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Nd^{3+} fluorescence quantum-efficiency measurements with photoacoustics

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We have investigated the use of photoacoustic techniques for obtaining absolute values of fluorescence quantum efficiencies in lightly doped Nd^{3+} laser materials. We have found that surface absorptions play an important role in gas-microphone measurements, and that thermal profiles are important in piezoelectric measurements. We have obtained fluorescence quantum efficiencies for Nd^{3+} in yttrium aluminum garnet, and in silicate and borate glasses that are in good agreement with lifetime measurements and Judd-Ofelt calculations.

I. INTRODUCTION

One of the principal parameters of interest for luminescence and quantum electronics applications is the absolute radiative quantum efficiency of the materials of interest. This determines, for example, the efficiency of optical pumping of lasers.

The precise determination of absolute fluorescence quantum yield by conventional luminescence means has proven to be very difficult.[1] In a luminescence measurement, the number of quanta absorbed from a beam of monochromatic light has to be compared with the number of quanta emitted in the polychromatic fluorescent light, whose distribution in space may be geometrically complicated. This comparison can be accomplished by determining a defined fraction of the fluorescent radiation. To that end various corrections (for geometry, reabsorption, re-emission, polarization, refractive index) must be taken into account. This is tedious and errors exceeding 5–10% are common. Details of this widely used method are reviewed by Demas and Crosby.[2]

Another technique involves the measurement of fluorescence lifetime.[3] Again this method suffers from several experimental difficulties, since a separate measurement of the nonradiative contribution to the lifetime of the fluorescent electronic state must be made, or alternatively the radiative lifetime must be calculated as with Judd-Ofelt calculations for rare-earth fluorescent ions.[4]

There is another method which has been somewhat neglected until recently: obtaining the radiative quantum efficiency by determining the nonradiative part of the absorbed energy through calorimetry.[2] Here the temperature rise of an irradiated luminescent sample is compared to the temperature rise of a nonluminescent material showing the same absorption. The main obstacle to this method is the relative insensitivity of common temperature sensors so that strongly absorbing samples usually have to be used.

The photoacoustic technique is a more sensitive means for performing calorimetric measurements, and it has been used quite successfully to obtain accurate absolute radiative quantum efficiencies in gases, liquids, and highly absorbing solids. Recently, photoacoustic experiments have also been performed on fluorescent laser materials that are only weakly absorbing, such as Nd:YAG (yttrium aluminum garnet) and Nd-doped glasses. Unlike the experiments on more highly absorbing solids, these experiments have given quantum-efficiency values considerably different from those usually measured or calculated for Nd:YAG and Nd-doped glasses.

We have investigated the problem of photoacoustic measurements of fluorescence quantum efficiencies, and have concluded that the discrepancies encountered in the experiments with the lightly doped samples are primarily due to the neglect of surface absorptions. We have used both gas-microphone and piezoelectric photoacoustic techniques, and have been able to obtain fluorescence quantum efficiencies for Nd^{3+} in YAG, silicate glasses and borate glasses which are in good agreement with lifetime measurements and Judd-Ofelt calculations.

II. QUANTUM-EFFICIENCY CALCULATION

For a sample of thickness d, with a bulk optical coefficient α such that $\alpha d < 1$, the photoacoustic signal at a wavelength λ_k and at a phase angle θ will be given by[5]

$$q_k(\theta) = S a_k p_k \sum_{ij} \phi_{ij}^{\mathrm{nr}} \frac{E_{ij}}{E_k} \cos\left[\psi' + \tan^{-1}\left(\frac{d}{\mu}\right) + \tan^{-1}\omega\tau_{ij} - \theta\right] , \quad (1)$$

where a_k is the absorbance of the sample and P_k is the incident power at λ_k, E_k is the energy of the absorbing electronic level, and S is the system sensitivity (V/W). The probability for nonradiative transitions between energy levels E_i and E_j is given by ϕ_{ij}^{nr} and $E_{ij} = E_i - E_j$. The various phase shifts are as follows: ψ', due to system electronics, cell, etc.; $\tan^{-1}(d/\mu)$ due to the heat flow in the sample which has a thermal diffusion length μ; and $\tan^{-1}\omega\tau_{ij}$, due to the lifetime of state E_i with $1/\tau_{ij}$ being the total transition rate for the decay $E_i \rightarrow E_j$.

