Controlling the Fluorescence Lifetime of Rare Earth Element in Amorphous Inorganic Solids via Very Small Compositional Adjustments**

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The ability to control the spontaneous emission rate (SER) of a point dipole impurity embedded in a wide variety of solid-state dielectrics is a key issue to be resolved. If this can be achieved it opens up new possibilities for the application of doped dielectrics in the quantum optics field in addition to their existing applications.[1-3] A rare earth element (REE) can be regarded as a good electric dipole photon-emitting source.[4-6] The intra-4f-configurational transitions of REE are particularly interesting as emission at various wavelengths ranging from deep ultraviolet to mid infrared can in principle be obtained. Tailoring SER of a REE by positioning it inside appropriate periodic arrays of a dielectric surrounding is possible,[7] although fabrication of such dielectric microstructures is usually not trivial. In this respect, it is important to search for solid-state

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dielectrics doped with REE inside which the SER is very sensitive to changes of the nearest neighbouring atoms surrounding it. Control of the SER would then be possible in such doped dielectrics by way of adjusting external conditions such as temperature, pressure and electric field. In this communication, we report that SER of a REE transition in amorphous inorganic solids (e.g. chalcogenide glasses in the well-known Ge-As-S (GAS) system) can be dramatically modified by compositional adjustment of the host tantamount to not more than 1 mol% without any elaborated thermal treatments. Specifically, it is possible to modify the SER of Dy^{3+} ($^{6}F_{11/2}$, $^{6}H_{9/2}$) $\rightarrow$ $^{6}H_{15/2}$ transition in the GAS glasses, which results in the 1.3 μm emission, through the selective addition of low levels of Ga and CsBr. Along with the SER change, the multiphonon relaxation rate (MPR) involved in the ($^{6}F_{11/2}$, $^{6}H_{9/2}$) state also varies significantly upon the minute compositional adjustment. The combination of these effects results in the measured lifetime of the fluorescing ($^{6}F_{11/2}$, $^{6}H_{9/2}$) level, which is reciprocal of sum of SER and MPR, being greatly enhanced. The results presented show the most extreme dependence of the fluorescence lifetime on small compositional changes reported compared to any other noncrystalline solid-state dielectric.

Due to the shielding of the REE $4f$ electrons by the outer-lying $6s$ and $5d$ configurations, oscillator strengths of the $4f$-$4f$ transitions are relatively insensitive to the local coordination structure compared to the case of transition metal elements. Again, as the perturbation of the crystal field to the $4f$ electronic configuration is weak, the oscillator strengths of the forced electric dipole transitions are not large; typically order of 10^{-6} in usual noncrystalline solid hosts. In an amorphous solid host, the SER of a $4f$-$4f$ transition can be changed through modification of either the crystal field at REE sites or the dielectric constant of the host medium. Typically such modification arises as a consequence of compositional change of the host. As a result the extent of the structural modification, and especially the dielectric constant, is usually assumed to be proportional to size of the constituent change. This reasoning then requires that a significant compositional adjustment is necessary to observe any sizable change in absorption and emission properties of REE. Some $4f$-$4f$

transitions, however, exhibit exceptional sensitivity towards local structural changes around the REE and are labelled hypersensitive.[8,9] Among the $4f$ configuration of Dy^{3+}, the $^6H_{15/2} \leftrightarrow {}^6F_{11/2}$ transition satisfies the selection rules for the hypersensitive transition that are $|\Delta J| \leq 2$, $|\Delta L| \leq 2$, and $\Delta S = 0$ for two $^{2S+1}L_J$ manifolds, whilst the $^6H_{15/2} \leftrightarrow {}^6H_{9/2}$ transition does not. This is significant as the $^6H_{9/2}$ and $^6F_{11/2}$ levels are of similar energy and usually considered together and thus denoted as the $(^6H_{9/2}, {}^6F_{11/2})$ level. The hypersensitive nature of the Dy^{3+} $^6H_{15/2} \leftrightarrow {}^6F_{11/2}$ transition was first observed experimentally from Dy^{3+} ions immersed in some liquids.[10] Since then reports of the hypersensitive nature of this transition have been infrequent.[11] In the case of noncrystalline inorganic solid hosts reported changes of the spectroscopic properties due to local structural modification around the REE have been modest, even for the hypersensitive transitions.[12]

