0$, ${}^3\text{P}_1$) and Pr^{3+} : (${}^3\text{F}_3$, ${}^3\text{F}_4$) [15–17]. Now, it is inferred that the decrease of W_m over temperature observed from the sample containing 0.5 mol% of Ga/CsBr is mainly due to the dominance of W_{SER} rather than W_{MPR} . We then presume that when the Ga/CsBr concentration is around 0.3 mol%, we have $\frac{dW_{\text{SER}}}{dT} \approx -\frac{dW_{\text{MPR}}}{dT}$, so that $\frac{dW_m}{dT} \approx 0$, as shown in Figure 2b.

To verify our reasoning, we need to check the temperature dependence of W_{20} and W_{30} for each sample in order to assess

Figure 3. Absorption cross-section spectrum for the ${}^6\text{H}_{15/2} \rightarrow ({}^6\text{H}_{9/2}, {}^6\text{F}_{11/2})$ transition of some representative samples measured at different temperatures.

Figure 4. The peak absorption cross-section of the glass samples plotted as a function of temperature.

the perturbations of the crystal fields more precisely. With this in mind, we have recorded absorption spectrum for ${}^6\text{H}_{15/2} \rightarrow ({}^6\text{H}_{9/2}, {}^6\text{F}_{11/2})$ transition at different temperatures ranging from 20 K to room temperature as displayed in Figure 3. As is already known, the absorption cross-section measured at 300 K tends to decrease with increasing concentration of Ga/CsBr (Figure 4), which implies that the higher the Ga/CsBr concentration, the lower W_{20} and W_{30} become. Figure 4 also reveals that the peak absorption cross-section changes with temperature for Dy^{3+} ions with fixed local structural environments given by fixed chemical compositions; the peak value of absorption cross-section tends to decrease over temperature for all the samples measured. Among the samples displayed in Figure 4, in particular, the sample containing 0.1 mol% Ga/CsBr features such a change most significantly. We note that a quite similar result was also observed from the same transition of Dy^{3+} ions doped in $\text{SiO}_2\text{-P}_2\text{O}_5\text{-GeO}_2$ glass [18]. In general, for rare earth ions embedded in a solid matrix, change(s) in absorption spectrum resulting from temperature variation would mainly rely on changes in refractive index and the odd parts of the crystal fields, which can be either static or dynamic in time [1]. Here, the symmetry and the size of the static and (or) vibrational odd distortions of the crystal fields would be influenced by the type of neighbors as well as covalence involved in the chemical bonds formed between rare earth ions and the neighboring ions. Previous experimental results already confirmed that upon the incorporation of a small amount of Ga/CsBr the doped Dy^{3+} ions experience a dramatic alternation in their local environments. Specifically, it is reasoned that in a glass fully modified with Ga/CsBr, Dy^{3+} ions would feel the crystal fields consisting of Br ions with the enhanced symmetry rather than those of S ions in the unmodified glass. A detailed assessment for such changes of the absorption cross-section over temperature in this series of samples is beyond the scope of this Letter. However, one thing clear is that the absorption cross-section is not fixed but varies with temperature as does the sum of

the radiative rates $W_{20} + W_{30}$. This further implies that in order to correctly evaluate $W_{\text{SER}}(T)$ for each sample one needs to take into consideration not only the Boltzmann distribution between the tightly spaced fluorescing levels but also the intrinsic radiative transition probability of each level involved, both of which are a sensitive function of temperature. This reasoning together with the lack of necessary experimental data makes a quantitative analysis quite complicated, hence the qualitative explanation given in this Letter.

4. Conclusions

In summary, the uncommon temperature dependence of the measured transition rate for Dy^{3+} : (${}^6\text{H}_{9/2}$, ${}^6\text{F}_{11/2}$) state observed from the amorphous Ge-As-S matrix containing very small amount of Ga and CsBr is qualitatively explained in terms of different temperature dependences of multiphonon relaxation rate and spontaneous emission rate. For Ga/CsBr concentration below ~ 0.3 mol%, W_{MPR} dominates over W_{SER} , so that $\frac{dW_m}{dT} > 0$. However, as the concentration is increased further, W_{MPR} becomes negligible compared with W_{SER} , so that $\frac{dW_m}{dT} < 0$. For Ga/CsBr concentrations close to 0.3 mol%, it is found that $\frac{dW_{\text{SER}}}{dT} \approx -\frac{dW_{\text{MPR}}}{dT}$, i.e., $\frac{dW_m}{dT} \approx 0$ thus athermal behavior may be obtained. The local structural modifications happening preferentially in the vicinity of Dy^{3+} ions are induced by the chemical effects of the incorporation of Ga and CsBr, which as a whole is responsible for our experimental observation. Through control of concentration of Dy relative to that of Ga/CsBr, it is thus feasible to engineer not only the lifetime itself but also its temperature dependence.

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References

- [1] Grller-Walrand, K. Binnemans, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 25, Elsevier, Amsterdam, 1998.
- [2] Y.G. Choi, R.J. Curry, B.J. Park, K.H. Kim, J. Heo, D.W. Hewak, Chem. Phys. Lett. 403 (2005) 29.
- [3] Y.G. Choi, J.H. Song, Opt. Commun. 281 (2008) 4358.
- [4] Y.G. Choi, R.J. Curry, B.J. Park, K.H. Kim, J. Heo, D.W. Hewak, J. Appl. Phys. 98 (2005) 023523.
- [5] Y.G. Choi, J. Lumin. 129 (2009) 620.
- [6] K. Wei, D.P. Machewirth, J. Wenzel, E. Snitzer, G.H. Sigel Jr., Opt. Lett. 19 (1994) 904.
- [7] Y. Guimond, J.L. Adam, A.M. Jurduc, J. Mugnier, B. Jacquier, X.H. Zhang, Opt. Mater. 12 (1999) 467.
- [8] Y.G. Choi, J.H. Song, J. Non-Cryst. Solids 355 (2009) 2396.
- [9] Y.G. Choi, K.H. Kim, S.H. Park, J. Heo, J. Appl. Phys. 88 (2000) 3832.
- [10] Y.B. Shin, J. Heo, J. Non-Cryst. Solids 256 and 257 (1999) 260.
- [11] L.A. Riseberg, H.W. Moos, Phys. Rev. 174 (1968) 429.
- [12] Y.B. Shin, J. Heo, H.S. Kim, Chem. Phys. Lett. 317 (2000) 637.
- [13] R.S. Quimby, B.G. Aitken, J. Non-Cryst. Solids 320 (2003) 100.
- [14] T. Schweizer, F. Goutaland, E. Martins, D.W. Hewak, W.S. Brocklesby, J. Opt. Soc. Am. B 18 (2001) 1436.
- [15] T. sun, Z.Y. Zhang, K.T.V. Grattan, A.W. Palmer, S.F. Collins, Rev. Sci. Instrum. 68 (1997) 3447.
- [16] T.B. Nguyen, S. Trpkovski, P.M. Farrell, G.W. Baxter, S.F. Collins, Opt. Commun. 186 (2000) 277.
- [17] Y.S. Han, J. Heo, J. Appl. Phys. 93 (2003) 8970.
- [18] I.S. Edelman, A.V. Malakhovskii, A.M. Potseluyko, T.V. Zarubina, A.V. Zamkov, J. Non-Cryst. Solids 306 (2002) 120.