Experimental studies of spontaneous emission from dopants in an absorbing dielectric

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We report the first measurements, to our knowledge, of the modification of spontaneous emission rates of Eu^{3+} ions in the visible region owing to an absorbing medium. Precise levels of the absorption coefficient are introduced by codoping with different amounts of Nd^{3+}. We use a binary glass system $PbO-B_2O_3$ as the host, the compositional variation of which leads to a change in the real part of the refractive index. Measured lifetimes are found to follow the real cavity model, and the data are analyzed by the model proposed by Scheel *et al.* [Phys. Rev. A **60**, 4094 (1999)]. We give estimates of the parameter that is related to the radius of the cavity around Eu^{3+}. © 2005 Optical Society of America

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The radiative lifetime of an atom in a dielectric is not only determined by the electronic wave functions of the atomic states involved but also by the photon density of states and the electromagnetic field strength of the photon modes at the position of the atom. The spontaneous decay rate of an atom placed in a dielectric can be modified when compared with its free-space rate, given by

$$\Gamma_0 = \frac{\mu^2 \omega^3}{3\pi\hbar\varepsilon_0 c^3},\tag{1}$$

where μ is the dipole moment and ω is the transition frequency. Modification of the spontaneous emission rate has been studied for various systems such as atoms embedded in a dielectric, free atoms in resonant cavities,[1–3] organic molecules,[4] Eu^{3+} complexes in solution,[5] III–V semiconductor quantum wells,[6] and Er^{3+}-doped SiO_2.[7] Rikken and Kessener[8] demonstrated the modification of lifetimes of Eu^{3+} complexes dissolved in different solvents and Shuurmans *et al.*[9] demonstrated the same in Eu^{3+} in supercritical CO_2 gas. The lifetimes in the presence of a bulk and transparent dielectric can be written as

$$\tau(n) = l(n)\frac{\tau_0}{n}.\tag{2}$$

Here $\tau(n)$ is the lifetime in the medium of (real) refractive index n; τ_0 is the free-space lifetime; and $l(n)$ is the local field correction factor, which in addition is also found to give rise to frequency shifts in a two-level system.[10] While calculating the local field, the atom is assumed to be at the center of a spherical cavity. The dimensions of such a cavity are assumed to be large compared with the dimensions of the atom and small compared with the wavelengths involved. Two distinct models, real and virtual for the nature of the cavities, have been proposed. The $l(n)$ for real and virtual cavities are $(2n^2+1)^2/9n^4$ and $9/(n^2+2)^2$, respectively.[11–13] In the real-cavity model it is assumed that the atom is at the center of the cavity and

the cavity itself has no other material. The virtual-cavity model is based on the work of Lorentz and assumes a uniform distribution of material within and outside the cavity. In a recent experiment[14] we measured the lifetimes of Eu^{3+} in bulk $PbO-B_2O_3$ glass. Our measurements were found to agree well with the real-cavity model.

In many real situations the radiating ion would be surrounded by an absorbing medium. Such a situation may arise from self-absorption, impurities, codopants, etc. In such situations the refractive index is no longer real and one has to take into account the complex nature of the refractive index of the medium. An exact theoretical treatment of the spontaneous decay of an excited two-level atom in the presence of a dispersive and absorbing dielectric medium was presented by Scheel *et al.*[15] Experimentally this situation can be created by suitably doping the radiating ion in an absorbing medium. Because of the well-known energy level structure of rare-earth elements, one can choose two rare-earth elements in such a way that the absorption of one of the elements overlaps the emission of the other. The energy transfer from Eu^{3+} to Nd^{3+} has been studied in various hosts, including glasses.[16] $PbO-B_2O_3$ glass as a host is attractive not only because it is easy to fabricate but also for its application in wavelength-division multiplexing.[17]