As long as the sample is thermally thick ($d > \mu$) at all modulation frequencies used, and as long as $\omega\tau_{ij} << 1$, then the phase of the photoacoustic signal will be independent of both ω and λ, and thus can be ignored, and Eq. (1) can be rewritten as

$$q_k = S a_k P_k \sum_{ij} \phi_{ij}^{\mathrm{nr}} \frac{E_{ij}}{E_k} \quad . \tag{2}$$

For a system where only one level is fluorescent, with a quantum efficiency η, we can show that

$$q_k = S a_k P_k \left[1 - \eta \frac{\lambda_\kappa}{\lambda_e} \right] \quad , \tag{3}$$

where λ_k is the exciting wavelength and λ_e is the mean emission wavelength. In the case of Nd^{3+} where there are several discrete emission wavelengths arising from transitions from the ${}^4F_{3/2}$ fluorescent state to the various ${}^4I_j$ terminal states, the mean emission wavelength is given by

$$\frac{1}{\lambda_e} = \sum_t \frac{b_t}{\lambda_t} \quad , \tag{4}$$

where the b_t's are the branching ratios to the various ground levels E_t, and the λ_t's are the corresponding emission wavelengths.

Clearly, in order to obtain an absolute value for η, we would need to know the sensitivity factor S, which in turn depends critically on such difficult-to-measure parameters as the volume of gas in the cell, the acoustic reflectivity of the cell walls, etc. The ratiometric approach, first used by Rockley[6] in a fluorescent study on gases, offers a convenient solution to this problem. If the photoacoustic signal is measured at two absorbing wavelengths λ_i and λ_j, the ratio of the two signals will be given by

$$\frac{q_i}{q_j} = \left[a_i P_i \left(1 - \eta \frac{\lambda_i}{\lambda_e} \right) \right] \Big/ \left[a_j P_j \left(1 - \eta \frac{\lambda_j}{\lambda_e} \right) \right] \quad . \tag{5}$$

And if we define a normalized photoacoustic signal $q^* = q/aP$, then the absolute quantum efficiency is determined by

$$\eta = \frac{(q_i^* - q_j^*)\lambda_e}{(q_i^* \lambda_j - q_j^* \lambda_i)} \quad . \tag{6}$$

It is important to note that an accurate evaluation of η requires very high accuracy in the determination of the photoacoustic signal, and particularly so for systems with low η since here $q_i^* \simeq q_j^*$. In general we find that errors or uncertainties in the q^*'s of only ±1% will result in errors or uncertainties in η of ±10%. In addition, it is important to have the quantity $(\lambda_j - \lambda_i)$ as large as possible or the uncertainties in η will become even greater.

III. PREVIOUS EXPERIMENTS

The first photoacoustic study (PAS) of fluorescence quantum efficiency in solids was reported by Murphy and Aamodt.[7] In this study the gas-microphone PAS signal of Cr^{3+} in Al_2O_3 was obtained, and in particular a comparison of the ${}^4T_1$ and ${}^4T_2$ band intensities was made as a function of Cr^{3+} concentration. Using rate equations for the different transitions allowed in ruby, Murphy and Aamodt were able to relate the ratio of the ${}^4T_1$ and ${}^4T_2$ PAS bands to the relative rates for radiative and nonradiative decay rates, and to obtain data on the quenching effects of increased Cr^{3+} concentration. In this experiment, however, absolute radiative quantum efficiencies were not obtained.

Quimby and Yen[8] (QY) also used a gas-microphone method to obtain the absolute quantum efficiency for Nd^{3+} ions in an Ed-2 glass matrix. They measured the PAS signal and the fluorescence lifetime for a number of samples as a function of Nd^{3+} concentrations and from these measurements obtained a value of η for lightly doped Nd:glass of 0.65 ± 0.05. This value is considerably less than the value of 0.9 found by the luminescence-sphere method,[9] and predicted by the exponential-energy-gap law.[10] Quimby and Yen have suggested that the reason for this discrepancy might be site selectivity resulting from their use of a narrow energy laser line for excitation, since as Brecher, Riseberg, and Weber have shown with fluorescence line-narrowing experiments, η can vary by as much as 50% between the various sites in Ed-2 silicate glass.[11]

