

# Spectroscopic data of the 1.8-, 2.9-, and 4.3- $\mu\text{m}$ transitions in dysprosium-doped gallium lanthanum sulfide glass

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Infrared emission at 1.8, 2.9, and 4.3  $\mu\text{m}$  is measured in dysprosium-doped gallium lanthanum sulfide (Ga:La:S) glass excited at 815 nm. Emission cross sections were calculated by Judd–Ofelt analysis, the Füchtbauer–Ladenburg equation, and the theory of McCumber. The  $\sigma\tau$  value for the 4.3- $\mu\text{m}$  transition is  $\sim 4000$  times larger in the Ga:La:S glass than in a dysprosium-doped  $\text{LiYF}_4$  crystal, which has lased on this transition. The large  $\sigma\tau$  value and the recently reported ability of Ga:La:S glass to be fabricated into fiber form show the potential for an efficient, low-threshold mid-infrared fiber laser. The fluorescence peak at 4.3  $\mu\text{m}$  coincides with the fundamental absorption of atmospheric carbon dioxide, making the glass a potential laser source for gas-sensing applications. © 1996 Optical Society of America

A number of important properties including low phonon energy, high refractive index, and high rare-earth solubility make the chalcogenide glass gallium lanthanum sulfide (Ga:La:S) an interesting host material for rare-earth ions. The low phonon energy of  $\sim 425\text{ cm}^{-1}$  results in low non-radiative decay rates of rare-earth energy levels, and the high refractive index of 2.4 results in high radiative emission rates. These two effects lead to much higher radiative quantum efficiencies for all transitions originating from energy levels with a small energy gap to the next-lower-lying level. This gives rise to new rare-earth transitions that cannot be observed in conventional silica glasses or low-phonon fluoride glasses such as ZBLAN. Examples of new transitions in other  $\text{Dy}^{3+}$ -doped chalcogenide glasses are the 1.34-, the 1.76-, and the 2.86- $\mu\text{m}$  fluorescence in Ge:Ga:S glass and the 2.98- and the 4.4- $\mu\text{m}$  fluorescence in  $\text{As}_2\text{S}_3$  glass.<sup>1,2</sup> Another effect of the low phonon energy is a shift of the multiphonon absorption edge to longer wavelengths, causing infrared transparency with a loss minimum near 5  $\mu\text{m}$ . All these properties make Ga:La:S glass an ideal candidate for a mid-infrared rare-earth laser host material.

We present spectroscopic measurements of  $\text{Dy}^{3+}$ -doped Ga:La:S glass. The emission cross sections of the 1.76-, the 2.83-, and the 4.27- $\mu\text{m}$  transitions were calculated from the fluorescence spectra by use of the Füchtbauer–Ladenburg equation and the results of a Judd–Ofelt analysis. These values are compared with those obtained from the absorption spectrum by use of the modified theory of McCumber after Miniscalco and Quimby.<sup>3</sup> Room-temperature laser operation on the 4.3- $\mu\text{m}$  transition was achieved by Barnes *et al.* in a  $\text{Dy}^{3+}$ -doped  $\text{LiYF}_4$  (YLF) crystal.<sup>4</sup> Comparisons of the emission cross sections and lifetimes of YLF and Ga:La:S show the potential of a 4.3- $\mu\text{m}$  laser in the glass with a much lower threshold than in YLF. We estimate a threshold 4000 times smaller, indicating the possibility of efficient diode pumping. A further

decrease of the threshold could be achieved with  $\text{Dy}^{3+}$ -doped Ga:La:S glass fiber.<sup>5</sup> A laser source at this important wavelength would find application in  $\text{CO}_2$ -gas sensing.

We melted a series of Ga:La:S glasses with the molar ratio  $70\text{Ga}_2\text{S}_3:30\text{La}_2\text{S}_3$  and doped them with  $\text{Dy}^{3+}$  by replacing 0.033–0.652 mol. % of the  $\text{La}_2\text{S}_3$  with  $\text{Dy}_2\text{S}_3$ . A sample of 7.8-mm thickness and doped with 9900 parts in  $10^6$  (ppm) by weight (0.652 mol. %) of  $\text{Dy}_2\text{S}_3$  was used for absorption measurements. The absorption spectrum from 500 to 3000 nm was measured with a Perkin-Elmer Lambda 9 spectrophotometer. A second spectrum, from 1540 to 3400 nm, was measured with a Fourier-transform spectrometer (Perkin-Elmer System 2000 FT-IR) and added to the first spectrum.

