

## Dependence of fluorescence lifetimes of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanoparticles on the surrounding medium

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The radiative lifetime,  $\tau_R$ , of the  $^5D_0$  metastable excited state of  $\text{Eu}^{3+}$  ions in nanocrystalline monoclinic  $\text{Y}_2\text{O}_3$  samples is about four times longer than that in the micron size powder of the same material. The  $\text{Eu}^{3+}$  radiative lifetime was measured in nanocrystals surrounded with air as well as those immersed in different liquids. It is shown that the radiative lifetime changes with the index of refraction of the immersion medium and provides a unique test of the standard formula relating  $\tau_R$  and the oscillator strength. The magnitude of the effect is determined by the "filling factor" (the fraction of the sample volume occupied by nanocrystals) which can therefore be determined. [S0163-1829(99)51144-2]

The prospect of modifying the radiative lifetime of centers in solids is a tempting goal with a variety of potential applications to lasers, displays, etc. One means to do this is to alter the local environment of the center by putting it in different hosts or by selecting certain sites. Such a process simultaneously alters the spectrum of the center. An alternative method modifies the radiation modes to which the center couples by placing the material in some sort of cavity. In the present, it is shown that the lifetime can be modified, within certain limits, without altering the spectral properties, by placing nanoparticles, whose size is much less than the wavelength of light, in different media. By this means, the local environment of the center remains unchanged while its coupling to the light is modified both by changing the density of radiative modes and by modifying the surrounding medium polarizability. While this idea has been previously discussed in an earlier work,<sup>1</sup> the particle size was about the same as that of the light wavelength, making a quantitative comparison with theory difficult, and only the modification of the effective index of refraction was considered; the effective polarizability change produced by altering the surrounding medium was not considered.

Nanocrystalline insulating materials doped with rare earth and transition metal ions exhibit optical properties which are significantly different from that of bulk materials.<sup>2-4</sup> Such differences are expected due to: (i) the confinement effects on the vibrational spectra of nanocrystals, (ii) the increased role of the impurity ions at the surface whose optical properties are modified by the disorder at the surface, and (iii) the alteration of the electronic bands of the matrix. This makes nanocrystals interesting both in terms of their fundamental properties and because of their potential in a variety of applications.

We report here the results of a study of the radiative lifetime,  $\tau_R$ , of the  $^5D_0$  metastable excited state of  $\text{Eu}^{3+}$  ions in nanocrystalline  $\text{Y}_2\text{O}_3$  which is drastically different from that in the bulk material.

The nanocrystalline  $\text{Y}_2\text{O}_3:0.1\%\text{Eu}^{3+}$  samples were prepared by condensation after laser evaporation as described previously.<sup>5</sup> In the present work nanocrystalline samples with particle size distributions centered at approximately 7 and 12 nm (according to transmission electron microscopy) were studied. The crystal structure of the nanocrystalline samples is monoclinic, in contrast to the cubic phase of  $\text{Y}_2\text{O}_3$  single crystals. For comparison, a micron particle size powder of monoclinic  $\text{Y}_2\text{O}_3:0.1\%\text{Eu}^{3+}$ , synthesized under high pressure, as well as a monoclinic  $\text{Gd}_2\text{O}_3:0.1\%\text{Eu}^{3+}$  single crystal, produced by the laser heated pedestal growth method, were also studied. In monoclinic  $\text{Y}_2\text{O}_3$  and  $\text{Gd}_2\text{O}_3$ , the  $\text{Eu}^{3+}$  ions are located at three kinds of centers; A, B and C all with  $C_s$  symmetry.<sup>6,7</sup> The  $^5D_0$  energy levels of the  $\text{Eu}^{3+}$  B and C sites are situated close together and their dynamical properties are similar,<sup>4</sup> whereas the A site levels are shifted further to the blue and their dynamical properties differ significantly from those of the B and C sites.<sup>4</sup>

The experiments were performed at  $T=1.5\text{K}$  and  $T=295\text{K}$ . The  $\text{Eu}^{3+}$  ions were excited via the  $^7F_0 \rightarrow ^5D_0$  transition with a Coherent CR599 cw single frequency dye laser. In order to avoid hole-burning effects, the laser frequency was continuously scanned over 500 MHz. For fluorescence lifetime measurements, temporally rectangular laser pulses of width between 1–3 ms were formed with an acousto-optical modulator. The  $^5D_0 \rightarrow ^7F_2$  fluorescence of  $\text{Eu}^{3+}$  was selected with a 10 nm bandpass interference filter and was detected with a photomultiplier tube. The fluorescence decay curves were averaged and stored in a digital oscilloscope. All observed fluorescence decay curves were exponential over two orders of magnitude; thus the decay could be well characterized with a single decay time.

