Measurement of Local Field Effects of the Host on the Lifetimes of Embedded Emitters

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(Received 4 April 2003; published 13 November 2003)

We report experimental results on the variation of the radiative lifetime of Eu^{3+} ion embedded in a dielectric with the refractive index n. We dope 1 mol % of Eu^{3+} into the binary glass system xPbO-$(1-x)B_2O_3$. By varying x we have achieved a fairly large variation of the refractive index from 1.7 to 2.2. This enables us to study the local field effects for the first time for ions doped in a solid glassy material. Our measurements are in agreement with the so-called real cavity model. The present measurements are free from the complications arising from reorganizational effects in solvents.

DOI: 10.1103/PhysRevLett.91.203903 PACS numbers: 42.65.Pc, 32.70.Cs, 42.70.Ce

It was recognized very early by Lorentz that in a dense medium the field acting on an atom is neither the external field nor the Maxwell field, but an effective field that depends on the presence of all the other atoms in the medium [1]. Lorentz presented a very simple argument to show how such fields can be calculated. A microscopic approach to local fields was developed by Ewald and Oseen [1]. The local field effects have been very extensively studied in linear optics and in nonlinear optics and have been reviewed [2–5]. The effect of local fields on the propagation of light in multilevel resonant media has also been examined [6–12]. In a resonant dense medium one discovers very interesting frequency shifts and excitation dependent local fields [6,8,11]. The effects of local fields on electromagnetically induced transparency and coherent population trapping have been examined [8,10,12]. While a large body of theoretical literature exists, the experiments on the local field effects have been far too few [7,11,13].

We note that most studies deal with the propagation of light in a dense medium which could be either linear or nonlinear. A question of considerable importance in recent times concerns the modification of the decay rate of an atom (or ion) in a host material (such as a dielectric), particularly when the host is itself a dense medium. This is due to the fact that the total field at the site of the atom (ion) is altered by the presence of the dielectric. Since, according to the Fermi golden rule, the spontaneous emission probability is proportional to the square of the magnitude of the field at the location, the local field produced by the dielectric can change the lifetimes of the radiating ion relative to its value in free space or that in an optically thin medium. This problem has been a subject of rather extensive study in recent years. In these works the calculation of the local field is based on the assumption that the radiating dipole (ion) is placed in a spherical cavity, whose dimensions are large with respect to that of the radiating ion, but small compared to the wavelengths involved. The radiative lifetime of the emitter embedded in the dielectric can then be expressed as $\tau(n) = \tau(0)l(n)/n$. Here $l(n)$ is the local field correction factor (LFCF), $\tau(0)$ is the free space radiative lifetime, and n is the refractive index at the wavelength of emission. In the absence of the local fields, the radiative lifetime follows a simple inverse relationship to the refractive index [14], i.e., $\tau(n) = \tau(0)/n$. One has to then determine the form of $l(n)$, which requires specification of the nature of the cavity. Two distinct models for the nature of cavities—real and virtual—have been proposed in the literature. The LFCFs, l, for the real and virtual cavities are $(2n^2 + 1)^2/9n^4$ and $9/(n^2 + 2)^2$, respectively [2,15,16].

In the real cavity model it is assumed that the atom is at the center of a cavity and that the cavity itself has no other material. The virtual cavity model is based on the work of Lorentz [2]. It is *a priori* not clear which model is more relevant for a given experimental situation. The existing experimental works were carried out either in liquids [17,18] or a gaseous [19] medium. However, the range of refractive indices obtainable in gases and liquids is not only small, but also the method used to obtain the refractive index variation is prone to complications. For example it is known that in a solution the solvent molecules tend to reorganize in the vicinity of the metal ion, thereby leading to a local dielectric constant, which could be different from the bulk value [20]. The choice of the host material and the emitters is very critical in understanding the local field related issues. Ideally a far better host material will be a solid matrix.