No experimental studies are available in the literature that take into account the effects of both the real and the imaginary components of the refractive index of the dielectric on the rates of spontaneous emission of an atom embedded in a medium. Here we present the first estimate, to our knowledge, of the spontaneous emission rates of an Eu^{3+} ion embedded in a dielectric of $PbO-B_2O_3$ with different concentrations of Nd^{3+} as a codopant. Because the absorption of Nd^{3+} overlaps with the emission spectrum of Eu^{3+} and both Eu^{3+} and Nd^{3+} can be introduced into the binary complex, this system seems to be an excellent probe for characterizing the spontaneous emission rates for dopants in an absorbing and dispersive dielectric medium.
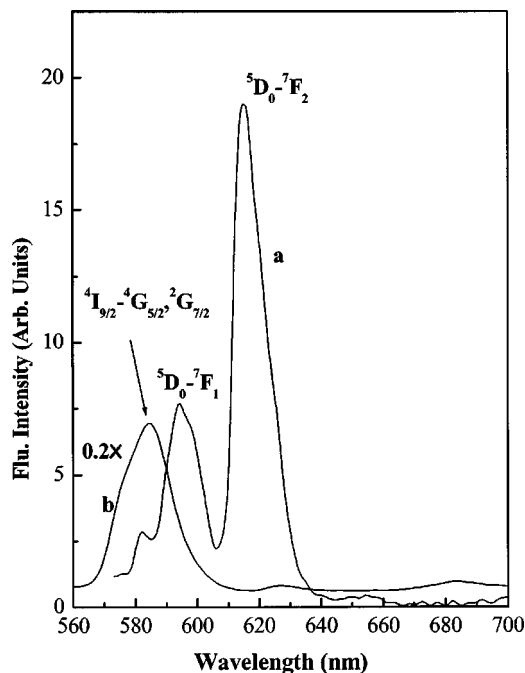
Fig. 1. a, Fluorescence spectrum of Eu^{3+} and b, absorption spectrum of Nd^{3+} magnified $5\times$ for clarity.

The binary lead borate glasses xPbO$+(100-x)$B$_2$O$_3$:1Eu$^{3+}+y$Nd^{3+} were prepared by the melt quench method. The concentration of PbO was varied in steps of 10 from 30 to 90, and concentrations of Nd^{3+} were chosen as 0, 0.05, 0.1, 0.25, 0.5, and 1 mol.%. The starting materials, PbO, H_3BO_3, Eu_2O_3, and Nd_2O_3, were ground in an agate mortar for 20 min under acetone. Then the mixture was subjected to heating at 200°C for 1 h; 500°C for 2 h; and 800–1000°C, depending on the composition, for 45 min. When a clear melt was achieved, it was poured into a copper mold and pressed by another copper plate. The glasses were then annealed at 250°C for 24 h. They were polished with cerium oxide to obtain clear and flat surfaces.

The relative compositional variation of PbO and B_2O_3 yields a change in the real part (η) of the refractive index and does not depend on either the Eu^{3+} or Nd^{3+} concentrations. Index η was measured by the Brewster's angle method with a He–Ne laser. The values of imaginary part κ of the refractive index were obtained by taking the area under the peak, $^4I_{9/2}$ to $(^4G_{5/2}, ^2G_{7/2})$, from the absorption spectrum of Nd^{3+} shown in Fig. 1. This transition is in resonance with the fluorescence from $^5D_0$ to $^7F_0$ of Eu^{3+} also shown in Fig. 1. The value of κ is 0.54×10^{-6} for the lowest Nd^{3+} concentration and 9.41×10^{-6} for the highest Nd^{3+} concentration. The fluorescence of Eu^{3+} is from $^5D_0$ to ^7F_j $(j=0,1,2,3,4)$. Figure 2 shows the fluorescence of Eu^{3+} with different concentrations of Nd^{3+} indicated by the numbers on each curve. The reduction in the fluorescence is mainly due to two factors; quenching by Nd^{3+} and partial absorption of the excitation energy (532 nm) by Nd^{3+} itself. The excitation spectra of Eu^{3+} in the absence and in the presence of Nd^{3+} are identical indicating that there is no

reverse energy transfer, i.e., from Nd^{3+} to Eu^{3+}. Hence the measured lifetimes are due to the energy transfer from $^5D_0$ of Eu^{3+} to $(^4G_{5/2}, ^2G_{7/2})$ of Nd^{3+}. The lifetimes of Eu^{3+} were measured at 613 nm, which is the strongest emission peak. Our measured decay times are the same for all the transitions from the $^5D_0$ to ^7F_j manifold as the upper level is nondegenerate.[9] The samples were excited with the second harmonic (532 nm) of the Nd:YAG laser. The pulse width was 6 ns with a 10-Hz repetition rate. The fluorescence was collected at 90° with a monochromator. The output from the photomultiplier tube was connected to a Tektronix TDS 220 digital oscilloscope. The decays showed a deviation from the single exponential nature for higher Nd^{3+} concentrations. The lifetimes for all the samples were taken to be as those obtained by a single exponential fit for better consistency. To analyze our experimental data, we used Eq. (53) of Ref. 15, which describes both radiative and nonradiative decay owing to dipole–dipole energy transfer in an absorbing medium:

$$\frac{\Gamma}{\Gamma_0} = \frac{9\varepsilon_I(\omega_A)}{|2\varepsilon(\omega_A)+1|^2}\left(\frac{c}{\omega_A R}\right)^3$$

$$+ \frac{9\varepsilon_I(\omega_A)[28|\varepsilon(\omega_A)|^2 + 12\varepsilon_R(\omega_A)+1]}{|2\varepsilon(\omega_A)+1|^4}\left(\frac{c}{\omega_A R}\right)$$

$$+ \frac{9\eta(\omega_A)}{|2\varepsilon(\omega_A+1)|^4}[4|\varepsilon(\omega_A)|^4 + 4\varepsilon_R|\varepsilon(\omega_A)|^2 + \varepsilon_R^{\;2}(\omega_A)]$$

$$- \varepsilon_I^{\;2}(\omega_A)] - \frac{9\kappa(\omega_A)}{|2\varepsilon(\omega_A+1)|^4}[4|\varepsilon(\omega_A)|^2 + 2\varepsilon_R(\omega_A)]$$

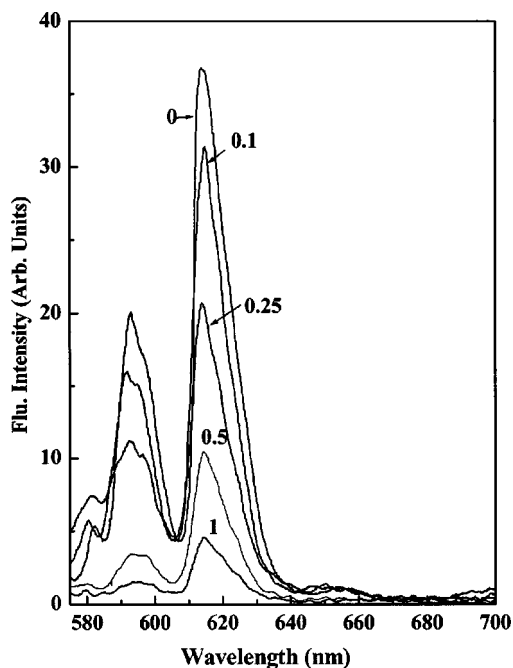$$+ O(R), \quad \varepsilon_R = \eta^2 - \kappa^2, \quad \varepsilon_I = 2\eta\kappa, \tag{3}$$

Fig. 2. Fluorescence spectrum of Eu^{3+} in the presence of varying amounts of Nd^{3+}. Number on each curve denotes the Nd^{3+} concentration.
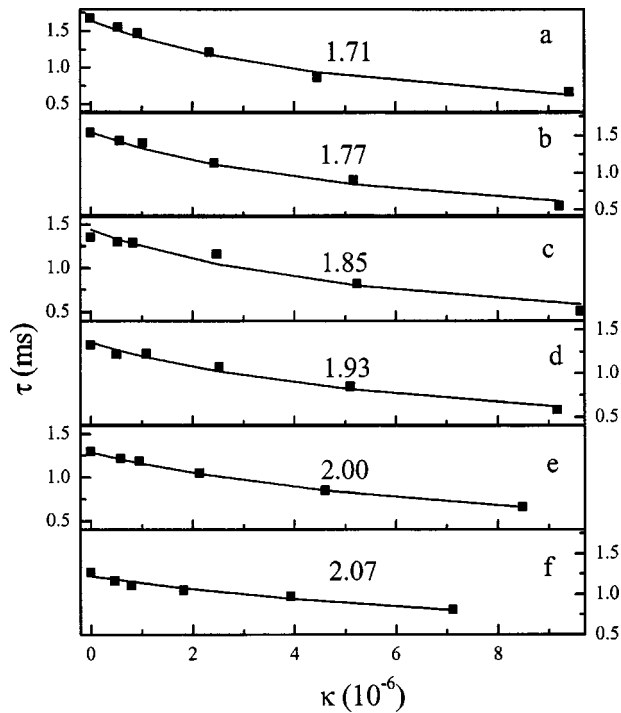
Fig. 3. Experimentally measured lifetimes, τ (filled squares) as a function of absorption, $\kappa(=\lambda\alpha/4\pi)$ for different real parts of the refractive index, indicated in each curve. The values of R (in nanometers) obtained by theoretical fit (solid curves) using Eq. (3) are a, 1.05; b, 1.01; c, 0.97; d, 0.97; e, 0.97; f, 1.04

