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Fluorescence lifetimes for neodymium-doped yttrium aluminum garret and yttrium oxide powders

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A simple theoretical model for the radiative lifetime of a fluorescent ion in a particle of a powder is described. The model predicts that the lifetime depends on the size of the particle, the density of the powder, and the refractive index of the surrounding medium. For a dilute system of very small particles the lifetime should be inversely proportional to the index of the surroundings. In Nd-doped yttrium aluminum garnet (YAG) and Y_2O_3 powders, prepared by different methods, the $Nd^{3+}{:}^4F_{3/2}$ decay rate was measured and compared to the particle size, the powder density, and the refractive index of the surroundings. In agreement with the theory the decay is slower the smaller the particles, the less dense the powder, and the lower the refractive index. For index-matched conditions the decay rate is close to what is observed in the bulk single crystal.

I. INTRODUCTION

There exists in the literature considerable disagreement about the proper numerical value to be assigned to the radiative quantum efficiency of the upper laser level in YAG:Nd. Theoretical calculations predict a quantum efficiency for $Nd^{3+}{:}^4F_{3/2}$ of 0.91.[1] Direct and indirect measurements give values from as low as 0.47 to values close to unity.[2-8] Investigations have shown that multiphonon relaxation cannot cause low quantum efficiency for the $^4F_{3/2}$ multiplet.[9] However, cross relaxation and energy migration could become significant even at a rather low doping concentration.[10]

An argument for a low quantum efficiency has been advanced by Singh *et al.*,[11] who compared the fluorescent lifetime of $Nd^{3+}{:}^4F_{3/2}$ in fine powders of YAG with the lifetime in the bulk single crystal, and found for the former a value of 420 μs compared to the typical value of 250 μs characteristic of the bulk. This difference led them to suggest that the quantum efficiency is close to unity in the powder but significantly smaller in the crystal, presumably because of defects created during high-temperature crystal growth which act as quenching centers.

In this paper we show that it is not possible to verify differences in the quantum efficiency by comparing lifetimes in powders with lifetimes in the bulk single crystal. The influence of optical environment on lifetime has been noted in a slightly different context, by Lukosz and Kunz[12] in their studies of the fluorescence of molecular thin films containing Eu. These studies indicate that the difference in lifetimes for fluorescent ions in powders and single crystals is of a more fundamental nature, and that the difference is more related to different radiative lifetimes than to different quantum efficiencies.

II. THEORY

The lifetime τ for spontaneous emission from ions excited to the state i in a dielectric medium with refractive index n is given, in the electric dipole approximation, by

$$\tau = \frac{3\pi\epsilon_0\hbar c^3 g_i}{n} \sum_j \frac{1}{\mu_{ij}^2 \omega_{ij}^3 g_j} , \qquad (1)$$

where the sum runs over all terminal states j. ϵ_0 and c are the permittivity and velocity of light in vacuum, respectively, g_i and g_j are the degeneracies of the i and j states,

$$\mu_{ij}=e\left\langle i\left|\sum_k \bar{r}_k\right|j\right\rangle$$

is the matrix element of the electric-dipole operator, and $\hbar\omega_{ij}$ is the energy difference between the i and j states.

The quantities g_i, g_j, μ_{ij}, and ω_{ij} are related to ionic properties and depend only on the emitting ions and their nearest neighbors, i.e., ions within a distance of 1 – 10 nm. The index n, on the other hand, depends on the modes of a cavity large compared to the wavelength of the emitted radiation and, therefore, on the properties of the medium surrounding the emitting ions within a distance of the order of the wavelength. Thus, for a particle much smaller than the wavelength, the refractive index to be considered cannot be the index for this material n_c but rather the index n_s for the medium surrounding the particle.

If τ_c is the lifetime of the ions in an infinite medium with index n_c, the lifetime τ_p in a single very small particle surrounded by a medium with index n_s is given by

$$\tau_p=\frac{n_c\tau_c}{n_s}=\frac{\tau_0}{n_s}\ , \tag{2}$$

where τ_0 is the lifetime in the small particle in vacuum. For a very small particle the lifetime therefore should be inversely proportional to the index of the surroundings. If the particle is not much smaller than the wavelength or the particle is part of a powder, it will be necessary to use an effective index with a value somewhere between n_c and n_s. Thus, the lifetime for ions in a powder is dependent on particle sizes and powder density, and the measured value will be between the theoretical value τ_p and the bulk single-crystal value τ_c.

