PHYSICAL REVIEW B **79**, 180202(R) (2009)

Evidence of formation of tightly bound rare-earth clusters in chalcogenide glasses and their evolution with glass composition

T. H. Lee,[1] S. I. Simdyankin,[1,2] L. Su,[1] and S. R. Elliott[1]
[1]*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom*
[2]*WPI Advanced Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan*

(Received 6 January 2009; revised manuscript received 4 March 2009; published 26 May 2009)

We present spectroscopic evidence for the formation of tightly bound Nd^{3+} clusters in chalcogenide glasses in which Nd^{3+} ions are so close that no appreciable fluorescence is observed. According to a theoretical calculation using the rate-equation modeling and comparison with experimental results, this type of cluster contributes as the main source of energy transfer among Nd^{3+} ions in Ga-free glasses, resulting in the strong fluorescence quenching. It is proposed that the total volume of such Nd^{3+} clusters sharply decreases with Ga doping, while the spatial distance among Nd^{3+} ions in clusters remains close enough for there to be no detectable fluorescence from these clustered Nd^{3+} ions. Such clusters are then completely dissolved in glasses once a critical Ga concentration is reached.

DOI: 10.1103/PhysRevB.79.180202 PACS number(s): 61.43.Fs, 78.55.Qr, 42.70.Hj

Cluster formation of rare-earth (RE) ions in glasses or crystals has been of great research interest due to its significant influence on the performance of optical-amplifier or laser devices.[1] In RE-doped oxide glasses, various experimental techniques have been employed to probe the formation of such clusters, using, e.g., nuclear magnetic resonance (NMR),[2] electron paramagnetic resonance (EPR),[3] and neutron diffraction.[4] Moreover, spectroscopic measurements intended to obtain information about the RE distribution from their fluorescence have also been performed, applying the fluorescence line-narrowing (FLN) technique,[5] fluorescence-decay analysis,[6] and the phenomenon of cooperative luminescence of Yb^{3+} ions.[7] The majority of researches mentioned above is, however, focused on RE clustering in silica-based oxide glasses due to their technological importance in optical-telecommunication systems.[1] In spite of such extensive work on this topic, knowledge of actual atomic structures is, however, still limited.

Although similar RE-cluster formation in chalcogenide glasses is strongly suspected, information as to the RE-cluster formation is even less than in oxide glasses since only a few studies[8] have been performed to probe RE clustering in this type of glass. The need for employing chalcogenide glasses as RE hosts is, however, evident in many applications due to their crucial advantages over oxides, including low phonon energies and consequent broad optical-transmission windows.[9] For example, these superior properties enable the development of optical amplifiers or lasers for the midinfrared or far-infrared region with high quantum efficiency.[10] More significantly, the high photosensitivity of these glasses,[11] along with the availability of selective chemical etching,[12] provides an elegant tool to fabricate RE-doped planar waveguide-type optical amplifiers for integrated optical circuits.

Nevertheless, as for oxide glasses, the performance of these chalcogenide-glass devices can be strongly degraded by RE clustering. Recently, we have proposed an atomistic structural model for rare-earth and Ga codoped chalcogenide glasses on the basis of the spatial distribution and the correlation of Ga atoms with rare-earth ions.[13] Structural information on such RE clusters is, though, still largely unavailable. In this study, as a prerequisite step for developing such chalcogenide-based optical devices, we have focused on investigating RE-cluster formation and annihilation, using spectroscopic methods together with the rate-equation modeling. Evidence for the formation of tightly bound RE clusters, where fluorescence from rare-earth ions is almost completely quenched, is shown. A quantitative estimation of the proportion of rare-earth ions in such clusters will also be discussed.