Fluorescence measurements were performed with the above-mentioned highly doped sample, which was excited by a Ti:sapphire laser operating at 815 nm. Two  $\text{CaF}_2$  lenses imaged the fluorescence onto the entrance slit of a 300-mm focal-length monochromator containing a grating blazed at 3  $\mu\text{m}$ . A third  $\text{CaF}_2$  lens imaged the exit slit onto an InSb detector cooled with liquid nitrogen. The measured signal was processed by a lock-in amplifier and a computer.

For correction measurements the sample was replaced by a blackbody source (Optronic Laboratories Model OL 480) operating at temperatures of 400, 760, and 900 °C for the 4.27-, the 2.83-, and the 1.76- $\mu\text{m}$  transitions, respectively. We performed lifetime measurements of the  ${}^6\text{H}_{11/2}$  and the  ${}^6\text{H}_{13/2}$  levels, using the chopped output of the Ti:sapphire laser at 815 nm and a suitable set of filters for wavelength selection of the levels. The 1.76- $\mu\text{m}$  emission of the  ${}^6\text{H}_{11/2}$  level was detected with an InGaAs detector, and the 2.83- $\mu\text{m}$  emission of the  ${}^6\text{H}_{13/2}$  level with an InSb detector. The fluorescence decay curves were averaged with a TEK2232 digital storage oscilloscope and transferred to a PC for the fitting procedure.

The absorption spectrum is shown in Fig. 1. The relatively weak absorption of the closely spaced  ${}^6\text{F}_{3/2}$

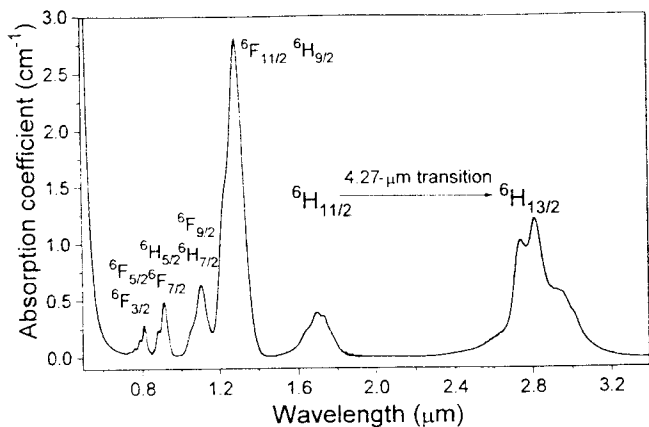


Fig. 1. Room-temperature absorption spectrum of 9900-ppm  $\text{Dy}^{3+}$ -doped Ga:La:S glass.

and  ${}^6F_{5/2}$  levels with a peak at 815 nm was used to excite the  $\text{Dy}^{3+}$  ions for fluorescence and lifetime measurements. The excited ions decay, mainly by fast nonradiative processes, to the metastable  ${}^6H_{11/2}$  and  ${}^6H_{13/2}$  levels. We measured three different infrared transitions originating from these two levels.

We used the 1.76- $\mu\text{m}$  transition ( ${}^6H_{11/2} \rightarrow {}^6H_{15/2}$ ) and the 2.83- $\mu\text{m}$  transition ( ${}^6H_{13/2} \rightarrow {}^6H_{15/2}$ ) to obtain the lifetimes of the  ${}^6H_{11/2}$  and the  ${}^6H_{13/2}$  levels, respectively. The measured lifetimes of the 9900-ppm  $\text{Dy}^{3+}$ -doped glass are 540  $\mu\text{s}$  for the  ${}^6H_{11/2}$  level and 510  $\mu\text{s}$  for the  ${}^6H_{13/2}$  level, compared with lifetimes of 1300 and 3600  $\mu\text{s}$ , respectively, for a  $\text{Dy}^{3+}$ -doped glass with the much lower ion concentration of 500 ppm. This shows that the sample used in the fluorescence experiments suffers from concentration quenching. It should be mentioned here that the measured  ${}^6H_{13/2}$  lifetime is influenced by the decay of the  ${}^6H_{11/2}$  level. For more-accurate measurements the  ${}^6H_{13/2}$  level should be excited resonantly near 2.7  $\mu\text{m}$ .