III. EXPERIMENTS

The fluorescent decay rate of the $^4F_{3/2}$ multiplet of Nd^{3+} was measured in YAG and Y_2O_3 powders. The Nd concentration was kept low to avoid concentration quenching. The Nd ions were excited with a pulsed dye laser tuned to a wavelength around 580 nm depending on the host. The Nd^{3+}:$^4F_{3/2}\rightarrow{}^4I_{9/2}$ fluorescence was selected with a monochromator and detected with a photomultiplier tube. The 10-ns excitation pulses were eliminated with a filter. After amplification the detected signal was processed in a computer of average transients and plotted on an X-Y recorder.

All the measured decays were nonexponential as expected if the powders have a distribution of particle sizes. In order to give numerical values for the decay rates, a time interval (e.g., 1.2 – 1.6 ms after the excitation) was selected, and a single "lifetime" was fitted to that part of the decay curve—i.e., the average decay rate was calculated in that interval.

A. YAG

Nd-doped YAG powders were intially prepared in a way similar to the procedure described by Singh *et al.*[11] X-ray analysis and fluorescence spectroscopy of these powders revealed that they were not all pure YAG. The powder which had the slowest decay of the fluorescence was a mixture of YAG and $YAlO_3$. By selective excitation and narrow band detection it was possible to separate the fluorescence from the two phases. The decay rate (measured 300 – 600 μs after the excitation) was 510±25 μs in YAG and 370±10 μs in $YAlO_3$. Although the value in YAG is considerably longer than the 420 μs reported by Singh *et al.*,[11] a direct comparison cannot be made without knowing precisely how they measured the lifetime.

Since the initial method of powder synthesis failed to give single-phase powders with slow fluorescence decays and because of the difficulties connected with selective decay-rate measurements in mixed powders, more powders were prepared under better controlled conditions. Five different YAG powders doped with 0.5% Nd were prepared. Traces of a foreign phase still were detected by x rays in some of the powders although the only fluorescence in the region 860 – 950 nm was characteristic of YAG:Nd for all powders. All the powders were agglomerated, and the decay rate of the fluorescence was close to the value for single crystals of YAG. The powder with the slowest decay rate was the least agglomerated, and grinding it up slowed the decay somewhat. It seems that the powders are too dense to get close to the single-particle decay rate, and grinding up the agglomerates totally is impractical.

B. Y_2O_3

To avoid the problems with the YAG powders Nd in Y_2O_3 powders (which are easier to prepare) was investigated. Six different Y_2O_3 powders doped with 0.5% Nd were prepared by both hydroxide and carbonate precipitation processes. X-ray diffraction showed pure, well-crystallized Y_2O_3 powders and fluorescence spectra in the region