Nd^{3+} ions were used as probe ions in a site-selective excitation study because of its simple Stark sublevel of the $^4F_{3/2}$ manifold. Eu^{3+} ions, which are normally employed for this type of study, however, were not able to be used since we have found that most Eu ions are not in a trivalent state, but presumably in a divalent state, in chalcogenide glasses. The stoichiometric "GAGS" glass compositions investigated were $Ge_{23.5}As_{(11.8-x)}Ga_xS_{64.7}$ ($0 \leq x \leq 3$ in atomic percent) [i.e., for $x=0$, $Ge_{23.5}As_{11.8}S_{64.7}$ is equivalent to $(GeS_2)_4(As_2S_3)$]. The concentration of Nd^{3+} ions was fixed at 0.01 at. %. Hereafter, the Ga-free glass with $x=0$ will be denoted as Ga0 and a similar notation will be applied for other Ga-containing glasses. Details of the sample-fabrication method and the laser experiments are described elsewhere.[14]

Figures 1(a) and 1(b) show near-infrared fluorescence at 12 K due to the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of Nd^{3+} ions in Ga0 and Ga0.6 glasses, respectively. These two glass compositions were selected for comparison because it is expected that most rare-earth ions in the former glass are clustered, while rare-earth ions in the latter are distributed rather randomly.[13] A series of fluorescence spectra was obtained by exciting Nd^{3+} ions to the inhomogeneously broadened $^4F_{3/2}$ energy level at nearly regular excitation-wavelength intervals [Fig. 1(d)]. As shown in this figure, the line shape of fluorescence spectra, especially the spectral linewidth, changes in a rather systematic manner with an increase in excitation wavelength. According to the Kramers' rule, the maximum number of Stark sublevels for the Nd^{3+} $^4I_{11/2}$ and $^4F_{3/2}$ manifolds are six and two, respectively. Because of the fast ther-

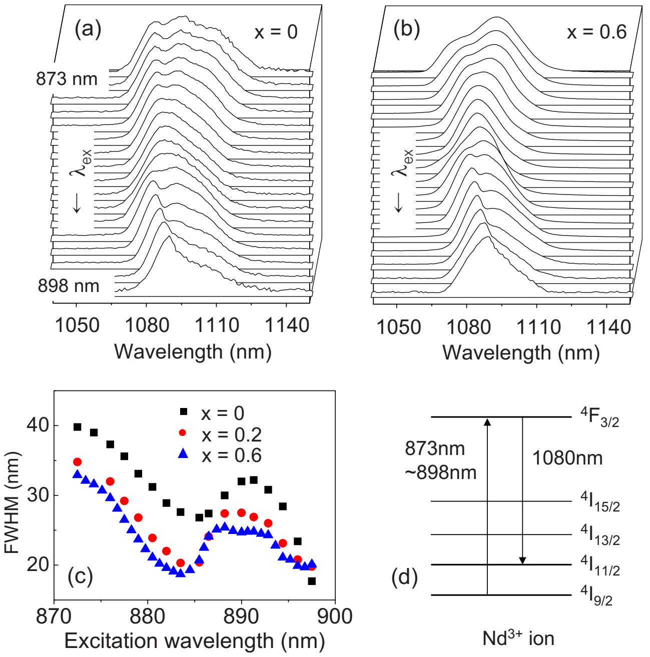

FIG. 1. (Color online) FLN spectra at 12 K of 0.01 at. % Nd^{3+}-doped GAGS glasses with (a) $x=0$ and (b) $x=0.6$. The interval between adjacent spectra is 1.5∼2 nm, and all fluorescence intensities were normalized to their peak intensities. (c) FWHMs of spectra shown in (a) and (b). The results for the glass with $x=0.2$ are also included. (d) A schematic energy-level diagram for the excitation and fluorescence processes.

malization within the Stark sublevels, most of the fluorescence originates from the lower Stark sublevel of the $^4F_{3/2}$ manifold. Each of the fluorescence spectra shown in Fig. 1 is thus presumably composed of six peaks for Stark transitions to the $^4I_{11/2}$ manifold. It is evident from the peak shift, together with a peak fit using Gaussian subpeaks, that subpeaks constituting a broad spectrum become closer to each other with increasing excitation wavelength within certain excitation-wavelength regions. To reveal such a narrowing more quantitatively, the full width at half maximum (FWHM) of each spectrum was monitored as a function of the excitation wavelength [Fig. 1(c)]. As shown in this figure, there are two regions where the FWHMs show a gradual decrease and an intervening transition region (∼885–890 nm) where the opposite trend, i.e., an increase in FWHM, is observed. A similar trend is also found for the Ga0.2 and Ga0.6 glasses, although the overall FWHMs are smaller than those for the Ga0 glass.