The fluorescence spectra of the 1.76-, the 2.83-, and the 4.27- $\mu\text{m}$  transitions are shown in Figs. 2 and 3. The peak of the 4.27- $\mu\text{m}$  emission spectrum overlaps exactly the fundamental absorption of the atmospheric  $\text{CO}_2$ , as shown in Fig. 2(a). Figure 2(b) shows the absorption of  $\text{CO}_2$  in the background spectrum of a Fourier-transform spectrometer with a mid-infrared light source. The two emission peaks of the corrected fluorescence spectrum in Fig. 2(c) can also be seen in the 2.83- $\mu\text{m}$  fluorescence spectrum but not in the 1.76- $\mu\text{m}$  fluorescence spectrum and might be caused by a Stark splitting of the  ${}^6H_{13/2}$  level into two groups.

The Judd-Ofelt parameters ( $\Omega_2 = 11.3 \times 10^{-20} \text{ cm}^2$ ,  $\Omega_4 = 1.0 \times 10^{-20} \text{ cm}^2$ ,  $\Omega_6 = 1.3 \times 10^{-20} \text{ cm}^2$ ) from Ref. 6 were obtained from the measured absorption spectrum excluding the absorption from the  ${}^6H_{15/2}$  ground state to the  ${}^6H_{13/2}$  level, which has a magnetic dipole contribution (selection rules:  $\Delta J = 0, \pm 1$ ,  $\Delta S = 0$ ,  $\Delta L = 0$ ,  $\Delta I = 0$ ). The electric and magnetic dipole contributions,  $A_{\text{ed}}$  and  $A_{\text{md}}$ , of the radiative transition rate  $A = A_{\text{ed}} + A_{\text{md}}$  were calculated from the equations given in Ref. 7 and are listed in Table 1. The branching ratios  $\beta$  and the radiative lifetimes  $\tau_r$  were derived from the radiative rates  $A = \beta/\tau_r$ . Comparison of  $\tau_r$  with the

measured lifetimes  $\tau_m$  gives the quantum efficiencies  $\eta = \beta \times \tau_m/\tau_r$ . The overall quantum efficiency of the  ${}^6H_{11/2}$  level (51%) and the quantum efficiency of the 4.27- $\mu\text{m}$  transition (7.4%) in particular are remarkably high considering the small energy gap of  $\sim 2350 \text{ cm}^{-1}$  to the next-lower-lying level. A second Judd-Ofelt calculation omitting the hypersensitive ( ${}^6H_{9/2}, {}^6F_{11/2}$ )  $\rightarrow {}^6H_{15/2}$  transition at 1.3  $\mu\text{m}$  yielded values for the radiative rates that lie in the range of accuracy ( $\approx 20\%$ ) of the previous calculation.