The MPR should also be considered in addition to the hypersensitive nature of the $^6H_{15/2} \leftrightarrow {}^6F_{11/2}$ transition. The MPR is dominant in determining the measured lifetime of the $(^6H_{9/2}, {}^6F_{11/2})$ level in an ordinary sulphur-based chalcogenide glass due to the presence of the small energy gap between the $(^6H_{9/2}, {}^6F_{11/2})$ and the next-lower-lying $^6H_{11/2}$ levels (see inset of Figure 1). Such strong MPR has been the major problem associated with practicality of the 1.3 μm emission of Dy^{3+}, despite possessing some superior characteristics to the $^1G_4 \rightarrow {}^3H_5$ transition of Pr^{3+} which is utilized in commercial fluoride optical fibers devices.[13] The measured lifetime of the 1.3 μm emission in some representative sulphide glasses is only ~35 μs indicating the quantum efficiency is quite low.[14,15] To reduce the MPR low phonon energy hosts are often considered. However, in general it is observed that the thermal and mechanical stability of a host medium gets worse as the phonon energy of the host is lowered. It has been shown that addition of at least 10 mol% of CsBr can be successful in increasing the lifetime of the Dy^{3+} 1.3μm emission in a Ge-Ga-S based glass.[16] Unfortunately, such significant modification on the host composition tends to deteriorate the thermal and mechanical properties. As such we postulate that such constituent modification (a few mol%) alters the parent glass structure itself as well as the nanostructure of surrounding the REE. In

addition to such structural changes we should also take into consideration the resulting localized change of the dielectric constant. Such changes affect both the optical density of state and the local field correction factor for the absorption and emission phenomena of an electric dipole impurity in a sensitive manner.[17] Based on these considerations, in this work, we aimed at tailoring only the nanostructure in the vicinity of REE through reducing the amount of compositional modification down to much lower doping levels.

The GAS hosts used in this study consisted of three Ge-rich and five As-rich glasses (inset of Figure 2) all doped with 0.02 mol% Dy. These compositions were chosen to make number of S atoms sufficient, stoichiometric, or deficient against the GeS_2-As_2S_3 tie line composition. The GAS hosts were modified by the inclusion of small amounts of Ga and CsBr and samples are designated hereafter as for example 0.5/1.0 with each number indicating molar percentage of included Ga and CsBr, respectively. The absorption spectra shown in Figure 2 clearly demonstrate that the modification of the glasses with small amounts of Ga and CsBr affects the electronic absorption edge, which will be further discussed later. Figure 3 shows the measured lifetimes of the 1.3 μm emission from the ($^6H_{9/2}$, $^6F_{11/2}$) → $^6H_{15/2}$ transition as a function of increasing the Ga and CsBr doping concentration in equal amounts for the As-rich GAS glass (circles). Also shown are the same measured lifetimes for Ge-rich but S-sufficient, S-exact and S-deficient glasses (square, inverted triangle, and triangle) doped with 0.5 mol% Ga and CsBr. In the As-rich glass the fluorescence lifetime is significantly increased upon the introduction of Ga + CsBr. The lifetime of the 0.5/0.5 sample in the As-rich host is ~340 μs, which is more than 10 times the lifetime of the unmodified 0.0/0.0 sample, and it further increases so long as the Ga ≤ CsBr condition is satisfied. The condition that Ga ≤ CsBr in order for the lifetime to be increased is common for all the host glass compositions studied. However, the size of the lifetime enhancement is also clearly dependent on the host composition in addition to the respective concentration of Ga and CsBr with their relative ratios. The measured lifetimes of the 0.5/0.5 As-rich samples are all longer than 300 μs

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regardless of the detailed host compositional changes. The Ge-rich samples however exhibit a different behaviour as shown in Figure 3. With equal doping concentrations of Ga and CsBr (0.5/0.5 in Figure 3) the abrupt lifetime enhancement is observed only in a host where excess sulphur atoms are present; in this case the lifetime is measured to be ~370 μs. Here, it should be noted that though in this case the abrupt lifetime enhancement does not appear both in the S-exact and S-deficient series, it does appear in these hosts when the doping condition Ga < CsBr is satisfied. For example, lifetime of 0.5/1.0 Ge-rich and S-exact composition is ~760 μs.