The observed variation in fluorescence with excitation energy can be properly understood in terms of successive site-selective excitations of subsets of Nd^{3+} ions, whose local environments are broadly distributed due to a site-to-site variation in Nd^{3+}-ligand structures. Each fluorescence observed is thus only from Nd^{3+} ions that are resonant with the excitation wavelength (λ_{ex}) of the laser source having a narrow spectral width. In the case of an energy level composed of only one Stark component, e.g., the $\mathrm{Eu}^{3+}:{}^5D_0$, a series of site-selective excitations over the absorption band was found to show generally a monotonic change in FWHM of fluorescence spectra due to a FLN effect.[15] Accordingly, in our case, it seems reasonable to assume that the observed FLN effect at longer wavelengths is due to excitation to the lower Stark sublevel while that at shorter wavelengths is due to excitation to the upper sublevel. Therefore, although the fluorescence is generated only from the transition of the lower Stark sublevel of the $^4F_{3/2}$ manifold, we can attribute the trend observed in the variation in FWHM to the existence of two Stark sublevels and their successive excitation.

The observation of the FLN effect is direct evidence that the measured fluorescence arises mostly from Nd^{3+} ions residing at sites relatively well dispersed in the glass matrix. Otherwise, an inhomogeneous distribution of Nd^{3+} ions, with a tendency to form clusters, generally leads to fast spectral diffusion and subsequent simultaneous excitation of Nd^{3+} ions in different local environments, thereby preventing any FLN effect from being observed.[5] It is, however, significant that a random distribution of Nd^{3+} ions inferred from this FLN result is not consistent with the previous expectation of a strong tendency of RE clustering in this glass system.[8,13] To explain such an abnormal result, we propose a structural model involving the formation of tightly bound RE clusters, in which the rare-earth ions are so close that most excited ions are relaxed to lower states via energy-transfer processes. In this model, the majority of rare-earth ions, participating in radiative transitions, is thus loosely bound to—or are far from—these clusters, thereby manifesting the FLN effect. This type of RE cluster should thus be differentiated from RE clusters in which rare-earth ions show appreciable fluorescence.[5] This RE-cluster model is further supported by a decay curve analysis and fluorescence intensity changes, details of which will be explained in a latter section.

Neither the experimental nor a theoretical estimation of the proportion of clustered rare-earth ions in a glass is a trivial task. In particular, a theoretical estimation requires some information on the microscopic structures of RE clusters. In the present case, however, the observation of tightly bound RE clusters gives us a simple route to approximate the proportion of rare-earth ions in clusters using rate-equation modeling. First, suppose that all Nd^{3+} ions are randomly distributed in the glass matrix. The fluorescence intensity (I) from rare-earth ions excited to energy level (i) can be expressed as $I_i = h\nu\beta A_r n_i$. Here, $h\nu$ is the photon energy, β is the branching ratio of the transition of interest, A_r is the radiative transition rate, and n_i is the population density of ions excited to the ith energy level. Under steady-state and weak pumping conditions, n_i can be written as $n_i = \phi\sigma_p\tau_m n_{\mathrm{Nd}}$, where ϕ is the flux of the pump photons, σ_p is the absorption cross section, τ_m is the measured lifetime, and n_{Nd} is the total Nd^{3+} dopant concentration.[16] The combination of these two relations, along with $\tau_m = 1/(A_r + W_{\mathrm{ET}})$, results in

$$I_i = h\nu\phi\sigma_p n_{\mathrm{Nd}}\beta\left(\frac{1}{1 + W_{\mathrm{ET}}/A_r}\right). \tag{1}$$

Here, W_{ET} is the energy-transfer rate from the ith level. It has been assumed here that the multiphonon relaxation from the $^4F_{3/2}$ level is negligible. Let us now consider the case in which rare-earth ions partially form tightly bound clusters,