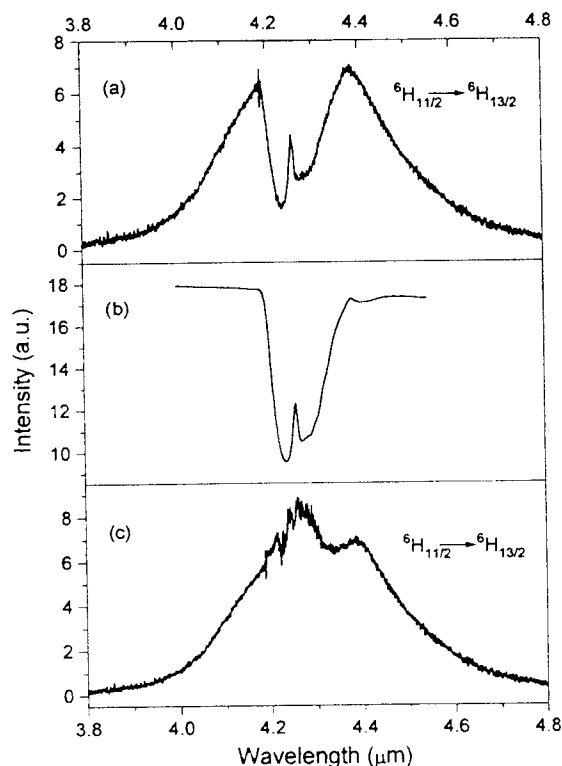


Fig. 2. (a) Uncorrected  $\text{Dy}^{3+}$  fluorescence spectrum ( ${}^6H_{11/2} \rightarrow {}^6H_{13/2}$ ). (b)  $\text{CO}_2$  absorption of a white-light source measured with the Fourier-transform infrared spectrometer. (c) Corrected  $\text{Dy}^{3+}$  fluorescence spectrum ( ${}^6H_{11/2} \rightarrow {}^6H_{13/2}$ ).

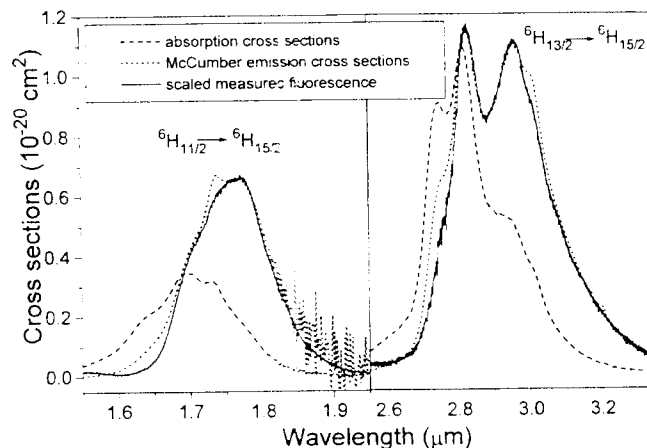


Fig. 3. Absorption cross sections and McCumber emission cross sections together with the scaled measured fluorescence spectra of the 1.76- and the 2.83- $\mu\text{m}$  transitions of  $\text{Dy}^{3+}$ -doped Ga:La:S glass.

Table 1. Radiative Properties of Dy<sup>3+</sup>-Doped Ga:La:S Glass

Transition	$\lambda$ ( $\mu\text{m}$ )	$A_{\text{ed}}$ ( $\text{s}^{-1}$ )	$A_{\text{md}}$ ( $\text{s}^{-1}$ )	$\beta$ (%)	$\tau_r$ ( $\mu\text{s}$ )	$\tau_m$ ( $\mu\text{s}$ )	$\eta$ (%)	$\sigma_{\text{em,FL}}$ ( $10^{-20}$ $\text{cm}^2$ )	$\sigma_{\text{em,MC}}$ ( $10^{-20}$ $\text{cm}^2$ )
${}^6H_{11,2} \rightarrow {}^6H_{13,2}$	4.27	42	15	14	2532	1300	7.4	1.17	—
$\rightarrow {}^6H_{15,2}$	1.76	338	—	86	2532	1300	44	0.57	0.64
${}^6H_{13,2} \rightarrow {}^6H_{15,2}$	2.83	129	30	100	6289	3600	57	0.92	1.16

The emission cross sections were calculated by two different approaches. First we used the Füchtbauer–Ladenburg equation as given in Ref. 8:

$$\sigma_{\text{em,FL}}(\lambda) = \frac{A\lambda^5 I(\lambda)}{8\pi n^2 c \int \lambda I(\lambda) d\lambda}, \quad (1)$$

where  $I(\lambda)$  is the measured intensity spectrum of the fluorescence. The refractive index  $n$  is 2.36 for all three transitions. The emission cross sections for the 1.76- and the 2.83- $\mu\text{m}$  transitions (Table 1) are slightly smaller than those reported for Dy<sup>3+</sup>-doped Ge:Ga:S glass, although the magnetic dipole contribution of the latter transition was not included in Ref. 1.