Powell, Neikirk, and Sardar[12] (PNS) have also used a PAS gas-microphone ratiometric technique to obtain absolute quantum efficiencies for Nd^{3+} in garnet, vanadate and phosphate host crystals. For the more highly concentrated samples PNS obtained results in good agreement with previous measurements and calculations. However, for lightly doped Nd:YAG, they obtained $\eta = 0.60$ while most previous measurements[3,13,14] and Judd-Ofelt calculations[15] indicate that η for a 1-at.% Nd:YAG is in the range of 0.9–0.88. In addition to this discrepancy, Powell *et al.* also observed that their photoacoustic signal varied as ω^{-1} for their lightly doped samples, whereas the Rosencwaig-Gersho theory[16] predicts an $\omega^{-3/2}$ behavior for these samples. Powell *et al.* have postulated that this discrepancy with the Rosencwaig-Gersho theory is a result of using a laser beam which is small compared to the total sample area. However, it has been shown both theoretically[17,18] and experimentally[17,19] that the Rosencwaig-Gersho theory is still valid under these conditions, and thus the PNS hypothesis appears invalid. Thus, neither the apparently low value of η nor the observed frequency dependence in the PNS experiment are adequately explained.

IV. ROLE OF SURFACE ABSORPTIONS

In both the QY and PNS experiments, a gas-microphone photoacoustic system was used, and in order to obtain sufficient signal strength, argon ion lasers in the 150–500-mW power range were employed as the light sources. In the QY experiment only the 514.5-nm laser line was used, while in the PNS experiment, both the 476.5- and the 514.5-nm lines were used. Both the 476.5- and 514.5-nm wavelengths are far from the major absorption bands of the Nd^{3+} ions. Thus, for the typical lightly doped laser materials, containing 1 wt. % or less of Nd_2O_3, the absorption coefficient of the Nd^{3+} ions at these two wavelengths is of the order of 0.1 cm^{-1} or less.

In a gas-microphone photoacoustic experiment, only the light absorbed within a thermal diffusion length below the surface is relevant.[16] The thermal diffusion length is given by

$$\mu = \left[\frac{2\kappa}{\rho C \omega} \right]^{1/2} , \qquad (7)$$

where κ is the thermal conductivity, ρ the density and C the specific heat of the sample, and ω is the frequency at which the light beam is modulated. At the modulation frequencies used in the QY and PNS experiments, the thermal diffusion lengths were generally less than 100 μm. Now the absorption term a in Eq. (6), is given by

$$a = (1 - e^{-\alpha\mu}) \simeq \alpha\mu \ , \qquad (8)$$

where α is the absorption coefficient. Thus, the total photoacoustic absorption due to the Nd^{3+} ions is less than 0.1% of the incident radiation. With such a low absorption due to the intrinsic bulk ions, it is imperative to consider the influence of any surface absorptions arising from contamination or surface-state effects. Unfortunately, the possible presence of a measurable non-Nd^{3+} surface absorption was not taken into account by either the QY or the PNS groups.

The anomalous ω^{-1} frequency dependence observed by PNS is a further indication that surface absorption terms may be of considerable importance. From the Rosencwaig-Gersho theory,[16] one can readily show that in the presence of both a surface absorption term of absorbance α_s, and of a weak bulk absorption with absorption coefficient α, the photoacoustic signal is given by

$$Q = I_0 \left[\frac{(1-i)\alpha_s}{\omega} - \frac{i\alpha\mu'}{\omega^{3/2}} \right] Z \ , \qquad (9)$$

where I_0 is the incident light intensity, Z is a frequency-independent term containing all the thermal and geometric parameters, and where μ' is a frequency-independent term given by

$$\mu'/\omega^{1/2} = \mu \ . \qquad (10)$$

We note that the first term, the surface absorption term, varies as ω^{-1}, while the bulk absorption term varies as $\omega^{-3/2}$. Furthermore, we see that the two terms are 45° out of phase. If the first term is much larger than the second term then an ω^{-1} dependence will be observed, and conversely, if the second term is larger, an $\omega^{-3/2}$ dependence will be seen.

