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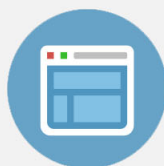
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Blue cooperative luminescence in Yb^{3+} -doped tellurite glasses excited at 1.064 μm

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Blue luminescence emission around 480 nm through cooperative upconversion from pairs of Yb^{3+} ions implanted into $60\text{TeO}_2-10\text{GeO}_2-10\text{K}_2\text{O}-10\text{Li}_2\text{O}-10\text{Nb}_2\text{O}_5$ tellurite glasses and excited by a cw laser at 1.064 μm is demonstrated. Cooperative luminescence emission enhancement owing to the temperature dependent multiphonon-assisted anti-Stokes excitation process of the ytterbium ions is also observed. The experimental results revealed a fourfold enhancement in the cooperative luminescence emission when the sample was heated in the temperature range of 20 $^\circ\text{C}$ –260 $^\circ\text{C}$. The thermally induced enhancement is assigned to the effective absorption cross-section for the ytterbium ions which is an increasing function of the medium temperature. © 2002 American Institute of Physics. [DOI: 10.1063/1.1463397]

I. INTRODUCTION

Intensive research has recently been dedicated to the conversion of near-infrared (NIR) radiation into visible light exploiting frequency upconversion in rare-earth doped solid-state materials for a wide range of applications including color displays, optical data storage, biomedical diagnostics, sensors, and undersea optical communications. The frequency upconversion process¹ is in general accomplished via sequential or multiphoton stepwise excitation, successive or cooperative energy transfer between pairs or triads of rare-earth ions in solids, and subsequent radiative depopulation of the excited-state levels with the emission of photons with energy higher than that of the excitation photons. In these upconversion excitation mechanisms one can have the participation of optical phonons in order to compensate for energy mismatches between the excitation photon and the pertinent energy levels of the activated rare-earth ion. When there is neither an intermediate nor a final energy level to be populated one still can convert near-infrared radiation into visible emission through the process referred to as cooperative upconversion first observed by Nakazawa and Shionoya in YbPO_4 ,² and later reported by many, mostly in crystals.^{3–6} In the cooperative luminescence emission, two infrared excited Yb^{3+} ions undergo a simultaneous de-excitation process producing the emission of a single visible wavelength photon, as pictured in the diagram of Fig. 1. The cooperative emission process relies upon Coulomb interaction between ions and strongly depends upon the distance separating them^{1–6} and its efficiency is determined by the nearest Yb^{3+} ions. Bearing that in mind, cooperative luminescence from Yb^{3+} pairs has been proposed as a probe of clustering in Yb^{3+} -doped glasses,^{4,7–9} and its potential application in a three-dimensional solid-state fluorescence display has recently been proposed.^{10,11} For technological applications and basic research, the study of cooperative luminescence in

novel crystals and glasses doped with high concentrations of ytterbium is very important in order to establish either limitations of applicability in devices like rare-earth doped optical amplifiers or to shed light onto unsolved research problems involving the optimization of materials composition in the synthesis of novel glasses for fiber and/or waveguide fabrication. In this work, we investigate blue cooperative upconversion emission around 480 nm in TeO_2 -based glasses doped with high various concentrations of Yb^{3+} ions and excited by cw radiation at 1.064 μm and the effect of temperature on the cooperative luminescence efficiency in these glasses.