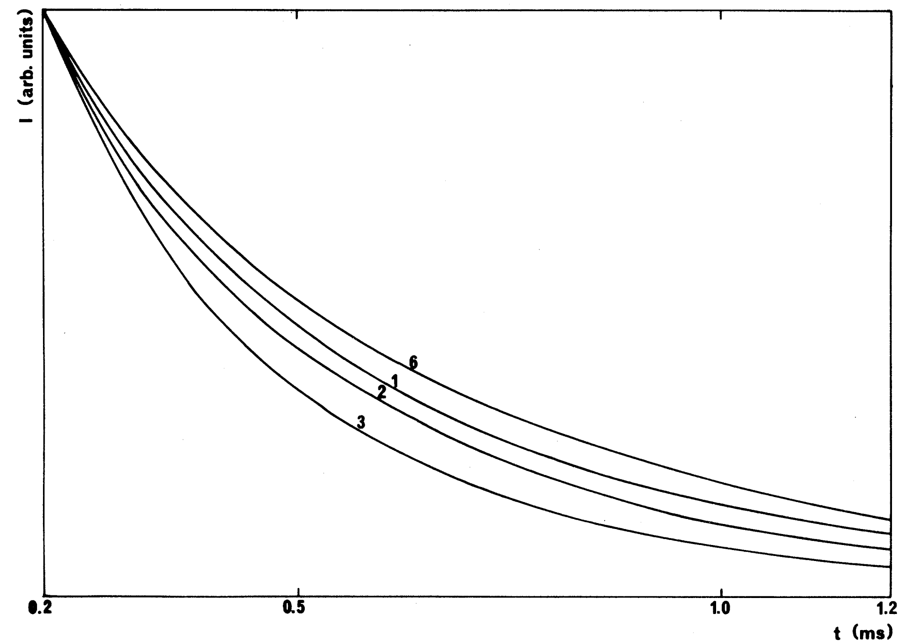

FIG. 1. Decay curves for Nd^{3+}:$^4F_{3/2}$ emission in Y_2O_3 powders Nos. 1, 2, 3, and 6. For all powders the intensity of the emission is given the same arbitrary value 0.2 ms after the excitation.

870–950 revealed no emission other than that characteristic of Y_2O_3:Nd. The fluorescent linewidths were comparable to those observed in Y_2O_3 single crystals.[13] An estimate of the particle size in powders Nos. 2, 3, and 6 was obtained from surface absorption measurements. The assumption that the particles occur as a uniform distribution of spheres leads to the following values of particle diameters: No. 2: 0.23 μm, No. 3: 0.42 μm, and No. 6: 0.11 μm.

The measured decay rates in the six Y_2O_3 powders were all different and nonexponential.

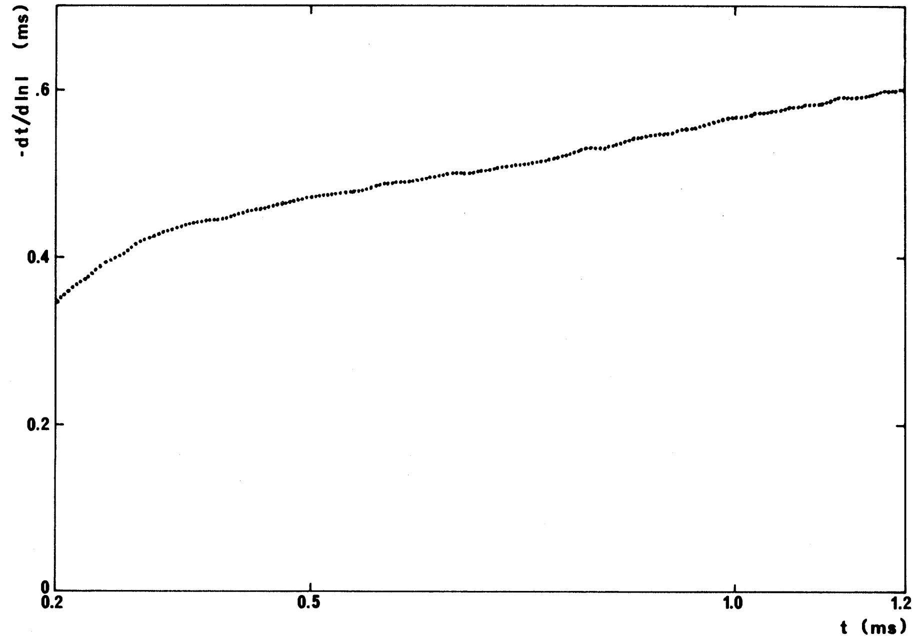

FIG. 2. Decay rate given as the differential lifetime $-dt/d\ln I$ for Nd^{3+}:$^4F_{3/2}$ emission in Y_2O_3 powder No. 6 as function of the time after the excitation.

TABLE I. Lifetime τ in μs for Nd^{3+}:$^4F_{3/2}$ emission in six different Y_2O_3 powders. The given values are those obtained by fitting to the decay curves 1.2—1.6 ms after the excitation. The uncertainty is less than 10%.

