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Effect of Radiation Trapping on Measured Excited-State Lifetimes in Solids

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Abstract

A refractive index matched experimental setup that largely eliminates the effects of radiation trapping on measured excited-state lifetimes in high refractive index solids is presented. An index-matched glass sphere was used to measure the room-temperature lifetimes of $^2F_{5/2}$ in YAG:1%Yb $^{3+}$ and $^4I_{11/2}$ in YLF:5%Er $^{3+}$, yielding the record low values of $948.9 \pm 0.6 \mu\text{s}$ and $3.85 \pm 0.01 \text{ ms}$, respectively. It is concluded that lifetimes from non index-matched experiments are most likely to be significantly overestimated in high refractive-index solids for excited states with a large radiative component to the ground-state multiplet and a high reabsorption cross section. The presented technique is easily applicable to room-temperature excited-state lifetime measurements of many luminescent solids.

Keywords: Geometrical optics - optical design, Total internal reflection, Spectroscopy - atomic - time-resolved

Introduction

Excited-state lifetimes are one key factor determining the performance of a solid-state laser material, and their measurement is part of any standard spectroscopic characterization. It is well known that the measured excited-state lifetime may be severely affected by reabsorption processes in the material. After the initial emission occurs from the sample each subsequent reabsorption event acts as a time "reset" on the relaxation of this excitation, and after a series of reabsorption/reemission processes, the result is an overall lengthening of the observed excited-state decay.

Overestimates of excited-state lifetimes and subsequent errors in derived quantities such as stimulated emission cross sections, threshold powers, or slope efficiencies are particularly pronounced for excited states with unity branching ratio such as $^2F_{5/2}$ of Yb $^{3+}$ or $^4I_{13/2}$ of Er $^{3+}$. In these cases, reabsorption may be very pronounced and should be considered especially at room temperature, a regime of particular importance to solid-state laser design.

The probability of a reabsorption/reemission event depends exponentially on the distance the emitted light has to travel in the sample. This path length is given not only by the size of the sample and the spatial emission distribution but also by the physical sample geometry and the sample refractive index. A considerable fraction of the light emitted within an ideal sample of high symmetry can be trapped by successive total internal reflections (TIR) at the sample/air interface [1]. Radiation trapping can be very pronounced in high refractive index solids since the critical angle for TIR decreases with increasing sample refractive index. In a real sample however, even light emitted in a direction subject to infinite TIR will eventually be scattered or reemitted in a new direction and leave the sample. As a result, excessive TIR strongly increases the path length in the sample and therefore enhances reabsorption effects such as the lengthening of observed excited-state lifetimes.

Sumida et al. investigated the effects of radiation trapping on the measured $^2F_{5/2}$ lifetime in Yb $^{3+}$ -doped Y $_3$ Al $_5$ O $_{12}$ (YAG) [2]. Motivated by the wide spread of $^2F_{5/2}$ lifetimes reported in the literature, ranging from $1080 \mu\text{s}$ [3] to $1300 \mu\text{s}$ [4], they proposed a refractive-index matched arrangement in an attempt to eliminate radiation trapping. A thin YAG:Yb $^{3+}$ sample was optically contacted between two larger, undoped YAG

crystals forming a sandwich structure. The elimination of TIR at the YAG:Yb³⁺/YAG interface allowed emitted light to pass into the undoped crystals. Using an aperture, luminescence striking the YAG/air interface near normal incidence and thus suffering the least Fresnel reflections was imaged onto the detector system. Sumida et al. measured a ²F_{5/2} lifetime of 951±15 μs for YAG:1%Yb³⁺ in this geometry, a significant improvement over previously reported values [3-5]. There remain, however, two unsolved problems with this experimental arrangement. First, although the low measured lifetime value suggests efficient suppression of TIR, there is, in principle, still the possibility of radiation trapping in the highly symmetric sandwich structure [1]. Hence it is uncertain if the measured 951 μs lifetime indeed corresponds to the intrinsic single-ion lifetime, or if it is still artificially lengthened by reabsorption processes. Second, the proposed geometry requires one doped and two undoped crystals, an approach which is not universally convenient. This paper addresses both these issues and compares the performance of a new refractive-index matched experimental geometry with lifetime results reported in the literature.

Results and Discussion

Radiation trapping is completely eliminated for a infinitely small sample, spherically surrounded by transparent material of identical refractive index. In this ideal case, emission would occur in the center of a sphere, pass into the index-matched material, and

Figure 1: Defining the sphere radius r with respect to the sample size (a^3) and the sample refractive index (n_s) such that no angle θ at the sphere/air interface is greater than the critical angle (θ_{crit}) for TIR.

Figure 2: Schematic of the actual design of the refractive-index matched glass sphere ($r=18$ mm) used in the experiments.

encounter the sphere/air interface at normal incidence. Internal Fresnel reflections still occur at this interface, but it is not possible to trap light by TIR in this point-source arrangement. Figure 1 shows an experimental geometry which is close to this ideal situation: a small sample, with refractive index n_s and assumed a cube with dimension a^3 , is positioned in the center of a glass sphere of radius r and immersed in a liquid of identical refractive index $n=n_s$. In order to avoid TIR at the sphere/air interface, the maximum possible angle of incidence $\sin \theta = a/2r$ has to be smaller than the critical angle for TIR $\sin \theta_{crit} = n_0/n_s$, where n_0 is the refractive index of air. Neglecting the finite thickness of the sphere walls, it therefore follows that

$$r > \frac{an_s}{2n_0} \quad (1)$$

Based on this condition, a glass sphere with $r=18$ mm has been designed. As schematically shown in Figure 2, the sphere contains a glass stage to position samples in the center and planar windows for optical excitation and detection. Both the sample and the refractive index liquid were inserted through the top port which can be sealed to avoid evaporation of liquid.