More detailed analyses have been carried out using As-rich host samples. The oscillator strengths of the 0.02 mol% Dy-doped samples are shown in Figure 4. The two closely spaced levels, $^{6}H_{9/2}$ and $^{6}F_{11/2}$, are least-squares fitted with respective Lorentzian lineshape functions based on the assumption that the electronic states are solely and independently represented by the corresponding term symbols and inhomogeneous broadening is moderate throughout the samples. The least-squares fits with a Lorentzian profile are found to be quite reproducible and a good approximation to the bandwidth of the crystal field splitting which is comparable with the energy discrepancy between centres of gravity of the two levels.[18] The overall oscillator strength of the $^{6}H_{15/2} \rightarrow (^{6}H_{9/2},$ $^{6}F_{11/2})$ transition decreases with increasing Ga-CsBr concentration. Whilst the decrease in magnitude of oscillator strength of the $^{6}H_{15/2} \rightarrow {}^{6}H_{9/2}$ transition is moderate, that of the hypersensitive $^{6}H_{15/2} \rightarrow {}^{6}F_{11/2}$ transition abruptly decreases for Ga (= CsBr) concentrations of above 0.1 mol%. At these concentrations the 'normal' $^{6}H_{15/2} \rightarrow {}^{6}H_{9/2}$ transition is dominant in the overall oscillator strength. In the 0.5/0.5 sample in the As-rich series, for example, the oscillator strength of the $^{6}H_{15/2} \rightarrow {}^{6}F_{11/2}$ transition is reduced to ~6 % of that measured in the unmodified parent glass. It is interesting to note that the sudden decrease of oscillator strength of the $^{6}H_{15/2} \rightarrow {}^{6}F_{11/2}$ transition occurs when the concentration of CsBr exceeds 10 times that of the Dy atoms. Another series of samples with the same host composition but doped with 0.01 mol% dysprosium have also exhibited

this tendency. This indicates that coordination number in the nearest-neighbouring shell of Dy^{3+} is between 5 and 10, which needs to be further confirmed.

As the oscillator strength of the $^6H_{15/2} \leftrightarrow {}^6F_{11/2}$ transition is found to be very sensitive to the concentration of Ga and CsBr when probed by the changes of the absorption cross-section spectra, it is reasonable to expect the emission spectra to behave correspondingly. As shown in Figure 5, the peak wavelength of the emission spectra blue shifts as Ga (= CrBr) concentration increases. With this increasing concentration, the oscillator strength of the lower energy $^6H_{15/2} \leftrightarrow {}^6F_{11/2}$ transition reduces compared to that of the higher energy $^6H_{15/2} \leftrightarrow {}^6H_{9/2}$ transition. As a result emission from the $^6H_{9/2} \rightarrow {}^6H_{15/2}$ transition becomes to dominate in the overall $({}^6H_{9/2}, {}^6F_{11/2}) \rightarrow {}^6H_{15/2}$ transition. As such the peak position of the $^6H_{15/2} \leftrightarrow ({}^6H_{9/2}, {}^6F_{11/2})$ absorption and emission is seen to blue shift with increasing amount of the constituent modification. Such behaviour is also observed from the Ge-rich series of samples.

The significant changes observed in the absorption and emission properties of the $^6H_{15/2} \leftrightarrow$ $({}^6H_{9/2}, {}^6F_{11/2})$ transition in our modified glasses can have a number of origins. From the viewpoint of the nanostructural rearrangement around Dy^{3+} sites, changes in coordinating atoms, interatomic distances, and their inversion symmetries have to be considered, whilst the microscopic dielectric constant and volume of the structurally modified region can also have an influence. Concerning the component atoms of our samples, existence of Ga and CsBr along with their relative concentrations is a critical prerequisite to invoke the effects observed. In this regard, we have investigated structural correlation between Ga and Br. The presence of Cs is found to play a less important role as we have obtained similar results when Cs is replaced with K or Rb. Based on Raman and EXAFS spectroscopic analyses of the samples modified with equal amount of Ga and CsBr in the As-rich region, gallium in the modified glasses is believed to form [Ga$_{3/2}$Br]$^-$ complexes.[20] Formation of such complexes needs to be charge compensated, and in this case Dy^{3+} would act as a charge compensator together with Cs^+. In this way incorporation of Dy^{3+} close to the Ga-Br related

complexes is achieved without high-temperature heat treatment being applied. Thus we presume that preferential highly symmetric coordination in nearest-neighbouring shell of dysprosium with bromine in the Ga-Br related complexes is mainly responsible for the reported behaviour. According to the previous experimental results reported for hypersensitive transitions, a decreased oscillator strength can result from enhancing the localised inversion symmetry.[9] Therefore we suggest that the local coordination structure around Dy^{3+} should possess enhanced site symmetry following the introduction of Ga and CsBr.