To check the above results we used the theory of McCumber after Miniscalco and Quimby<sup>3</sup> to calculate the emission cross sections  $\sigma_{\text{em,MC}}$  of the two ground-state transitions at 1.76 and 2.83  $\mu\text{m}$  from the absorption cross sections  $\sigma_{\text{abs}}$ :

$$\sigma_{\text{em,MC}}(\lambda) = \sigma_{\text{abs}}(\lambda) \frac{Z_l}{Z_u} \exp\left(\frac{E_{ZL} - 10^4/\lambda}{kT}\right), \quad (2)$$

where  $Z_l$  and  $Z_u$  are the partition functions of the lower and the upper manifolds, respectively,  $E_{ZL}$  is the energy gap between the lowest Stark level of the ground-state manifold and the lowest Stark level of the upper manifold measured in inverse centimeters,  $\lambda$  is the wavelength in micrometers, and  $k = 0.695 \text{ cm}^{-1} \text{ K}^{-1}$  is the Boltzmann constant.  $Z_l$ ,  $Z_u$ , and  $E_{ZL}$  are usually obtained from the energy levels of the manifolds and the Stark levels within these manifolds. As this information is not available for Ga:La:S glass, the parameters  $Z_l$ ,  $Z_u$ , and  $E_{ZL}$  can be obtained from a simplified model.<sup>3</sup> The Stark levels of a given manifold are assumed to be equally spaced. The width of the ground state is given by the long-wavelength half-width of the emission spectrum measured from the peak of the spectrum to the point where the spectrum falls to 5% of the peak value. The width of the excited manifold is obtained in a similar way from the short-wavelength half-width of the absorption spectrum. The width of a manifold divided by the number of Stark levels gives the energy spacing of the Stark levels that is necessary for the calculation of the partition functions  $Z_l$  and  $Z_u$ . The values for  $Z_l/Z_u$  are 1.84 and 1.07 for the 1.76- and the 2.83- $\mu\text{m}$  transitions, respectively.  $E_{ZL}$  can be taken as the average of the absorption and the emission peaks. The calculated emission cross section spectra of the 1.76- and the 2.83- $\mu\text{m}$  transitions are shown in Fig. 3 together with the absorption spectra and the measured fluorescence spectra, which were multiplied by  $\lambda^5$  and a constant  $C$ . The good spectral correspondence of the calculated emission cross sections and the scaled measured fluorescence shows that the modified McCumber theory is capable of producing absolute emission cross sections and the correct emis-

sion shape without a detailed knowledge of the electronic structure of the Dy<sup>3+</sup> ions.

The emission cross sections obtained from the theory of McCumber (Table 1) confirm the values calculated from the Judd–Ofelt calculations and the Füchtbauer–Ladenburg equation. They are slightly larger, especially for the  ${}^6H_{13,2} \rightarrow {}^6H_{15,2}$  transition, but lie in the range of accuracy.<sup>3</sup>

To date laser action on the 4.27- $\mu\text{m}$  transition could be achieved only in a low-phonon YLF crystal.<sup>4</sup> The reported emission cross section for this transition and the  ${}^6H_{11,2}$  lifetime in Dy<sup>3+</sup>-doped YLF are  $0.44 \times 10^{-20} \text{ cm}^2$  and 0.83  $\mu\text{s}$ , respectively. Thus the  $\sigma\tau$  product of Dy<sup>3+</sup>-doped Ga:La:S glass, which is a measure of the laser threshold, should be  $\sim 4000$  times larger than the  $\sigma\tau$  product of YLF. The laser threshold in turn should be  $\sim 4000$  times smaller. Together with the recent progress in Ga:La:S glass fiber fabrication these calculations show the potential of a diode-pumped Dy<sup>3+</sup>-doped fiber laser operating at 4.27  $\mu\text{m}$ , which would be useful for CO<sub>2</sub> gas sensing.<sup>5</sup>

In conclusion, we have presented infrared absorption, lifetime, and fluorescence measurements of Dy<sup>3+</sup>-doped Ga:La:S glass. Emission cross sections for three infrared transitions were calculated by Judd–Ofelt calculations, the Füchtbauer–Ladenburg equation, and the modified theory of McCumber and yielded promising  $\sigma\tau$  values for the 4.27- $\mu\text{m}$  transition compared with those from the existing 4.34- $\mu\text{m}$  laser in a bulk YLF crystal. A Dy<sup>3+</sup>-doped Ga:La:S glass fiber would make use of the advantages of the fiber geometry and could provide a more efficient and compact laser source with 0.8- or 1.3- $\mu\text{m}$  laser diodes used for pumping.

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