At low temperatures the fluorescence decay of the  $\text{Eu}^{3+} ^5D_0$  state is entirely due to radiative transitions. This follows from the fact that at 295 K the fluorescence lifetime decreases by only a few percent relative to its value at 1.5 K. Thus the room temperature fluorescence lifetime is almost

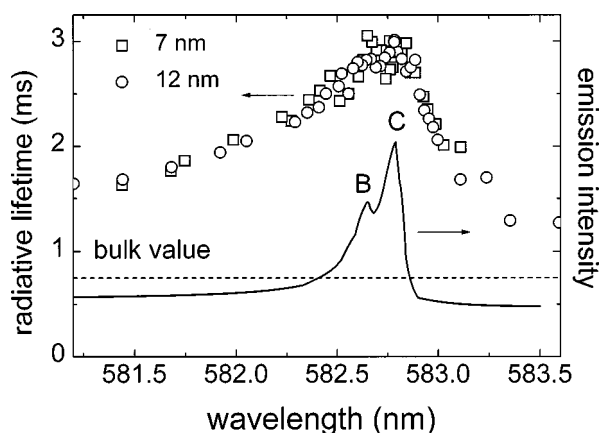


FIG. 1. The dependence of the  ${}^5D_0$  radiative lifetime,  $\tau_R$ , for the  $\text{Eu}^{3+}$  B and C sites on excitation frequency inside the  ${}^7F_0 \rightarrow {}^5D_0$  transition in 7 and 12 nm nanocrystalline  $\text{Y}_2\text{O}_3:0.1\%\text{Eu}^{3+}$  samples ( $T=1.5$  K). Solid line—excitation spectrum of  ${}^5D_0 \rightarrow {}^7F_2$  fluorescence. The dotted line represents the radiative lifetime in the micron size “bulk” material.

entirely due to radiative relaxation; nonradiative decay processes are still not significant. The results of fluorescence lifetime measurements at  $T=1.5$  K for excitation inside the inhomogeneously broadened profile of the B and C sites for the  ${}^7F_0 \rightarrow {}^5D_0$  transition are shown in Fig. 1. At 1.5 K the homogeneous width of the transition is much smaller ( $<0.001$   $\text{cm}^{-1}$ ) than the inhomogeneous broadening.<sup>4</sup> The excitation spectrum of the  ${}^5D_0 \rightarrow {}^7F_2$  fluorescence of the B and C sites is also shown. The significant inhomogeneous broadening of the transition as well as the background fluorescence around the lines are due to increased disorder in nanoparticles and/or the contribution of ions at the particles’ surfaces. The spectral dependence of the fluorescence lifetime is the same for the 7 and 12 nm  $\text{Y}_2\text{O}_3\text{Eu}^{3+}$  samples. The lifetime is a maximum at the C site line center and decreases in the wings of the B and C site line shape. This spectral dependence may be explained taking into account the nature of inhomogeneous broadening. Indeed, only the “ideal” centers responsible for the line center possess exactly  $C_s$  symmetry. The ions forming the wings of  ${}^7F_0 \rightarrow {}^5D_0$  transition are in distorted sites, which, strictly speaking, possess only  $C_1$  symmetry. The larger is the distortion of the  $C_s$  site, the stronger is the line shift. This reduction of the  $C_s$  symmetry may increase the radiative transition probabilities for ions excited in the wings of inhomogeneously broadened transition and thus be responsible for their shorter lifetimes.