A small change in the oscillator strength of the hypersensitive $^6H_{15/2} \leftrightarrow \, ^6F_{11/2}$ transition gives rise to a much greater change of SER for the $^6F_{11/2} \to \, ^6H_{15/2}$ transition compared to that for the 'normal' $^6H_{9/2} \to \, ^6H_{15/2}$ transition. In the framework of Judd-Ofelt theory,[21,22] the line strength for electric dipole transitions is proportional to the reduced matrix elements, $\langle A \| U^{(\lambda)} \| B \rangle^2$, between the two electronic states involved, $\langle A |$ and $| B \rangle$, where $U^{(\lambda)}$ is the tensor operator of rank $\lambda = 2$, 4 or 6. The three values of the reduced matrix elements are 0.9394, 0.8299 and 0.2061, respectively, for the $^6F_{11/2} \to \, ^6H_{15/2}$ transition, and 0.0000, 0.0166 and 0.2017 for the $^6H_{9/2} \to \, ^6H_{15/2}$ transition.[23] Values for transitions from the $^6F_{11/2}$ state to other remaining underlying states (Figure 1) are also larger than the corresponding cases for the $^6H_{9/2}$ state. As such SER of the $^6F_{11/2}$ level is much more sensitive to the changes of the oscillator strengths than that of the $^6H_{9/2}$ transition. Thus, the decreased oscillator strengths of the $^6H_{15/2} \leftrightarrow \, ^6F_{11/2}$ transition, which arises as a consequence of the local structural changes at the Dy^{3+} sites, results in a significant decrease of SER of the $^6F_{11/2}$ state in the modified GAS glasses. On the other hand the refractive index measured at 1.3 μm is found to decrease with increasing concentrations of Ga and CsBr, though the corresponding changes are all less than ~0.02. Therefore the changes of dielectric constant would not fully account for the observed SER changes, though the microscopic dielectric constant around the Dy^{3+} is not clearly known at this time.

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Together with the decreased SER, reduced MPR is also responsible for the far enhanced lifetimes of the 1.3 μm emission in our modified glasses. Population of the $^6H_{11/2}$ level is fed from the above lying ($^6H_{9/2}$, $^6F_{11/2}$) level mainly through multiphonon relaxation processes. The intensity of the 1.3μm emission increases compared to the 1.7 μm emission from the $^6H_{11/2} \rightarrow {}^6H_{15/2}$ transition with increasing Ga (= CsBr) concentration as shown in Figure 1. This evidence clearly indicates that the decreased MPR in the modified samples must be taken into consideration. Raman spectra reveal that a molecular vibration associated with the Ga-Br chemical bond appears at ~260 cm^{-1} in the modified samples,[20,24] which is smaller than the representative phonon energy of these sulphide glasses, ~350 cm^{-1}.[25] In this regard we postulate that as we surround the Dy^{3+} with Br we are reducing the local phonon energy around the ion from that of the host glass (~350 cm^{-1}) to ~260 cm^{-1}, and then the ~260 cm^{-1} phonons participate in the MPR process of the ($^6H_{9/2}$, $^6F_{11/2}$) level in the modified glasses.

The glass transition temperature and the onset temperature of crystallization of the samples are all identical to each other within the measurement uncertainty, ±2 K. TEM investigations suggest absence of any crystalline phases inside the modified materials. Based on these results, we assume that the compositional modification carried out in this study does not bring about any apparent crystallization or reduce the thermal stability of the glasses.

As previously mentioned, locating Dy^{3+} close to the Ga-Br related complexes depends on not only the concentration of Ga and CsBr but also on the host composition, though a clear understanding of the underlying mechanisms remains to be resolved. However, differences in the chemical bond energies of the heteropolar Ge-S and As-S bonds as well as homopolar Ge-Ge, As-As and S-S bonds along with their relative ratios would result in such a dependence on the host composition. Besides the reported abrupt changes of the spectroscopic properties of Dy^{3+}, the electronic absorption edge of the host glass itself is significantly changed as Ga and CsBr are introduced (Figure 2). Though the bulk thermal properties of the host glasses remain unchanged

following the introduction of small amounts of Ga and CsBr, it is perhaps more surprising that the band gap energy of the host glass is modified to such an extent.

The results presented suggest that these modified glasses show promise for applications in fibre-optic amplifiers. The GAS glasses exhibit excellent thermal stability that is still maintained after the low-level addition of Ga and CsBr. Indeed, propagation loss of air-clad fibre drawn from a 0.2/0.2 As-rich glass preform is quite low, i.e., 0.7 dB/m at 1.6 μm.[26] The ability to deposit thin films of these glasses would be more advantageous as just low levels of Ga and CsBr are necessary to invoke the extreme hypersensitivity. In addition, the supersensitivity of the fluorescence lifetime upon the changes of the local structural coordination of Dy^{3+}, which is altered by environmental conditions such as temperature as well, would result in some novel behaviour. In fact, we have experimentally demonstrated that via careful selection of concentrations of Ga and CsBr it is possible to make the temperature dependency of lifetime to be positive, negative or even zero in the temperature range from ~78 K to ~300 K.[26]