where Γ and Γ_0 are the decay rates in the presence of an absorber and in free space, respectively, and $O(R)$ contains the higher-order terms of R. Clearly decay rate Γ sensitively depends on the radius of cavity R through ε_I, i.e., absorption in the medium. In particular the R^{-3}-dependent terms can be regarded as arising due to nonradiative decay through dipole–dipole energy transfer from the Eu^{3+} ion to the Nd^{3+} ion. In a purely dispersive medium, $\varepsilon_I = 0$, and this equation reduces to the equation for the case of a transparent dielectric. The refractive index can be measured by other techniques, whereas the radius cannot be measured directly. Therefore the measurement of the lifetimes in the presence of absorption permits the determination of R. We prepared six sets of samples, each with a different real part of the refractive index. In each set, increasing the amount of the codopant Nd^{3+} gradually increases absorption. The lifetimes decreased with the increase of the absorption. All six sets of data were analyzed individually with Eq. (3). η and κ were assigned the measured values. The free-space lifetime was taken from Ref. 14. Figure 3 shows the lifetimes of Eu^{3+} as a function of absorption with a different real part of the refractive index and the fittings using the equation. The error in the measurement of the lifetimes is approximately 5%, which is due to the glass preparation, concentration variation, etc. The least-squares fit yielded the radius

of the cavity to be 1 ± 0.05 nm. This is to our knowledge the first time that the radius of the cavity has been experimentally determined in a dielectric. The values of R of the order of 1 nm are not unreasonable, as experiments involving energy transfer from one rare-earth element to another have shown that multipolar interactions can occur over distances of 2 nm.[18]

In summary, we have measured the lifetimes of europium in the presence of absorption as a function of refractive index. The data have been analyzed with the equation derived by Scheel et al.[15] for an emitter in an absorbing dielectric. Parameter R related to the radius of the cavity around the europium is found to be of the order of 1 nm, which is in the expected range.

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References

1. G. S. Agarwal, Phys. Rev. A **12**, 1475 (1975).
2. D. J. Heinzen, J. J. Childs, J. E. Thomas, and M. S. Feld, Phys. Rev. Lett. **58**, 1320 (1987).
3. D. J. Heinzen and M. S. Feld, Phys. Rev. Lett. **59**, 2623 (1987).
4. F. De Martini, G. Innocenti, G. R. Jacobovitz, and P. Mataloni, Phys. Rev. Lett. **59**, 2955 (1987).
5. F. De Martini, M. Marrocco, P. Mataloni, L. Crescentini, and R. Loudon, Phys. Rev. A **43**, 2480 (1991).
6. Y. Yamamoto, S. Machida, Y. Horikoshi, K. Igeta, and G. Björk, Opt. Commun. **80**, 337 (1991).
7. A. M. Vredenberg, N. E. J. Hunt, E. F. Schubert, D. C. Jacobson, J. M. Poate, and G. J. Zydzik, Phys. Rev. Lett. **71**, 517 (1993).
8. G. L. J. A. Rikken and Y. A. R. R. Kessener, Phys. Rev. Lett. **74**, 880 (1995).
9. F. J. P. Schuurmans, D. T. N. de Lang, G. H. Wegdam, R. Sprik, and A. Lagendijk, Phys. Rev. Lett. **80**, 5077 (1998).
10. R. Friedberg, S. R. Hartmann, and J. T. Manassah, Phys. Rep. Phys. Lett. **7C**, 101 (1973).
11. R. J. Glauber and M. Lewenstein, Phys. Rev. A **43**, 467 (1991).
12. P. W. Milonni, J. Mod. Opt. **42**, 1991 (1995).
13. C. J. F. Bottcher, *Theory of Electric Polarization* (Elsevier, Amsterdam, 1973).
14. G. M. Kumar, D. N. Rao, and G. S. Agarwal, Phys. Rev. Lett. **91**, 203903 (2003).
15. S. Scheel, L. Knoll, and D. G. Welsch, Phys. Rev. A **60**, 4094 (1999).
16. S. Murakami, M. Herren, M. Morita, S. Ohkubo, and T. Suzuki, J. Lumin. **66&67**, 294 (1996).
17. L. C. Hwang, S. C. Lee, and T. C. Wen, Opt. Commun. **228**, 373 (2003).
18. R. Reisfeld and L. Boehm, J. Solid State Chem. **4**, 417 (1972).