No.	τ
1	553
2	519
3	442
4	436
5	472
6	598

Nonexponential decay has also been reported for Nd in Y_2O_3 single crystals.[14] Nd ions can occupy two different sites in Y_2O_3,[15] but one of the sites has inversion symmetry, so the emission from ions on these sites is very weak, but at extremely long times after the excitation, the contribution from the inversion site could be significant. For the powders it is most likely that the decay is an infinite sum of exponential decays with slightly different lifetimes arising from particles of different sizes.

The decay curves for four of the powders are shown in Fig. 1. To indicate the nonexponentiality of the decays, the differential lifetime ($-dt/d\ln I$) for one of the powders is shown in Fig. 2. The "lifetimes" fitted to the decay curves 1.2—1.6 ms after the excitation are given for all six powders in Table I. The "lifetimes" 1.2—1.6 ms after the excitation for the three powders examined in the surface adsorption experiment are plotted as a function of the estimated particle size in Fig. 3. In agreement with the theory the decay is slower for the smaller particles.

When the agglomerated grains of powder No. 5 were crushed, the decay rate in agreement with the theory, decreased from 472±29 μs to 527±26 μs measured 1.2—1.6 ms after the excitation. The decay curves before and after grinding are shown in Fig. 4.

TABLE II. Lifetime τ in μs for Nd^{3+}:$^4F_{3/2}$ emission in Y_2O_3 powders Nos. 3 and 6 in air and immersed in liquids with different refractive index n_s. The given values are those obtained by fitting to the decay curves 0.5—0.9 ms after the excitation. The uncertainty is less than 10%.

Surroundings	n_s	τ No. 3	 No. 6
Air	1.00	400	495
Water	1.33		400
Oil	1.70		315
Oil	1.92	270	280
Oil	2.00		265

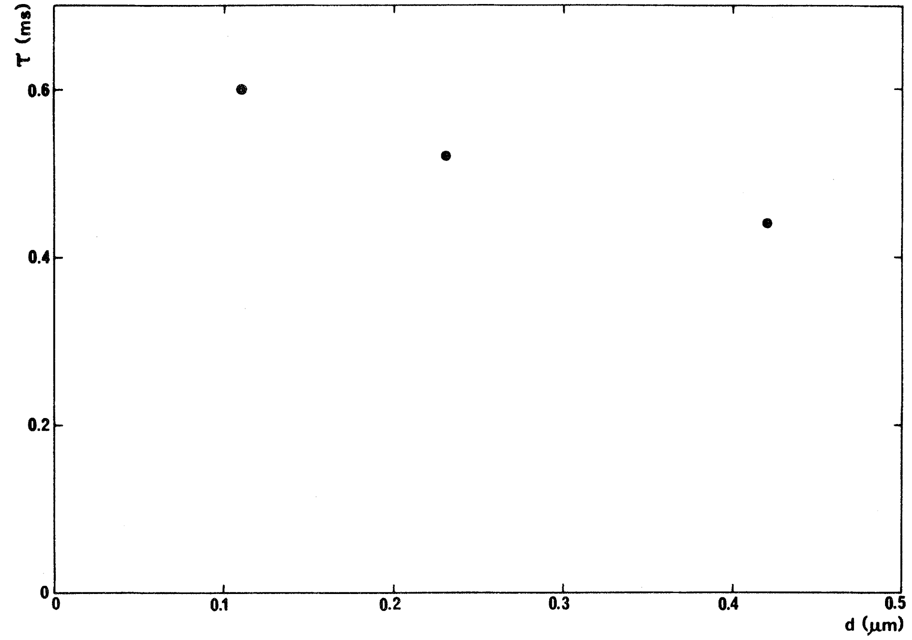

FIG. 3. Lifetime τ for Nd^{3+}:$^4F_{3/2}$ emission in Y_2O_3 powders versus estimated particle size d. The values used are those obtained by fitting to the decay curves 1.2—1.6 ms after the excitation.