To test this concept we studied several lightly doped Nd:glass (Ed-2 silicate) samples using a gas-microphone photoacoustic system with a xenon lamp and monochromator optical system. With this optical system we were able to measure the photoacoustic signal both at a wavelength of strong Nd^{3+} absorption (585 nm) and at a wavelength of very low Nd^{3+} absorption (550 nm). We found that the 550-nm signals were 45° out of phase and that these signals had different frequency dependencies. Figure 1 shows

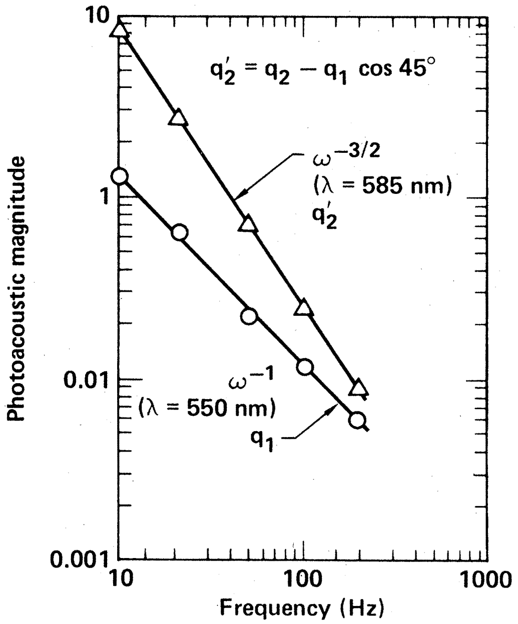

FIG. 1. Dependence of photoacoustic signal with frequency in Nd-doped silicate glass at 550 nm (q_1) and at 585 nm (q_2'). The signal at 585 nm has been corrected for background ($q_2' = q_2 - q_1 \cos\pi/4$).

the frequency dependence of the photoacoustic signal at both wavelengths. The signal at 585 nm has been corrected for background by proper vector subtraction of the signal at 550 nm. We see that the 550-nm signal shows an ω^{-1} dependence while the 585-nm signal shows an $\omega^{-3/2}$ dependence. These results strongly indicate that the 550-nm signal is indeed primarily a surface absorption signal while the 585-nm signal is due to bulk Nd^{3+} absorption. Also, our results show that the surface absorption in our samples is not negligible, and in fact at the argon laser wavelengths of 476.5 and 514.5 nm, the signal is found to be predominantly due to surface absorption, particularly, at frequencies greater than 50 Hz. We found a significant surface-absorption contribution to the total photoacoustic signal even in ultraclean samples at these two wavelengths.

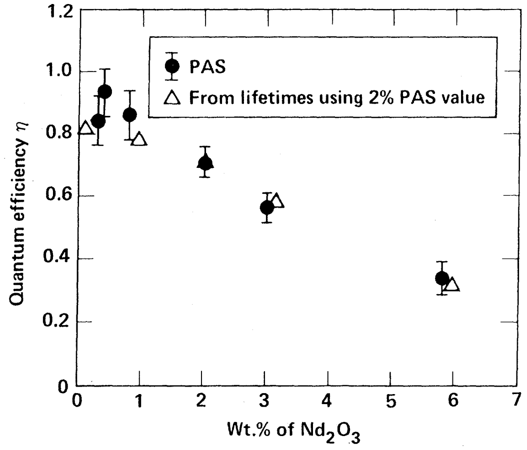

FIG. 2. Photoacoustic and relative lifetime fluorescence quantum efficiencies vs Nd_2O_3 concentration in ED-2 silicate glasses.

V. GAS-MICROPHONE PAS MEASUREMENTS

We employed a conventional gas-microphone photoacoustic system to perform these measurements. The incident radiation is from a xenon lamp and monochromator arrangement which provides us with tunable optical radiation in the 1-mW power range at ~5-nm bandwidth. We use a mechanical chopper at 10 Hz, a frequency low enough so that no measurable phase shift occurs as a result of the lifetime of the $^4F_{3/2}$ energy level. This then allows us to use Eq. (2). The two absorbing wavelengths used are at 585 and 750 nm, both positions of relatively strong Nd^{3+} absorption. In addition, measurements are also made at 550 and 700 nm, where there is essentially no Nd^{3+} absorption. These two latter measurements provide us with the needed correction for the background surface-absorption term.

