Spectroscopic data of the 1.8-, 2.9-, and 4.3-μm transitions in dysprosium-doped gallium lanthanum sulfide glass

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Infrared emission at 1.8, 2.9, and 4.3 μm 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 Fuchtbauer–Ladenburg equation, and the theory of McCumber. The στ value for the 4.3-μm transition is ~4000 times larger in the Ga:La:S glass than in a dysprosium-doped LiYF₄ crystal, which has based on this transition. The large στ 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 μm 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 ~125 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 Dy³⁺-doped chalcogenide glasses are the 1.34-, the 1.76-, and the 2.86-μm fluorescence in Ge:Ga:S glass and the 2.98- and the 4.4-μm fluorescence in As₂S₃ glass. 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 μm. 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 Dy³⁺-doped Ga:La:S glass. The emission cross sections of the 1.76-, the 2.83-, and the 4.27-μm transitions were calculated from the fluorescence spectra by use of the Fuchtbauer–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. Room-temperature laser operation on the 4.3-μm transition was achieved by Barnes et al. in a Dy³⁺-doped LiYF₄ (YLF) crystal. Comparisons of the emission cross sections and lifetimes of YLF and Ga:La:S show the potential of a 4.3-μm 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 Dy³⁺-doped Ga:La:S glass fiber. A laser source at this important wavelength would find application in CO₂-gas sensing.

We melted a series of Ga:La:S glasses with the molar ratio 70Ga₂S₃:30La₂S₃ and doped them with Dy³⁺ by replacing 0.033–0.652 mol. % of the La₂S₃ with Dy₂S₃. A sample of 7.8-mm thickness and doped with 9900 parts in 10⁶ (ppm) by weight (0.652 mol. %) of Dy₂S₃ 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 CaF₂ lenses imaged the fluorescence onto the entrance slit of a 300-mm focal-length monochromator containing a grating blazed at 3 μm. A third CaF₂ 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-μm transitions, respectively. We performed lifetime measurements of the 6H₁₁/₂ and the 6H₁₃/₂ 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-μm emission of the 6H₁₁/₂ level was detected with an InGaAs detector, and the 2.83-μm emission of the 6H₁₃/₂ level with an InSb detector. The fluorescence decay curves were averaged with a Tektronix 2232 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 6F₃/₂
and $^{6}F_{5/2}$ levels with a peak at 815 nm was used to excite the Dy$^{3+}$ ions for fluorescence and lifetime measurements. The excited ions decay, mainly by fast nonradiative processes, to the metastable $^{6}H_{11/2}$ and $^{6}H_{13/2}$ levels. We measured three different infrared transitions originating from these two levels.

We used the 1.76-μm transition ($^{6}H_{11/2} \rightarrow ^{6}H_{15/2}$) and the 2.83-μm transition ($^{6}H_{13/2} \rightarrow ^{6}H_{15/2}$) to obtain the lifetimes of the $^{6}H_{11/2}$ and the $^{6}H_{13/2}$ levels, respectively. The measured lifetimes of the 9900-ppm Dy$^{3+}$-doped glass are 540 μs for the $^{6}H_{11/2}$ level and 510 μs for the $^{6}H_{13/2}$ level, compared with lifetimes of 1300 and 3600 μs, respectively, for a 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 $^{6}H_{13/2}$ lifetime is influenced by the decay of the $^{6}H_{11/2}$ level. For more accurate measurements the $^{6}H_{13/2}$ level should be excited resonantly near 2.7 μm.

The fluorescence spectra of the 1.76-, the 2.83-, and the 4.27-μm transitions are shown in Figs. 2 and 3. The peak of the 4.27-μm emission spectrum overlaps exactly the fundamental absorption of the atmospheric CO$_2$, as shown in Fig. 2(a). Figure 2(b) shows the absorption of 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-μm fluorescence spectrum but not in the 1.76-μm fluorescence spectrum and might be caused by a Stark splitting of the $^{6}H_{13/2}$ level into two groups.

The Judd–Ofelt parameters ($\Omega_{1} = 11.3 \times 10^{-20}$ cm$^2$, $\Omega_{2} = 1.6 \times 10^{-20}$ cm$^2$, $\Omega_{3} = 1.3 \times 10^{-20}$ cm$^2$) from Ref. 6 were obtained from the measured absorption spectrum excluding the absorption from the $^{6}H_{15/2}$ ground state to the $^{6}H_{15/2}$ level, which has a magnetic dipole contribution (selection rules: $\Delta L = 0, \pm 1, \Delta S = 0, \Delta J = 0$). The electric and magnetic dipole contributions, $A_{e}$ and $A_{m}$, of the radiative transition rate $A = A_{e} + A_{m}$ 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 $^{6}H_{11/2}$ level (51%) and the quantum efficiency of the 4.27-μm transition (7.4%) in particular are remarkably high considering the small energy gap of $\sim 2350$ cm$^{-1}$ to the next-lower-lying level. A second Judd–Ofelt calculation omitting the hypersensitive ($^{6}H_{9/2}, ^{6}H_{11/2} \rightarrow ^{6}H_{15/2}$) transition at 1.3 μm yielded values for the radiative rates that lie in the range of accuracy ($\pm 20\%$) of the previous calculation.
The emission cross sections were calculated by two different approaches. First we used the Fuchtbauer–Ladenburg equation as given in Ref. 8:

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

where $I(\lambda)$ is the measured intensity of the line, $\lambda$ is the wavelength in micrometers, and $M(\lambda)$ is the wavelength in centimeters, and $\Delta$ is the energy spacing of the Stark levels of the Stark levels. $Z_i$ and $Z_u$ 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 $Z_i$, $Z_u$, and $Z_{uL}$ can be obtained from a simplified model. 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 first order 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 of the Stark levels. The cross sections for the calculation of the partition functions $Z_i$ and $Z_u$ are calculated by the absorption spectra and the measured fluorescence spectra, which are multiplied by $\lambda^2$ and a constant. The good spectral correspondence of the calculated emission cross sections and the measured fluorescence spectra shows that the modified McCumber theory is capable of producing absolute emission cross sections and the correct emission shape without a detailed knowledge of the electronic structure of the Dy³⁺ ions.

The emission cross sections obtained from the theory of McCumber (Table 1) confirm the values calculated from the Judd–Ofelt calculations and the Fuchtbauer–Ladenburg equation. They are slightly larger, especially for the first transition, but lie in the range of accuracy.

To date laser action on the 4.27-μm transition could be achieved only in a low-phonon YLF crystal. The reported emission cross section for this transition and the 6.11.2 lifetime in Dy³⁺ doped YLF are 0.44 × 10⁻²⁰ cm² and 0.13 μs, respectively. Thus the $\sigma \tau$ product of Dy³⁺ doped Ga:La:S glass, which is a measure of the laser threshold, should be about 4000 times larger than the $\sigma \tau$ product of YLF. The laser threshold in turn should be about 4000 times smaller. Together with the recent progress in Ga:La:S glass fiber fabrication these calculations show the potential of a diode-pumped Dy³⁺ doped fiber laser at 4.27 μm, which would be useful for CO₂ gas sensing.

In conclusion, we have presented infrared absorption, lifetime, and fluorescence measurements of Dy³⁺ doped Ga:La:S glass. Emission cross sections for three infrared transitions were calculated by Judd–Ofelt calculations, the Fuchtbauer–Ladenburg equation, and the modified theory of McCumber and yield promising $\sigma \tau$ values for the 4.27-μm transition compared with those from the existing 4.34-μm laser in a bulk YLF crystal. A Dy³⁺ 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-μm laser diodes used for pumping.

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### References