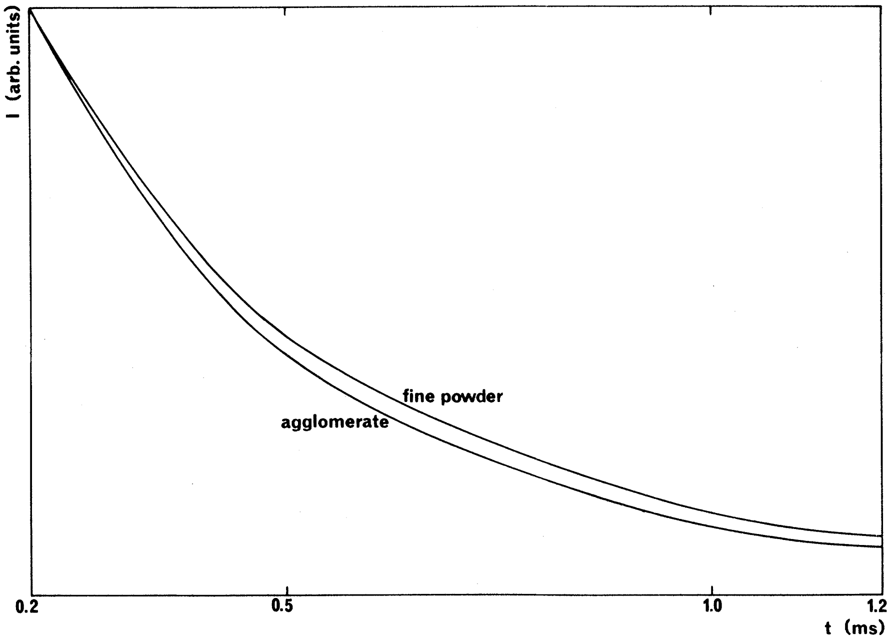

FIG. 4. Decay curves for Nd^{3+}:$^4F_{3/2}$ emission in Y_2O_3 powder No. 5 before (agglomerate) and after (fine powder) grinding. For both decays the intensity is given the same arbitrary value 0.2 ms after the excitation.

To investigate the effect of the surrounding medium, a few of the powders were immersed in water and three different index-matching fluids. The lifetimes fitted to the decay curves 0.5–0.9 ms after the excitation are given in Table II. In agreement with the theory the decay rates increase with increasing index of the surroundings. For index-matched conditions [$n_2=1.92$ (Ref. 13)] the decay rates for the two different powders become equal within the experimental accuracy. The re-

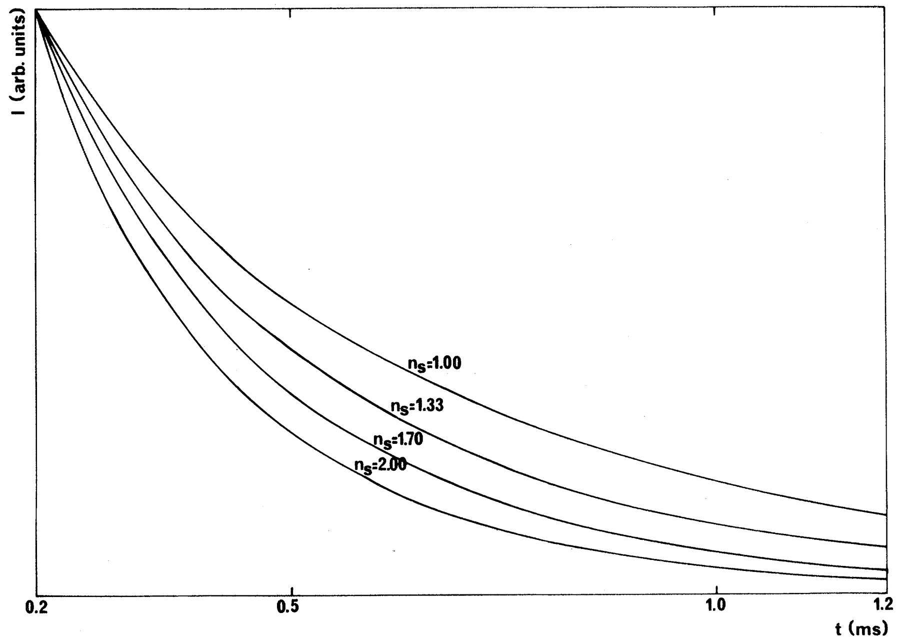

FIG. 5. Decay curves for Nd^{3+}:$^4F_{3/2}$ emission in Y_2O_3 powder No. 6 in air ($n_s=1.00$) and immersed in three liquids with different refractive index n_s. For all decays the intensity is given the same arbitrary value 0.2 ms after the excitation.