In this Letter, we report experimental results on the decay of europium ions in specially prepared glasses. We explain later the advantages of our choice of dopants and the host material. We are able to cover a wide range of the refractive index of the host material. Moreover our results are free from the complications of the gaseous or liquid host materials. Our data support the real cavity model. A

precise knowledge of lifetimes and their variation with the refractive index is important as rare earth doped glasses are extensively used as laser materials and as amplifiers in optical communications.

It should be noted that the above analysis is valid only for a lossless (nonabsorbing) medium, i.e., n is real. More recently Scheel *et al.* [21] demonstrated that in a strongly absorbing medium the lifetime would also depend on the radius of the real cavity. Further Crenshaw *et al.* [22] also presented a microscopic calculation of two level emitters in an absorbing and dispersive dielectric and obtained the result $\tau(n)/\tau(0) = \mathrm{Re}(n^2 + 2)/3$. These considerations, however, do not apply here, for the material chosen in the present study is absorption free.

In our studies we use glasses with the rare earth as a dopant. Glass preempts reorganization of the medium in the microenvironment of the metal ion. Therefore the bulk dielectric constant represents more satisfactorily the environment of the metal ion. Glass is not only easy to prepare but also the refractive indices in the range of 1.5–2.5 can be achieved. Of the several binary glasses the PbO-B_2O_3 system is found to form good glass with the desired range of refractive indices [23]. PbO is a high-density material and B_2O_3 is a low-density material. Different refractive indices for the glass are achieved through relative variation of PbO and B_2O_3. For the rare earth ion, Eu^{3+}, the observed intra f-f transitions are shielded by the closed shells of $5s$ and $5p$. It should be noted that the Eu^{3+} has a large quantum yield and the lifetime is in the range of a millisecond making it a natural choice for this experiment.

The glass system x PbO + $(1 - x)$ B_2O_3: Eu_2O_3 (1 mol %), $x = 1.0, 0.9, \ldots, 0.3$, is prepared by the melt quench method. The stoichiometric quantities of the initial materials PbO, H_3BO_3, and Eu_2O_3 are ground in an agate mortar with acetone for 20 min to ensure the formation of a homogenous mixture. The mixture taken in a silica crucible is subjected to three steps of heating, 1 h at 200 °C, 2 h at 500 °C, and 45 min at 800–1000 °C (depending on the composition). The first two steps ensure a complete formation of B_2O_3. The third step of heating leads to the formation of a clear melt. The melt is quenched on a hot copper mold at ~150 °C and pressed with another hot copper plate.

Differential scanning calorimetric studies were carried out to determine the melting temperature of each composition. The glasses were then annealed for 24 h at 50 °C below the melting temperature. The x-ray diffraction studies carried out on all compositions show no sharp peaks indicating the formation of good glass for every composition. The refractive indices are measured by the Brewster's angle technique with the He-Ne laser. The refractive index of the $x = 1.0$ glass is 2.2 and for $x = 0.3$ is 1.7.

Lifetime studies are done with the 6 ns pulsed Nd:YAG laser. The second harmonic of the Nd:YAG laser at 532 nm is focused into a Raman cell filled with 25 atm hydrogen. The first anti-Stokes line of hydrogen at 435 nm is focused on to the sample. The fluorescence is collected in the 90° geometry on to a 1 m double monochromator with a photomultiplier tube (PMT) as the detector. Figure 1(a) shows the fluorescence spectra of Eu^{3+}. All the bands originate from the level $^5D_0$. The lifetimes are measured at 613 nm, which is the strongest emission line and corresponds to the transition $^5D_0 - {}^7F_2$. The PMT signal is viewed on a digital oscilloscope TDS 220 and is grabbed using a CCD camera, which in turn is interfaced to a computer. Figure 1(b) shows a typical decay curve, which is single exponential for all the compositions.