The performance of the index-matched sphere shown in Figure 2 was studied by means of room-temperature lifetime measurements of YAG:1%Yb³⁺ (Y₃Al₅O₁₂) and YLF:5%Er³⁺ (YLiF₄). Both crystals were cut to cubes ($a_{YAG}=2.8$ mm, $a_{YLF}=1.0$ mm), optically polished on all faces, centered in the index-matched sphere, and excited by grazing a focused pulsed

laser beam (~970 nm, 10 Hz, ~500 μ J/pulse) along the front surface of the sample. Although the chosen sample size was small, front-surface excitation further reduces the path length of the emitted light in the sample, i.e. it minimizes the unavoidable fraction of reabsorption present in samples of finite size. Lifetimes were obtained from single exponential fits to the luminescence transients. A perfect refractive-index match was achieved for YLF ($n_s=1.46$) by immersing the crystal in a liquid of identical refractive index (Cargille Laboratories). In the case of YAG, the high refractive index of 1.82 prevented a perfect index match due to the very high toxicity of the arsenic-containing index-matching liquids of $n>1.8$. Radiation trapping exhibits a threshold behavior in the sense that a minimum difference between the sample and the surrounding medium refractive indices is required for infinite TIR to occur [1]. For YAG cube in particular it can be shown that radiation trapping is not possible if $n \geq \sqrt{2/3}$ $n_s=1.49$. In the case of YAG this makes it possible to use low-toxic, chemically stable, and only slightly colored index-matching liquids which are commercially available up to $n=1.64$.

For YAG:1%Yb³⁺, a ²F_{5/2} lifetime of 1242±0.7 μ s was measured without refractive-index matching, i.e. having the crystal surrounded by air. By subsequently immersing the crystal in $n=1.64$ index-matching liquid the observed lifetime dropped by almost 25% to 948.9±0.6 μ s. This lifetime measured in the index-matching sphere is only a very slight improvement over the one obtained from the YAG/YAG:Yb³⁺/YAG sandwich structure [2], hence confirming the results reported by Sumida et al. The index-matching however yields a record low value which is most likely only slightly contaminated by reabsorption arising from the imperfect index match ($n_s=1.82$ vs. $n=1.64$) and the finite sample size. It is therefore conceivable that the 948.9±0.6 μ s lifetime is very close to the intrinsic single-ion lifetime.

For YLF:5%Er³⁺, a drop of the ⁴I_{11/2} lifetime from 4.12±0.01 ms to 3.85±0.01 ms was observed upon refractive-index matching, significantly improving over the reported 4.00 ms lifetime derived from an unmatched experiment [6]. The index-matching induced 6.6% reduction of the measured lifetime in YLF:5%Er³⁺ is less pronounced than the 25% reduction observed in YAG:1%Yb³⁺, suggesting that the ⁴I_{11/2}→⁴I_{15/2} transition of YLF:5%Er³⁺ suffers less reabsorption/reemission events than the ²F_{5/2}→²F_{7/2} transition in YAG:1%Yb³⁺. Three factors are most likely to govern this behavior: (i) the refractive index of YLF ($n=1.46$) is smaller than the one of YAG ($n=1.82$), resulting in a lower probability for TIR and thus a shorter average path length in non refractive-index

matched YLF, (ii) the oscillator strength of the ⁴I_{15/2}↔⁴I_{11/2} transition in Er³⁺ is more than an order of magnitude smaller than of the ²F_{7/2}↔²F_{5/2} transition in Yb³⁺, leading to a much smaller reabsorption probability in YLF:5%Er³⁺ compared to YAG:1%Yb³⁺, and (iii) in contrast to the ²F_{5/2} (Yb³⁺) excited state which relaxes purely radiatively to the ²F_{7/2} ground state, both radiative and multiphonon relaxation processes compete with the ⁴I_{11/2}→⁴I_{15/2} emission, giving reabsorbed ⁴I_{11/2}→⁴I_{15/2} photons a certain chance not to be reemitted in the same transition.

Conclusions

Efficient elimination of reabsorption effects in YAG:1%Yb³⁺ and YLF:5%Er³⁺ is achieved by a refractive-index matched sphere, yielding record low values for the ²F_{5/2} and ⁴I_{11/2} lifetimes, respectively. Reductions of up to 25% in the measured excited-state lifetimes were achieved upon refractive-index matching. This, along with lifetime values from other non index-matched experiments, suggests that the lifetimes reported in the literature for a variety of samples might be significantly overestimated, making it necessary to repeat certain experiments. The artificial lengthening of the observed excited-state lifetimes is found to be a result of excessive reabsorption and reemission in the sample. It is most pronounced in samples with a high refractive index, a high oscillator strength of the reabsorbing transition, and a large radiative relaxation component to the ground state with respect to the total excited-state decay rate constant.

In contrast to other index-matched arrangements, the index-matched sphere presented here is easily realizable and offers the flexibility for convenient application to a wide variety of materials and experiments.

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