In order to obtain accurate values for η, careful measurements of both the incident power at the sample (P), and of the sample absorption coefficients at 585 and 750 nm were made. It is crucial to measure the sample absorption coefficients with the same optical system as is used for the photoacoustic measurements, because of the asymmetry of the inhomogeneously broadened Nd^{3+} absorption bands. Our measured quantum efficiencies for a set of Nd^{3+}-doped ED-2 glasses are plotted in Fig. 2 with probable error bars shown. We see that the quantum efficiency at low Nd^{3+} concentration approaches 0.9, in good agreement with both luminescence and lifetime values.

Also in Fig. 2 we have plotted the quantum efficiencies that would be determined from relative average fluorescence lifetime measurements[20] after assuming the PAS value of 0.71 for the 2-wt.% sample to be correct. We see that the photoacoustic η's and the relative lifetime η's agree very well with respect to the dependence on Nd^{3+} concentration. This then indicates that when dealing with a set of similar samples that have different concentrations of Nd^{3+}, we would need to obtain an absolute value of η with photoacoustics for only one sample, and then obtain the other η's from the easier-to-measure relative fluorescence lifetimes.

The sizable decrease in quantum efficiency at higher Nd^{3+} concentration is, of course, a result of ion-ion quenching. Using both the PAS-measured quantum efficiency at low concentration and the lifetime measurements, we can then obtain absolute values for the nonradiative decay rates for Nd^{3+} in Ed-2 glass.

The quantum efficiency η is simply the ratio of radiative to total decay rates. That is

$$\eta = \frac{\omega_r}{\omega_t} = \frac{1/\tau_r}{1/\tau} , \tag{11}$$

where ω_r and ω_t are the radiative and total decay rates and τ_r and τ are the radiative and total lifetimes. For a Nd^{3+} concentration near zero, $\eta \simeq 0.9$ as determined by PAS, and $\tau \simeq 400$ μsec as determined by fluorescence-lifetime measurement. This then gives $\omega_r \simeq 2250$ sec^{-1}. Now

$$\omega_t = \omega_r + \omega_{nr} , \tag{12}$$

where ω_{nr} is the nonradiative decay rate. Since ω_r is essentially independent of concentration c over the concentration range used, we can obtain $\omega_{nr}(c)$ from a study of $\tau(c)$. We depict the $\omega_{nr}(c)$ so obtained in Fig. 3. In general the nonradiative decay rate will be composed of two terms; a concentration-independent term which arises from multiphonon processes, and an ion-ion quenching term that varies as c^2. These two terms are clearly visible in Fig. 3. The multiphonon term dominates until $c > 1\%$, after which the

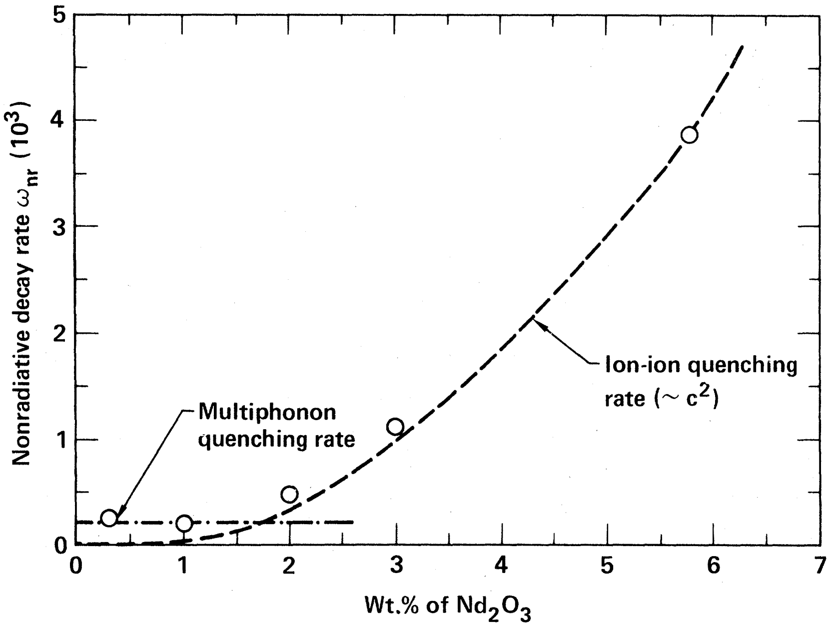

FIG. 3. Nonradiative decay rate vs Nd_2O_3 concentration in ED-2 silicate glasses.