Figure 2 shows the plot of refractive indices versus the lifetime for the $^5D_0$ level. The experiment is performed with the three different sets of samples and repeated several times to ascertain the reproducibility of the lifetimes and to determine the error. An error bar of ±5% has been introduced based on the above procedure. This error is mainly due to the variations in quenching

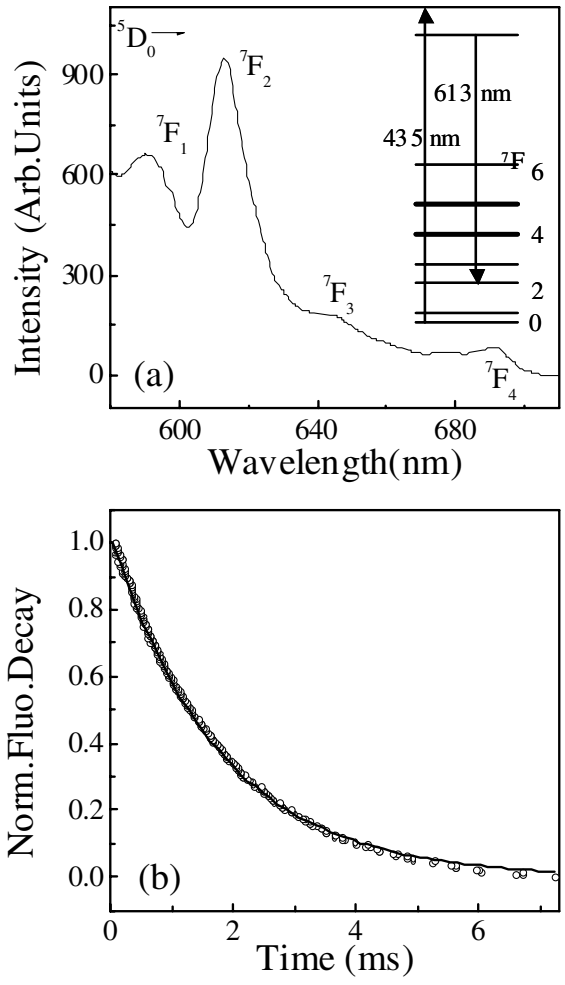

FIG. 1. (a) The fluorescence spectrum of Eu^{3+} excited with 435 nm; the inset shows the representative energy levels. (b) A typical fluorescence decay curve.

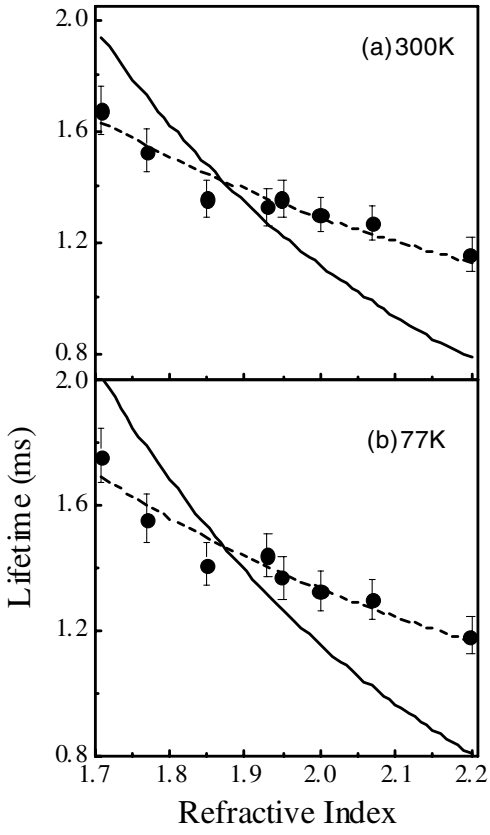

FIG. 2. Lifetimes plotted as a function of the refractive index at (a) 300 K and (b) 77 K. Circles are the experimental data; the dashed lines are the fits for the real cavity and the solid lines for the virtual cavity model.

temperatures and local inhomogeneities created during the process of quenching and annealing.