The lifetime in nanoparticles is throughout the spectrum significantly larger than the lifetime in the micron sized samples (shown in Fig. 1 by the dashed line). The difference between the lifetimes at the C site line center in nanometer- and micron-sized particles is about a factor of four. Similar differences in lifetimes were observed for the A site.

This strong particle size dependent effect on the  ${}^5D_0$  lifetime cannot be explained by multiple reabsorption of light by  $\text{Eu}^{3+}$  ions since the absorption even at line center is very weak (absorption coefficient  $<0.1$   $\text{cm}^{-1}$ ) and a significant increase of the lifetime is observed even in the distant wings of the line where the absorption is even a few orders of magnitude lower. There is small (if any) difference in position of the spectral lines in the micron and nanometer sized

particles, so the effect cannot be explained by the different local structure of the  $\text{Eu}^{3+}$  centers in the nanocrystals. It is also unlikely that the effect may be explained by the modification of the density of photonic states due to periodicity, as in photonic bandgap materials,<sup>8</sup> because there is no periodic structure in the material with a length scale of the order of the wavelength of light.

The significant difference in  $\tau_R$  between the nanocrystalline and micron size samples can be understood by considering the changes produced by the medium surrounding the nanoparticle. When the particles are much smaller than the light wavelength the local electric field acting on the  $\text{Eu}^{3+}$  is determined by the combined effects of the  $\text{Y}_2\text{O}_3$  medium contained within the nanoparticle and that of the medium filling the voids. In order to examine the role of the medium surrounding the nanoparticle, we compared the measured fluorescence lifetime of the  ${}^5D_0$  state of  $\text{Eu}^{3+}$  in 7 nm  $\text{Y}_2\text{O}_3$  nanoparticles surrounded by air ( $n=1$ ) and when they were immersed in liquids with different refractive indices. The media chosen included methanol,  $\text{CH}_3\text{OH}$  ( $n=1.326$ ) and carbon disulphide,  $\text{CS}_2$  ( $n=1.628$ ). A strong effect of the surrounding medium on the lifetime was observed; the lifetime of  ${}^5D_0$  state decreased monotonically as the index of the immersion medium was increased.

The radiative lifetime of the electronic transitions of an ion embedded in a medium is described by the formula<sup>9</sup>

$$\tau_R \sim \frac{1}{f(\text{ED})} \frac{\lambda_0^2}{\left[ \frac{1}{3}(n^2+2) \right]^2 n} \quad (1)$$

where  $f(\text{ED})$  is the oscillator strength for the electric dipole transition,  $\lambda_0$  is the wavelength in vacuum and  $n$  is the refractive index. The dependence of  $\tau_R$  on the index of refraction,  $n$ , arises from (i) the change in the density of states for photons in the medium of reduced light velocity and (ii) the modification of the polarizability of the surrounding medium. Since the nanoparticles occupy only a small fraction of the total volume, in order to compare the experimental results with the Eq. (1) it is necessary to introduce an effective index of refraction for the medium,  $n_{\text{eff}}$ , which consists of the  $\text{Y}_2\text{O}_3$  nanoparticles surrounded by the media with refractive index  $n_{\text{med}}$ . We define  $n_{\text{eff}}(x) = x \cdot n_{\text{Y}_2\text{O}_3} + (1-x) \cdot n_{\text{med}}$ , where  $x$  is the “filling factor” showing what fraction of space is occupied by the  $\text{Y}_2\text{O}_3$  nanoparticles. For the nanoparticles,  $n$  in Eq. (1) is replaced by  $n_{\text{eff}}(x)$ . The use of  $n_{\text{eff}}$  is valid when the average size of the particles is much smaller than the wavelength of light, a condition that is very well satisfied for the case of these nanoparticles. In Fig. 2 the  ${}^5D_0$  state lifetimes for the C and A sites of  $\text{Eu}^{3+}$ , measured at  $T=295$  K, are plotted versus  $n_{\text{med}}$ . Also plotted are the data points for the micron sized monoclinic  $\text{Y}_2\text{O}_3$ , which corresponds to  $n_{\text{med}} = n_{\text{Y}_2\text{O}_3}$ , and that of the single monoclinic crystal of  $\text{Gd}_2\text{O}_3:\text{Eu}$ , for which  $n_{\text{med}} = n_{\text{Gd}_2\text{O}_3} = 2.1$ . Unfortunately since we could not find data on the index of refraction of monoclinic  $\text{Y}_2\text{O}_3$  we used  $n_{\text{med}} = n_{\text{Y}_2\text{O}_3} = 1.91$ , the value for the cubic phase, assuming that they should be quite similar. Of course the data point for  $\text{Gd}_2\text{O}_3:\text{Eu}$  should be considered as providing only a semi-quantitative value for the life-