TABLE I. Calculated Judd-Ofelt intensity parameters ($\Omega_{2,4,6}$) for Nd^{3+} ions with different Ga-doping concentrations (x) of GAGS glasses. The four excited levels used for the Judd-Ofelt analysis are $^4F_{3/2}$, ($^2H_{9/2}$, $^4F_{5/2}$), ($^4S_{3/2}$, $^4F_{7/2}$), and ($^2G_{7/2}$, $^4G_{5/2}$). Because of the fundamental glass absorption as well as weak oscillator strengths for some transitions, only these four absorption bands were used for the fitting.

x	Ω_2 (10^{-20} cm^3)	Ω_4 (10^{-20} cm^3)	Ω_6 (10^{-20} cm^3)
0	11.9 ± 0.8	8.1 ± 0.8	6.6 ± 0.6
0.6	11.4 ± 0.6	8.6 ± 0.4	6.4 ± 0.3
1.2	11.5 ± 0.3	8.8 ± 0.3	6.0 ± 0.1

and there is approximately no fluorescence from these clusters. This condition can be simply expressed by replacing n_{Nd} in Eq. (1) by the effective total Nd^{3+} concentration defined by $R_{eff}n_{Nd}$. Here, R_{eff} is the proportion of Nd^{3+} ions that are loosely bound to clusters or well dispersed in the glass matrix. The rate W_{ET} in this model is thus attributed to the energy transfer among rare-earth ions outside clusters. Physically, this model describes glasses in which rare-earth ions in two different groups, i.e., either in tightly bound clusters or not, are spatially well separated, and thus as an approximation can be treated independently in the rate-equation modeling.

On the basis of the model presented above, R_{eff} can be computed from the measured fluorescence-intensity ratios, namely, $I_{Gax}/I_{Ga1.2} \approx R_{eff}/(1+W_{ET}/A_r)$. Here, Nd^{3+} ions are assumed to be completely randomly distributed in the Ga1.2 glass.[13] Accordingly, A_r is assumed to be equal to the measured lifetime for Ga1.2 (viz., 80 μs). In addition, it turns out from the Judd-Ofelt intensity parameters (Table I) that other parameters, i.e., σ_p and β, are insensitive to small compositional modifications. Fluorescence intensities at 1080 nm, along with W_{ET} evaluated from $1/\tau_m - 1/\tau_r$, are shown in Fig. 2(b), and the calculated variation of $1-R_{eff}$ is depicted in Fig. 2(a). It is evident from this result that most Nd^{3+} ions in the Ga0 glass form clusters—as expected—and only about 3% of them are rather well dispersed. As the Ga-doping concentration (x) increases, the proportion of clustered Nd^{3+} ions, i.e., $1-R_{eff}$, decreases sharply, the Nd^{3+} ions being dissolved almost randomly in the glasses once x exceeds 0.5 at. %.

Before we discuss the mechanism for such an effective dissolution of Nd^{3+} clusters with small Ga doping, it is instructive to rationalize the approximation made above by pursuing a deeper investigation of tightly bound RE clusters proposed from the FLN experiment. First, we examined the time evolution of fluorescence from the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition. Figure 2(c) shows fluorescence-decay curves measured at 1080 nm for Ga0 and Ga0.6 glasses. The Ga0.6 sample shows a single exponential decay with the average lifetime (τ_m) of 80 μs defined by $\tau_m = \int I(t)dt / I(0)$, which corresponds to the radiative lifetime of the $^4F_{3/2}$ level. On the other hand, fluorescence from the Ga0 sample shows nonexponential decay with an average lifetime of 56 μs. A double-exponential fit was then performed for this decay curve with a fast decay ($\tau = 8\,\mu s, 25\%$) and a slow one ($\tau = 80\ \mu s, 75\%$), and the result is shown in Fig. 2(c). Interestingly, the lifetime of the slowly decaying part is exactly equal to that for Ga1.2, indicating that the latter part of the decay curve is due to Nd^{3+} ions well dispersed in the Ga0 glass. It is noted that in our model, the fast decaying part is due to the energy transfer among rare-earth ions residing outside clusters, whose effect is described in W_{ET}.