Since the lifetime is the inverse of the sum of the radiative transfer rate and the nonradiative transfer rate, to determine the role of the nonradiative decays it is measured at another temperature, 77 K. We observed an increase in the lifetimes for all the compositions by about 5% with respect to the lifetimes measured at 300 K. This increase in the lifetimes is very uniform for all the compositions indicating that the role played by the nonradiative relaxations to the fluorescence decay time is almost the same for all the compositions. Thus even though we cannot rule out the role and the percentage of contribution by the nonradiative relaxations, we can say that the contribution has remained the same for all the samples. Infrared absorption spectra were recorded at room temperature for all the compositions to further assess the contribution from the nonradiative relaxations. This spectrum shows the strongest peaks at 1319 and 914 cm^{-1}. Compositional variation of the constituents of the glass only shifts these peaks slightly. The integrated area under these peaks shows a small variation of about 7%, indicating that the nonradiative decay is almost constant for all the compositions of the glass. Further nonradiative decay by these vibrations would mean a multiphonon decay involving about 13 phonons, which makes the probability of this process very low. We conclude that the measured variation in the lifetimes can be attributed to the local field effect. The data have been fitted to real and virtual cavity models. It is clearly seen that the data fit well to the real cavity model, where the chi square for the real cavity is 1.9×10^{-3} and 5.6×10^{-2} for the virtual cavity. The value for $\tau(0)$, the free space lifetime, comes out to be 4.57 ms for the real cavity and 8.92 ms for the virtual cavity. The virtual cavity fit not only gives a poor fit but also leads to a very high value for the free space lifetime. We have also fitted the data to a more general model [Ref. [17], Eq. (8)], $l(n) = [\{(2n^2 + 1) - f(n^2 - 1)\}/3n^2]^2$ and find that excellent fit is obtained for f of the order of 0.001 or less. This further confirms the good agreement of our data with the real cavity model.

It should be noted that Lorentz local field factors are relevant to a dense medium of one type of atoms. For the case of dopants in a host material, the density of dopants is very low so that the Lorentz local field becomes irrelevant. The Lorentz local field is relevant for the glass for the determination of its refractive index. However, since we use the measured refractive index for the glass, any Lorentz type of local field is automatically induced in the measured values of the refractive index. It is for these reasons the real cavity model is more appropriate for our data.

In order to confirm that our measurements are not due to the variations in the dopant concentrations, we investigated the effect of the dopant concentration on the lifetimes. We have prepared the glasses with a composition $60PbO + 40B_2O_3{:}xEu^{3+}$, with x ranging from 0.1 to 5 mol %. We found (Fig. 3) that the lifetime is almost a constant at 1.3 ms, which is within the experimental error.

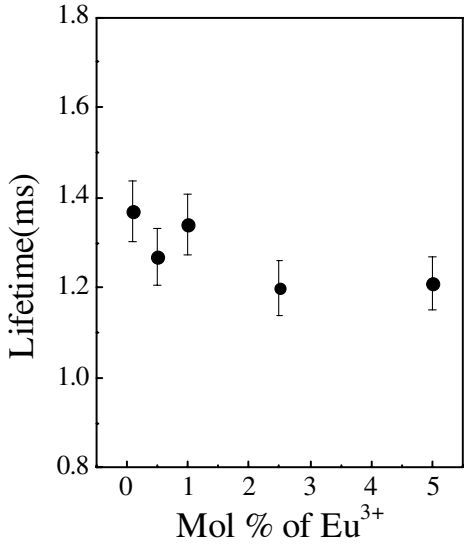

FIG. 3. The effect of the Eu^{3+} concentration on the lifetime.

In conclusion, our measurements on the effects of the local field on the radiative lifetimes of the Eu^{3+} doped in glasses follow the real cavity model. A solid matrix, which is close to the real system, has been used for the first time. Note that a precise knowledge of the lifetime and its variation with the refractive index is quite important for the utilization of rare earth doped materials for lasing and amplification of signals and for the core cladding of the fiber amplifiers. Finally we mention that it would be very interesting to study the effect of local fields on the energy transfer from one excited ion to another.

We are extremely thankful to Dr. M. Vittal, Osmania University, Hyderabad, India, for allowing us to use his laboratory facilities for the preparation of the samples and for many useful discussions we had with him. G. M. K. thanks the CSIR for financial assistance. G. S. A. thanks Bob Boyd and S. Dutta Gupta for many discussions on local field effects.

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