ion-ion term quickly becomes the factor determining the fluorescence quantum efficiency. It should be kept in mind that both the radiative and nonradiative decay rates of Nd^{3+} in a glass vary considerably from site to site because of the large variations in site environments in a glass. Brecher, Riseberg, and Weber have shown that the nonradiative decay rates for Nd^{3+} in a silicate glass can range from 0 to 850 sec^{-1}.[21] However, Layne, Lowdermilk, and Weber[10] have also shown that the average multiphonon rate for ED-2 glass is ~200 sec^{-1} in good agreement with our result in Fig. 3.

VI. PIEZOELECTRIC PAS MEASUREMENTS

Although it is possible to obtain fairly reliable measurements of the absolute radiative quantum efficiency with gas-microphone photoacoustics, the pervasive presence of a sizable surface-absorption term makes this method difficult, particularly for lightly doped samples in which the surface-absorption term may be comparable to the bulk-absorption term.

We have, therefore, developed an alternative procedure which employs a piezoelectric photoacoustic technique. As shown in Fig. 4, a mirror is bonded to a ceramic piezoelectric transducer, and the mirrored transducer is then acoustically bonded with phenylsalicylate to the side of the sample. The mirror serves to minimize background signal due to the absorption of scattered light by the transducer. The same optical system as was used in the gas-microphone experiment is used in this experiment, and once again the optical beam is chopped at 10 Hz. The signal from the piezoelectric transducer is amplified with a charge amplifier (Princeton Applied Research model 184), and then processed by a lock-in amplifier.

In a gas-microphone system, only the light absorbed within a thermal diffusion length beneath the sample surface plays a role in determining the photoacoustic signal. In a piezoelectric system, however, all of the light absorbed throughout the entire sample

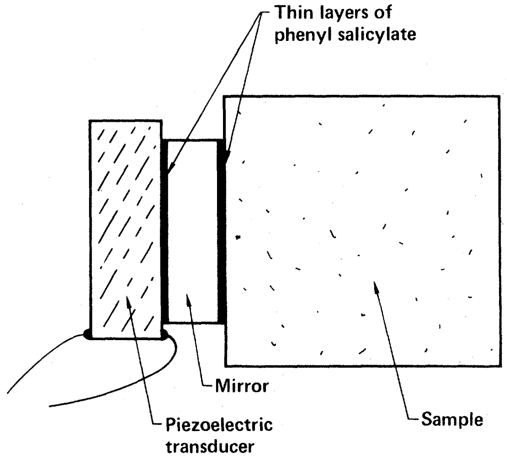

FIG. 4. Sample-detector mounting arrangement for piezoelectric photoacoustic experiments.

TABLE I. Radiative quantum efficiencies for Nd^{3+} laser materials.

Sample	PAS (gas microphone)	PAS (piezoelectric)	Other methods	(References)
ED-2 silicate glass				
0.3 wt.% Nd_2O_3	0.85 ±0.08		0.90	(20)
0.4 wt.% Nd_2O_3	0.93 ±0.08	0.91 ±0.05	0.90	(20)
0.8 wt.% Nd_2O_3	0.86 ±0.08		0.90	(20)
1.0 wt.% Nd_2O_3		0.93 ±0.05	0.87	(20)
2.0 wt.% Nd_2O_3	0.71 ±0.05		0.79	(20)
3.0 wt.% Nd_2O_3	0.56 ±0.05		0.64	(20)
5.8 wt.% Nd_2O_3	0.34 ±0.05	0.40 ±0.05	0.37	(20)
Borate glass				
0.2 wt.% Nd_2O_3		0.16 ±0.07	0.16	(21)
$Y_3Al_5O_{12}$				
1.2 at.% Nd		0.97 ±0.02	0.91	(3)
			0.88	(15,20)
			1.00	(13)
			0.98	(14)
			0.56	(24)
			0.63	(25)
			0.60	(12)

contributes to the photoacoustic signal. Since the samples are 0.2 to 1 cm thick, this provides us with a bulk-absorption signal considerably greater than the surface-absorption signals, and thus surface absorptions generally present no problems in a piezoelectric measurement. Nevertheless, we still take measurements at both 550 and 700 nm to subtract out any other background signals.