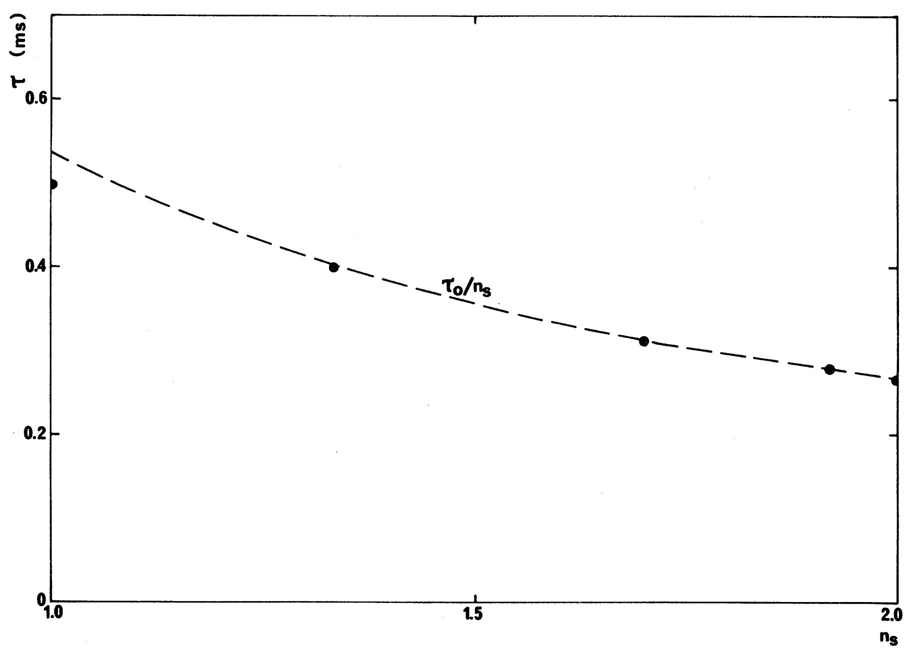

FIG. 6. Lifetime τ for Nd^{3+}:$^4F_{3/2}$ emission in Y_2O_3 powder No. 6 versus the refractive index n_s of the surrounding medium. The values used are those obtained by fitting to the decay curves 0.5–0.9 ms after the excitation. The broken curve is the theoretical prediction for emission from ions in a very dilute powder of very small particles. τ_0(=538 μs) is selected so the curve goes through the experimental point for index-matched conditions ($n_s=1.92$).

ported lifetime for Nd^{3+}:$^4F_{3/2}$ emission in Y_2O_3 single crystals doped with 0.5–1.0 mole% Nd vary from 260 to 350 μs.[13–15] This covers the range of decay rates in the powders under index-matched conditions as predicted by the theory. The decay curves for powder No. 6 in air, water, and two different oils are shown in Fig. 5. The lifetime 0.5–0.9 ms after the excitation for the same powder is plotted as a function of the refractive index of the surroundings in Fig. 6. It is seen that the $1/n_s$ law is followed within experimental error.

IV. CONCLUSIONS

The experimental results support the proposed simple theoretical model. The measurements on the Y_2O_3 powder have clearly shown that the radiative lifetime for ions in a dielectric particle depends on the size of the particle and the environment outside the particle. If the particle is part of a powder, the lifetime also depends on the powder density. The decay is slower the smaller the particles, the less dense the powder, and the lower the refractive index of the surrounding medium.

Difficulties with the powder preparation have prevented conclusive measurements on YAG powders, but the trend was the same as for the Y_2O_3 powders, and it seems safe to conclude that there is a fundamental theoretical explanation of the longer lifetime for YAG:Nd powder than for YAG:Nd single crystals.

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