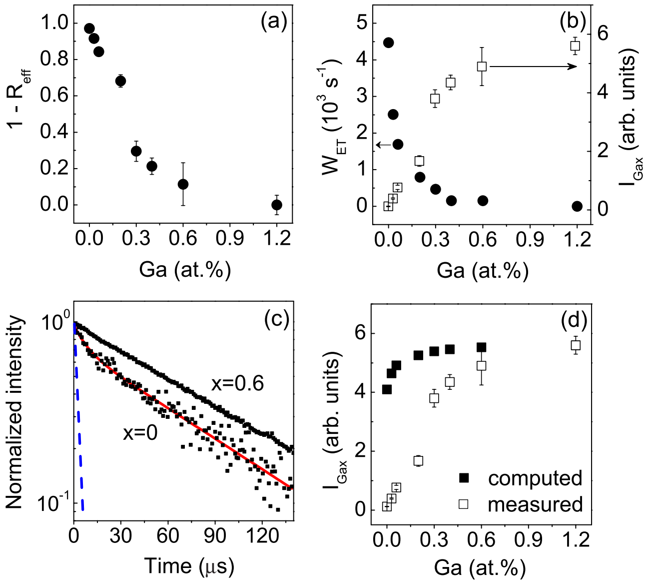

FIG. 2. (Color online) (a) Proportion of Nd^{3+} ions in tightly bound clusters calculated based on Eq. (1) as a function of Ga content. (b) Parameters of W_{ET} and fluorescence intensity (I_{Gax}) used for the calculation of $1-R_{eff}$. (c) Normalized decay curves of fluorescence measured at 1080 nm for Ga0 and Ga0.6 glasses. The blue dotted line corresponds to the estimated decay curve for the Ga0 glass, and the red solid line is a fit using a double-exponential decay model. (d) Measured and computed fluorescence intensities (see text for details).

Two crucial observations are evident in the decay profile of the Ga0 glass, namely, that (1) no decaying part, which is fast enough to explain the fluorescence-intensity changes, is found, and (2) the proportion of well-dispersed Nd^{3+} ions, exceeding 70% of total Nd^{3+} ions, is too large compared to the weak fluorescence intensity. As will be shown, these two abnormal results can be eventually understood by our RE-cluster model. The dotted line in Fig. 2(c) shows the expected decay curve for the Ga0 sample estimated from Eq. (1). If all Nd^{3+} ions participate in radiative and nonradiative processes then there should appear a fast decaying part, with a lifetime shorter than 2 μs, in order to describe the large fluorescence quenching. The absence of such a fast decaying part therefore should be associated with Nd^{3+} ions which do not contribute to the measured fluorescence-decay curve. We also theoretically estimated fluorescence intensities from the measured average lifetimes, using the relation $I_{Gax}/I_{Ga1.2} \approx \tau_{m,Gax}/\tau_{m,Ga1.2}$, and the results are shown in Fig. 2(d), with the measured fluorescence intensities for comparison. It is clear from this figure that the lifetimes tend to overestimate the fluorescence intensities, and the difference between the two becomes larger as the Ga concentration decreases. This means that the measured lifetime is not properly reflecting the population dynamics of Nd^{3+} ions as the Ga concentration decreases. Since all fluorescence-quenching processes, i.e., energy transfers, should be manifested in the measured lifetime, the large fluorescence quenching (not revealed from the measured lifetime) should again involve a group of Nd^{3+} ions which do not participate in the fluorescence process. The most plausible explanation for these two discrepancies between measured decay curves and fluorescence intensities is thus the formation of tightly bound RE clusters in Ga-deficient glasses, as expected from the FLN experiment.