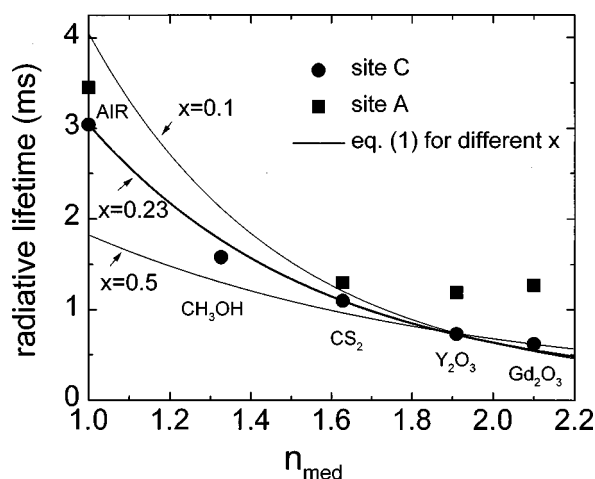


FIG. 2. The dependence of the  ${}^5D_0$  radiative lifetime,  $\tau_R$ , for the  $\text{Eu}^{3+}$  C and A sites on the index of refraction of the media  $n_{\text{med}}$  at  $T=295$  K. Solid lines—fits for nanocrystalline samples (site C) with Eq. (1) and different filling factors.

time at  $n_{\text{med}}=2.1$  because the local structure of Eu centers in  $\text{Gd}_2\text{O}_3$  is very slightly different from that of the  $\text{Y}_2\text{O}_3$  leading to a slight difference in the oscillator strength. The difference is expected to be small because the spectra of  $\text{Eu}^{3+}$  in  $\text{Gd}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  are very similar; spectral line shifts of less than 1 nm are observed. Also, the comparison of  $\text{Gd}_2\text{O}_3$  point with the fitting curve should be done carefully because this point corresponds exactly to a filling factor of  $x=0$  which is different from all the other plotted points. However for  $n_{\text{med}}=2.1$  the  $\tau_R$  given by Eq. (1) depends only weakly on  $x$  and for  $x=0.23$  is only a few percent larger than for  $x=0$ ; thus the presence of the  $\text{Gd}_2\text{O}_3$  points in Fig. 2 is justified.

The data points for the C site in Fig. 2 are fitted to Eq. (1) using  $x$  as an adjustable parameter, such that the data point for the bulk  $\text{Y}_2\text{O}_3$  lies on the fitted curve. The data point for the micron powder was taken as the value of  $\tau_R$  in the bulk, since single crystals of monoclinic  $\text{Y}_2\text{O}_3$  are not available. This is justified because the particle size for the powder is much larger than the wavelength of light. The best fitted curve, shown in Fig. 2 with the heaviest solid line, corresponds to  $x=0.23$  indicating that the  $\text{Y}_2\text{O}_3$  nanocrystals occupy 23% of the sample space. The other curves show the results of using Eq. (1) with other filling factors,  $x$ . The data for the A site cannot be fitted as well with Eq. (1), but the data do qualitatively show the same dependence on  $n_{\text{med}}$ . The experiments show that the difference in radiative lifetimes of the  ${}^5D_0$  state of  $\text{Eu}^{3+}$  in the bulk and in nanocrystalline  $\text{Y}_2\text{O}_3$  samples may be explained by the difference in the effective indices of refraction and polarizabilities of the media. For “dry” nanocrystalline samples the radiative lifetime depends on  $x$ ; this explains the observed  $\sim 25\%$  decrease in fluorescence lifetime in the sample dried after immersion in methanol compared to a “fresh” sample, if, after drying, one assumes that the sample is compacted. This also implies that different batches of sample may be expected to show different lifetimes depending on the filling fraction,  $x$ .