In summary, we observe that it is possible to modify fluorescence lifetime of the ($^6H_{9/2}$; $^6F_{11/2}$) states of Dy^{3+} in noncrystalline Ge-As-S alloys through the selective addition of low levels of Ga and CsBr. We show that the change in SER + MPR is more sensitive to the local coordination structure of the Dy^{3+} compared to other hypersensitive transitions that have been observed so far in solid-state dielectric hosts. Preferential highly symmetric coordination in nearest-neighbouring shell of dysprosium with bromine in $[GaS_{3/2}Br]^{\bullet}$ complexes, which are formed spontaneously during vitrification process of the host materials, is believed to be responsible for the behaviour. As such the control of absorption and emission properties, especially fluorescence lifetimes, is possible through minute compositional adjustment by co-utilizing many hypersensitive transitions of REE and those host materials used in this study.

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Experimental

We fabricated Dy-doped GAS glasses modified with or without Ga, Cs and Br. All the starting materials were in their element forms apart from Cs and Br which were in their compound form, CsBr. Purity of the starting materials were all > 99.999 % aside from CsBr of > 99.9 % purity. A rocking furnace was used for 12 h-long melting of batches inside sealed silica ampoules, which were subsequently quenched in air following by annealing at a suitable temperature (e.g. ~490 K for the As-rich region samples). Our sample preparation procedure was the same as the conventional sulphide glass fabrication.[25] After annealing the samples did not undergo any further thermal treatment.

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Figure caption

Fig. 1. Fluorescence emission spectra of some of the modified GAS glasses in the As-rich region. Pump wavelength is at 800 nm, and the intensities are normalized with respect to that of $^6H_{11/2} \rightarrow {}^6H_{15/2}$ transition. The inset denotes the schematic energy level structure of Dy^{3+} in the GAS glasses.

Fig. 2. UV-Vis-NIR absorption spectra of some selected samples. The inset shows the parent GAS host compositions used in this study. Ga and CsBr are introduced with expense of As, whilst Dy replaces Ge. Note that the steps at ~760 nm marked with asterisk result from an instrumental feature.

Fig. 3. Measured lifetimes of the modified GAS glasses of a) the Ge-rich and S-sufficient, b) the Ge-rich and S-exact, c) the Ge-rich and S-deficient, and d) an As-rich. Lifetimes here indicate the e^{-1} times of the emission intensities. The error bars include the sample-to-sample variations in the measured lifetimes as well as uncertainties involved in the measurements. The inset shows typical experimental data obtained from the three Ge-rich samples.

Fig. 4. Changes of oscillator strengths of each transition as a function of Ga (= CsBr) concentration in a series of the As-rich GAS samples doped with 0.02 mol% Dy. The oscillator strengths of $^6H_{15/2} \rightarrow {}^6H_{9/2}$ and $^6H_{15/2} \rightarrow {}^6F_{11/2}$ transitions are computed with using the Lorentzian fit values, whilst that of $^6H_{15/2} \rightarrow ({}^6H_{9/2}, {}^6F_{11/2})$ transition is calculated directly from the measured absorption spectra. The inset shows two representative examples of the least-squares fits to the absorption cross-section spectra.