In piezoelectric photoacoustic detection, the magnitude and phase of the photoacoustic signal are both complex functions of the thermal spatial profile produced in the sample through the absorption of the optical beam.[22,23] To minimize this very difficult problem we attempt to have the same spatial thermal profile at both of the absorbing wavelengths. Thus, we do not use the 585-nm wavelength, but rather a wavelength nearby that has the same optical absorption as that measured for 750 nm. In addition, since the absorption bands have quite different line shapes at the two wavelengths we use, we have found it best to work only with lightly doped samples to attempt to obtain identical thermal profiles at the two wavelengths.

In Table I, we list the fluorescence quantum efficiencies measured for some of the ED-2 silicate glass samples with both the piezoelectric and gas-microphone methods. There is quite good agreement between the two sets of values, and the probable error for the low-concentration samples is better in the piezoelectric measurements. The good agreement between the gas-microphone and piezoelectric measurements provides further confidence in the value of 0.9 for η that we obtain for Ed-2 silicate glass.

VII. BORATE GLASS

We repeated the silicate piezoelectric photoacoustic experiment with Nd^{3+}-doped borate glass. Borate glass has a high nonradiative multiphonon decay rate at room temperature of $\sim 14\,000\ \text{sec}^{-1}$, resulting in an average quantum efficiency substantially less than unit.[21] For the sample used in our experiment, the lifetime-determined η is ~ 0.16.[21] We obtain with the piezoelectric photoacoustic technique a value for η for this sample (see Table I) of 0.16 ± 0.07, a value in excellent agreement with the lifetime measurement. The relatively large uncertainty in our value is a result of the increased probable error that occurs when the quantum efficiency is low and the quantity $(q_i^* - q_j^*)$ in Eq. (6) becomes very small.

VIII. Nd:YAG

There has been, for many years, considerable interest in the absolute fluorescence quantum efficiency of Nd:YAG, a widely used laser material. In spite of many different experiments there is still uncertainty about the value of η for this material. Judd-Ofelt and lifetime calculations[15] indicate that a 1-at.% Nd:YAG sample should have an η of ~ 0.91. Luminescence measurements by Dianov *et al.*,[3] an optical refrigeration experiment by Kushida and Geusic,[13] and temperature studies of fluorescence lifetimes by Liao and Weber[14] agree with this prediction, and provide measurements of η for such a sample that range from 0.98–0.88. However, a luminescence measurement by Singh *et al.*,[24] and a thermal loading experiment by Kennedy and Barry[25] generate values of η in the 0.63–0.56 range.

Thus the photoacoustic experiment of Powell, Neikirk, and Sardar[12] is of considerable interest since it appears to confirm the lower values of η for Nd:YAG. However, the results of Powell *et al.* are unfortunately suspect, as we have shown, because of their neglect of surface-absorption terms.

We have measured the quantum efficiency of a 1.2-at.% Nd:YAG sample using the piezoelectric photoacoustic technique, and have obtained a value for η of 0.97 ± 0.02. Our result clearly supports the contention that the quantum efficiency for Nd:YAG is close to unity. In fact, our value of 0.97 is actually somewhat higher than the 0.91–0.88 value that would be predicted from Judd-Ofelt calculations and fluorescence lifetime measurements. We believe that this relatively minor discrepancy is a result of not being able to select two wavelengths in Nd:YAG for which the photoacoustic thermal profiles are exactly identical. This condition is particularly difficult to achieve in a crystal like YAG because of the narrow absorption bands.

IX. CONCLUSIONS

The photoacoustic technique provides a reliable means for obtaining absolute values for the radiative quantum efficiency. This technique, is, however, not without its particular problems. We have shown that in lightly doped laser materials with relatively weak bulk absorptions, surface absorptions from contamination or from surface energy states can play a major role in gas-microphone photoacoustic measurements. We believe that it was neglect of this surface absorption that led to anomalous results in previous experiments. We have also shown that a piezoelectric photoacoustic technique is an attractive alternative procedure that is relatively immune to surface-absorption effects. However, here too, care must be taken. This technique works best for weakly absorbing samples with measurements made at two wavelengths having equal absorptions.

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