Now let us discuss the evolution of such RE clusters with Ga doping. As shown in Fig. 2, most rare-earth ions form tightly bound clusters without Ga doping (Ga0). Although the actual shapes and sizes of these clusters are unknown and such factors are not critical in the following discussion, let us simply suppose that clusters are dispersed randomly in the glass matrix with various sizes. Valuable information is then extracted from Fig. 2(d). As shown in this figure, a considerable difference between computed and measured fluorescence intensities exists up to $x=0.5$ at. % and also no fast decaying part was found in any decay curves of Ga-doped glasses (not shown). Interesting insight from this observation as to the evolution of RE clusters might be that unless more than a critical concentration ($>\sim 0.5$ at. %) of Ga is incorporated, rare-earth ions still form tightly bound clusters without any noticeable fluorescence. The role of Ga is thus to reduce the cluster size and/or the number of clusters and then these clusters are completely dissolved once a certain critical Ga concentration is reached. The rare-earth ions that are accordingly detached from such clusters then might reside in Ga-rich regions, which can provide suitable well-dispersed sites for rare-earth ions.[13] Finally, it is noted that the structural model presented here might give an insight into other RE-doped glasses, particularly, RE-doped silica-based glasses, since we notice several similarities in the observed phenomena with RE/Al codoping.[2,3,6]

In summary, we have demonstrated evidence for the formation of tightly bound RE clusters in which most rare-earth ions decay nonradiatively via energy transfer and almost negligible fluorescence from these rare-earth ions is observed. It was found that the total volume of such clusters then decreases with Ga doping, while the distance among rare-earth ions in clusters remains close enough to account for the persistent absence of fluorescence from these clusters. Once a critical Ga concentration dependent on a relevant RE concentration is reached then rare-earth ions are likely to be completely dissolved in glasses without forming clusters.

We acknowledge financial support from the UK Home Office. T.H.L. is grateful for a Korea Research Foundation Grant (MOEHRD) (Grant No. KRF-2006-352-D00102).

---

[1] E. Desurvire, *Erbium Doped Fiber Amplifier: Principles and Applications* (Wiley, New York, 1994).

[2] S. Sen and J. F. Stebbins, J. Non-Cryst. Solids **188**, 54 (1995).

[3] K. Arai, S. Yamasaki, J. Isoya, and H. Namikawa, J. Non-Cryst. Solids **196**, 216 (1996); A. Saitoh, S. Matsuishi, M. Oto, T. Miura, M. Hirano, and H. Hosono, Phys. Rev. B **72**, 212101 (2005).

[4] J. M. Cole, A. C. Hannon, R. A. Martin, and R. J. Newport, Phys. Rev. B **73**, 104210 (2006).

[5] M. J. Lochhead and K. L. Bray, Chem. Mater. **7**, 572 (1995).

[6] K. Arai, H. Namikawa, K. Kumata, T. Honda, Y. Ishii, and T. Handa, J. Appl. Phys. **59**, 3430 (1986).

[7] P. Goldner, B. Schaudel, and M. Prassas, Phys. Rev. B **65**, 054103 (2002), and references therein.

[8] B. G. Aitken, C. W. Ponader, and R. S. Quimby, C. R. Chim. **5**, 865 (2002).

[9] J. S. Sanghera, I. D. Aggarwal, L. B. Shaw, L. E. Busse, P. Thielen, V. Nguyen, P. Pureza, S. Bayya, and F. Kung, J. Optoelectron. Adv. Mater. **3**, 627 (2001).

[10] L. B. Shaw, B. Cole, P. A. Thielen, J. S. Sanghera, and I. D. Aggarwal, IEEE J. Quantum Electron. **37**, 1127 (2001).

[11] *Photo-induced Metastability in Amorphous Semiconductors*, edited by A. V. Kolobov (Wiley-VCH, Weinheim, 2003).

[12] L. Su, C. J. Rowlands, T. H. Lee, and S. R. Elliott, Electron. Lett. **44**, 472 (2008), and references therein.

[13] T. H. Lee, S. I. Simdyankin, J. Hegedus, J. Heo, and S. R. Elliott (unpublished).

[14] T. H. Lee and J. Heo, Phys. Rev. B **73**, 144201 (2006).

[15] M. J. Weber, J. A. Paisner, S. S. Sussman, W. M. Yen, L. A. Riseberg, and C. Brecher, J. Lumin. **12-13**, 729 (1976).

[16] T. H. Lee and J. Heo, J. Appl. Phys. **98**, 113510 (2005).