Fig. 5. The centres of gravity of the two absorption transitions, i.e., $^6H_{15/2} \rightarrow {}^6H_{9/2}$ and $^6H_{15/2} \rightarrow {}^6F_{11/2}$, and peak positions of the $({}^6H_{9/2}, {}^6F_{11/2}) \rightarrow {}^6H_{15/2}$ emission and $^6H_{15/2} \rightarrow ({}^6H_{9/2}, {}^6F_{11/2})$ absorption transitions. The centres of gravity are obtained from the Lorentzian fits. The inset denotes some representative normalized emission spectra of the As-rich GAS samples.
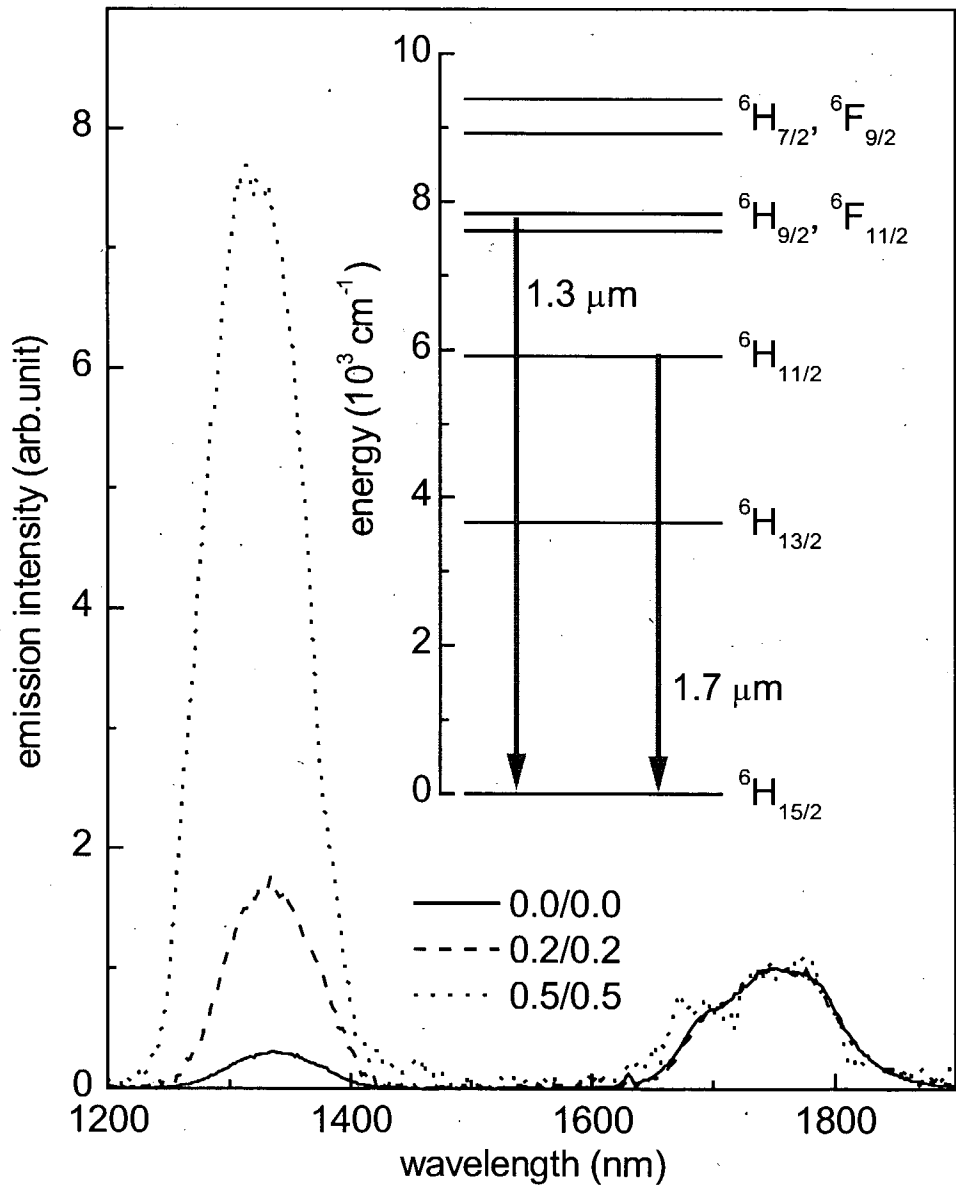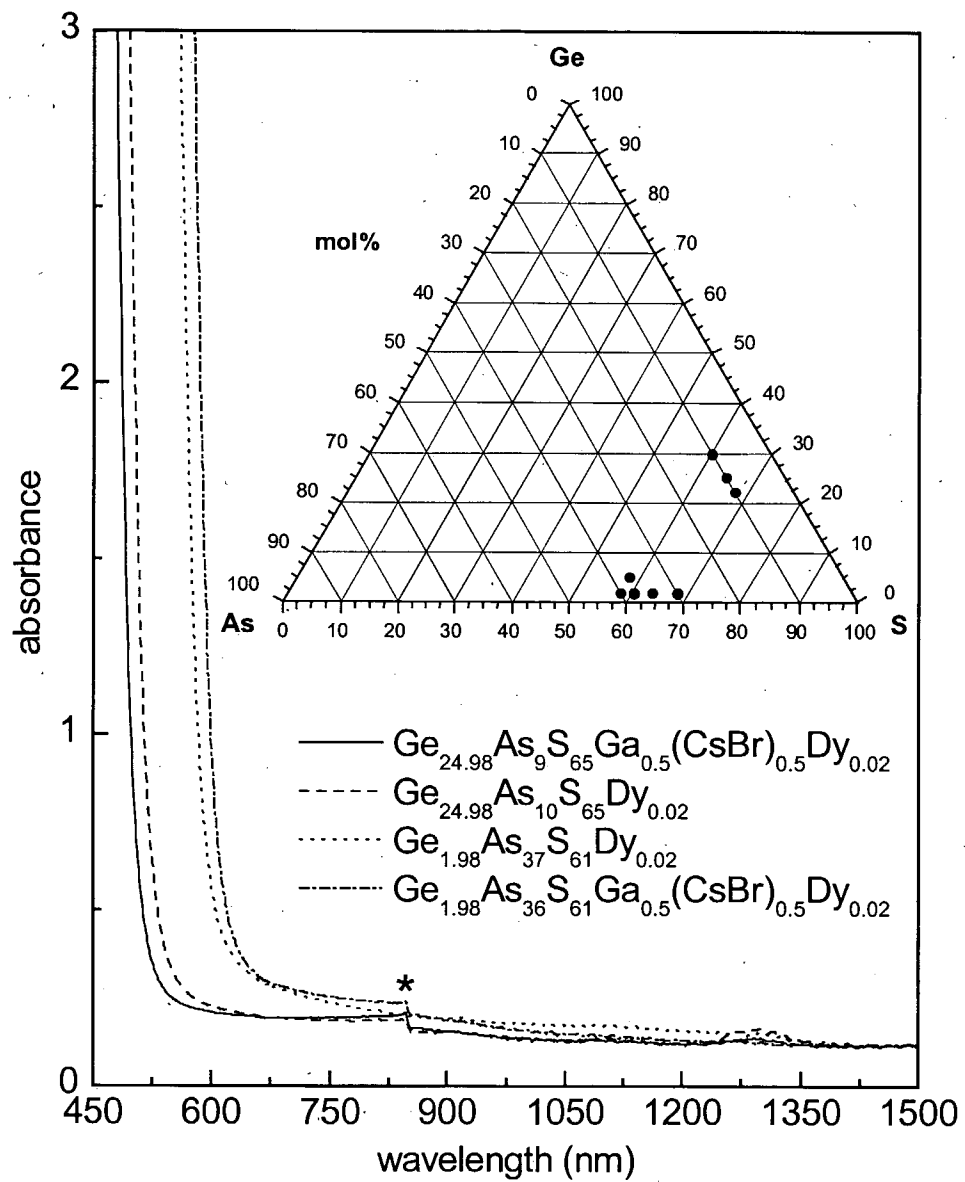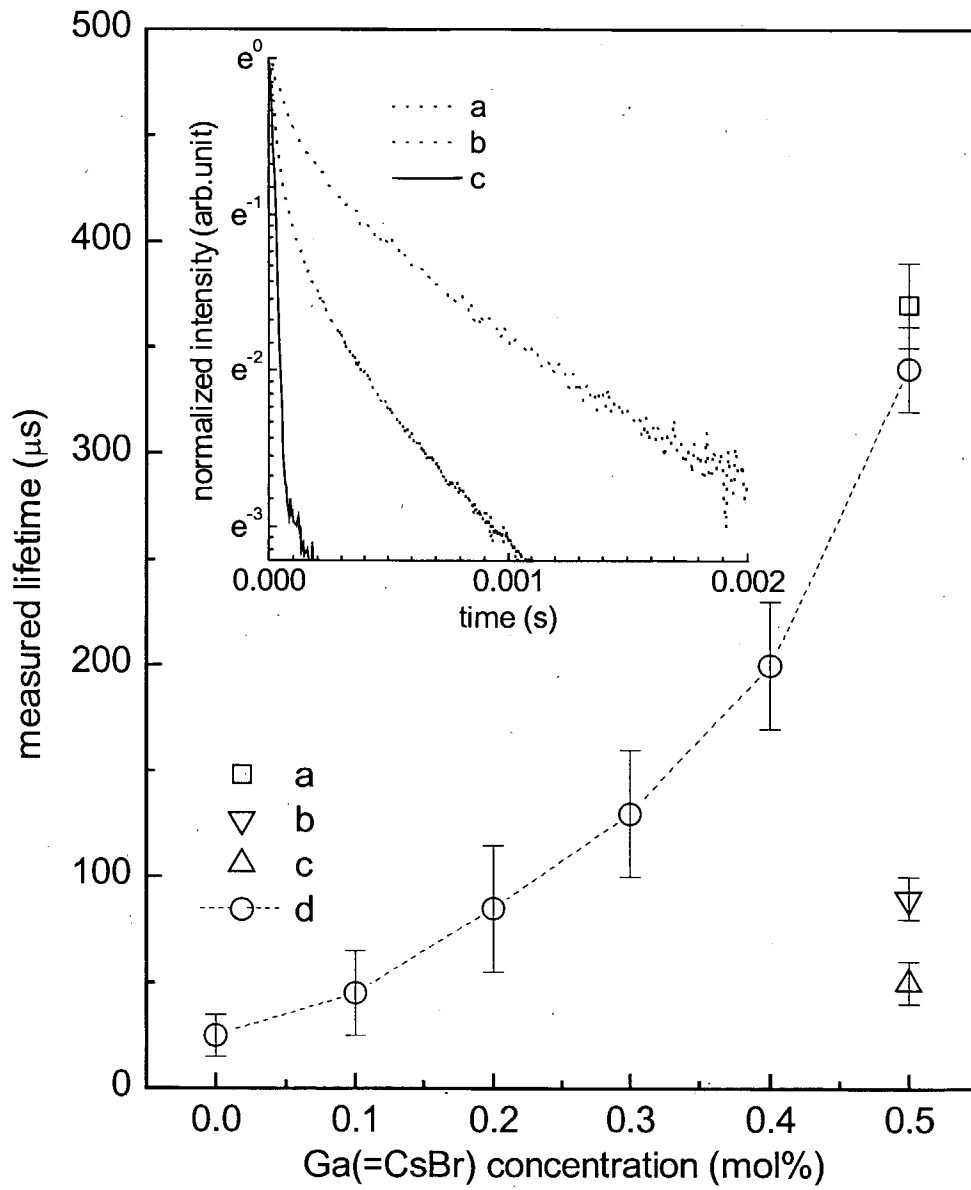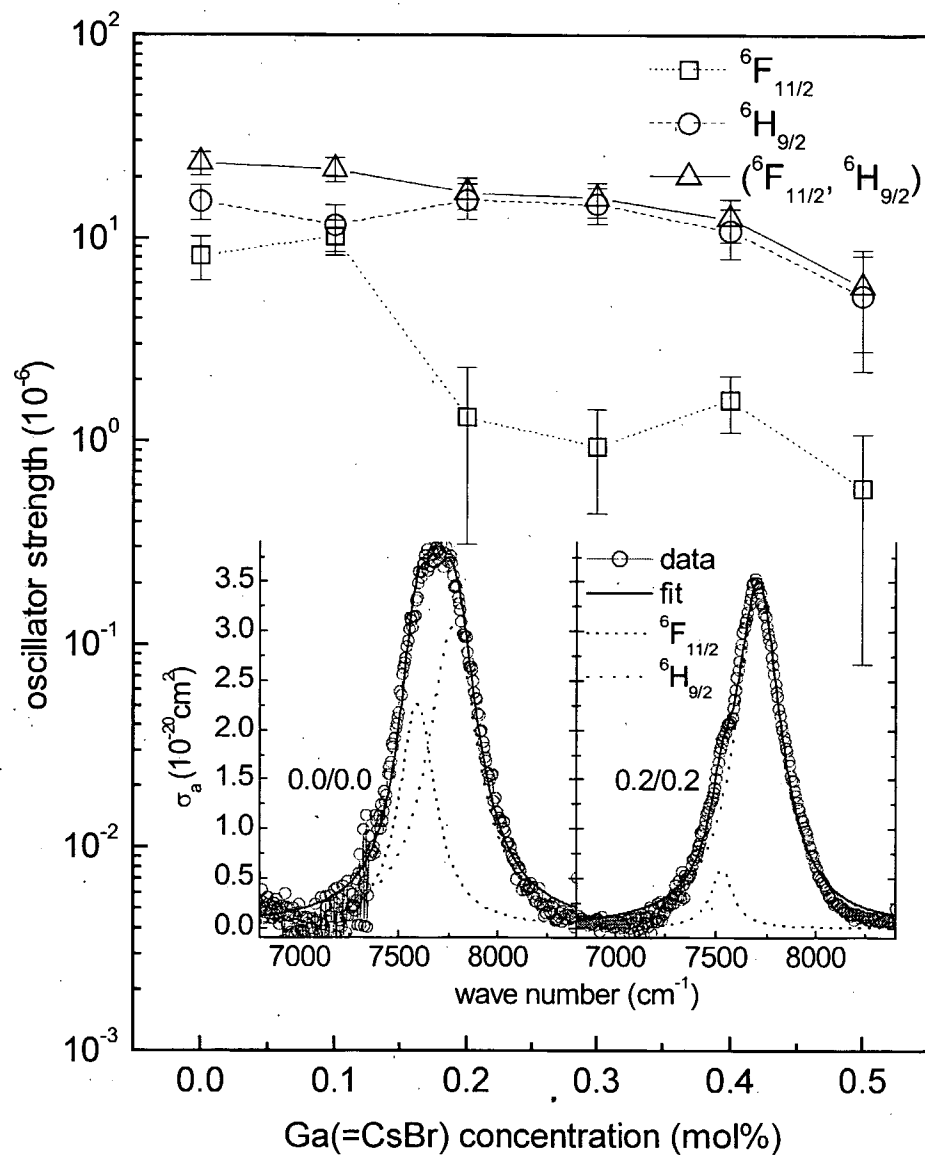
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