In Ref. 1 the fluorescence lifetimes of  $\text{Nd}^{3+}$  in  $\text{Y}_2\text{O}_3$  110–420 nm particle size powders were measured and it was suggested that the radiative lifetime is affected by the index of

refraction of the surrounding media. Though qualitatively the results in Ref. 1 are similar to those reported here, some comments should be made:

(i) An effective index of refraction should be introduced instead of the index of the surrounding medium. This is especially important if, as was the case in Ref. 1, the size of the crystallites is comparable to the wavelength of light since a significant fraction of the ion’s environment (characteristic scale  $\sim \lambda$ ) is occupied by the crystalline matrix.

(ii) The assumption that  $\tau_R \sim 1/n$ , used in Ref. 1, takes into account only the modification of the density of photon states but it does not consider the dependence of the lifetime on the polarizability of the media; Eq. (1) includes both effects and therefore should have been applied.

Local field effects on the radiative lifetime of rare earth ions have also been described for  $\text{Eu}^{3+}$ -ligand complexes in different liquids<sup>10</sup> and in a supercritical  $\text{CO}_2$  gas as a function of pressure.<sup>11</sup> In both cases, two models for the local field effects were considered: the empty real spherical cavity and the virtual spherical cavity. While in both cases, the data were best described with the empty-cavity model, we find for the nanoparticles immersed in a dielectric that the results are best fitted with the virtual spherical cavity model [Eq. (1)]. Attempts to fit the data with the empty-cavity model yielded a value for the filling factor,  $x=0.02$ , which is inconsistent with the TEM pictures of these samples. The important differences between our experiments and those in Refs. 10 and 11 are the following:

(i) In nanoparticles,  $\text{Eu}^{3+}$  ions are better isolated from the surrounding medium than in complexes where the influence of the surrounding molecules and the pressure differences on the  $\text{Eu}^{3+}$  environment may cause additional effects.

(ii) In contrast to nanoparticles, the Eu complexes may rotate in the medium and thus averaging of the local field over the radiative lifetime may occur, making a different local field model applicable.

While the formula for  $n_{\text{eff}}$  described above is not exactly correct, it gives a reasonable estimate. A more precise calculation would utilize the Clausius Mosotti equation to obtain the polarizabilities of the two media; the value of  $n_{\text{eff}}$  for the mixed system should then be obtained from the Clausius Mosotti equation by adding the polarizabilities of the two media, weighted according to their filling factors. The differences in  $n_{\text{eff}}$  obtained by such a calculation and the method described above are less than 5% for  $x=0.5$ , and much smaller at other values of  $x$ ; thus we have used the simple expression described earlier for obtaining  $n_{\text{eff}}$ .

The experimental results reported here show that the radiative lifetimes of the excited states of impurity ions strongly depend on the effective index of refraction of the media consisting of nanoparticles and the substance filling the space between them. In these experiments the lifetime varied as much as a factor of four. It follows from Eq. (1) that the lifetime of any nanoparticle materials can be increased from its bulk value by a factor of  $n(n^2+2)^2/9$  when the materials is total dispersed as individual particles in air (vacuum). For  $\text{Y}_2\text{O}_3$  with  $n=1.91$ , the maximum lifetime enhancement is a factor of 6.77. By placing the nanoparticles in a materials of greater index of refraction, the lifetime may be reduced. Such lifetime variations may be important in applications, for example, for fluorescent materials made of

doped nanoparticles embedded in glass or polymer matrices. Usually the effect of the refractive index on lifetime cannot be observed directly because when the host matrix is changed, the local structure of the impurity center is also altered so that the oscillator strength becomes different. Nanocrystalline materials are unique as they provide a possibility to change the refractive index of the medium without

changing the centers' local structure. Thus, this provides a unique test of Eq. (1) connecting the oscillator strength and the radiative lifetime. The observed effect may be also used to determine the "filling factor," e.g., the fraction of the sample volume occupied by the nanocrystals.

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