II. EXPERIMENT

The tellurium-oxide glass samples used in our measurements had a composition of $60\text{TeO}_2-10\text{GeO}_2-10\text{K}_2\text{O}-10\text{Li}_2\text{O}-10\text{Nb}_2\text{O}_5$ doped with concentrations 1000 ppm/wt, 5000 ppm/wt, and 30 000 ppm/wt of ytterbium. Glasses were prepared with high purity (99.9999%) rare-earth oxides and all special care was taken in the lab during the glass preparation in order to avoid contamination due to other rare-earth ions than ytterbium itself. The glass host material presents very good optical quality, is stable against atmospheric moisture, it exhibits low optical attenuation from 400 nm to 5.0 μm , and due to the relatively high refractive index (≥ 2.0), it is expected to produce significantly high radiative transition rates from excited-states of rare-earth ions. The material also exhibits high solubility allowing the incorporation of high lanthanide concentrations apart from being nonhygroscopic and possess high thermal stability against crystallization. The samples thickness were ~ 2.5 mm and the excitation source was a continuous-wave Nd:YAG laser operated at 1.064 μm with the pump beam focused down onto the samples by a $\times 10$ microscope objective. The detection system comprised a 0.34 m scanning spectrograph with operating resolution of

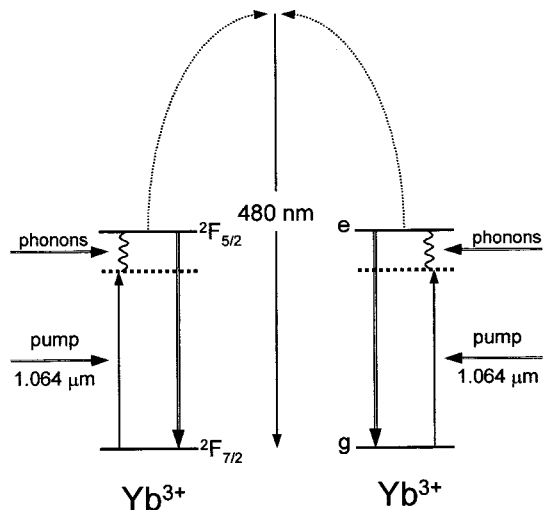


FIG. 1. Simplified energy-level diagram for the Yb^{3+} - Yb^{3+} pair pumped at $1.064 \mu\text{m}$ indicating the participation of phonons in the Yb^{3+} absorption.

0.5 nm equipped with an S-20 uncooled photomultiplier tube for visible wavelength detection and a 0.64 m spectrometer and a germanium photodetector for the infrared spectral region. A lock-in amplifier in conjunction with a storage-scope coupled to a microcomputer was used for data acquisition and storage.

III. RESULTS AND DISCUSSION

The blue cooperative luminescence emission around 480 nm was recorded at room temperature for all samples, and the result is presented in the typical power spectrum portrayed in Fig. 2(a). The spectrum has shown no structure and the 480 nm signal presented a bandwidth of ~ 17 nm. It is important to point out that the blue emission around 480 nm was intense enough that could easily be seen by naked eyes. The blue emission signal generation was ascribed to the simultaneous de-excitation of a pair of Yb^{3+} ions which forms a dimeric system³ yielding the emission of the blue light signal and also the near-infrared radiation corresponding to the ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} ions. The recorded near-infrared absorption and fluorescence signals are shown in the spectra depicted in Fig. 2(b). The absorption spectrum exhibits three peaks centered around 925, 955, and 975 nm, which correspond to transitions from the lowest Stark level to the multiplet ${}^2F_{7/2}$ into the various Stark levels of the ${}^2F_{5/2}$ excited multiplet. The near-infrared fluorescence spectrum presents four peaks centered around 975, 1002, 1018, and 1043 nm which are ascribed to the transitions from the lowest Stark level of the excited multiplet ${}^2F_{5/2}$ to the ${}^2F_{7/2}$ ground-state multiplet. A theoretical cooperative emission spectrum can be obtained by the convolution of the recorded infrared spectrum of Fig. 2(b). As can be seen, good agreement was attained as indicated by the dotted line convolution spectrum of Fig. 2(a). We have also extended the latitude of our spectral observation [see Fig. 2(c)] and performed measurements well beyond the visible region (300–900 nm) seeking for the presence of parasitic upconversion emission signals originating from remnant amount of Er^{3+} and/or Tm^{3+} in the glass samples. It is well known that Er^{3+} produces green upcon-

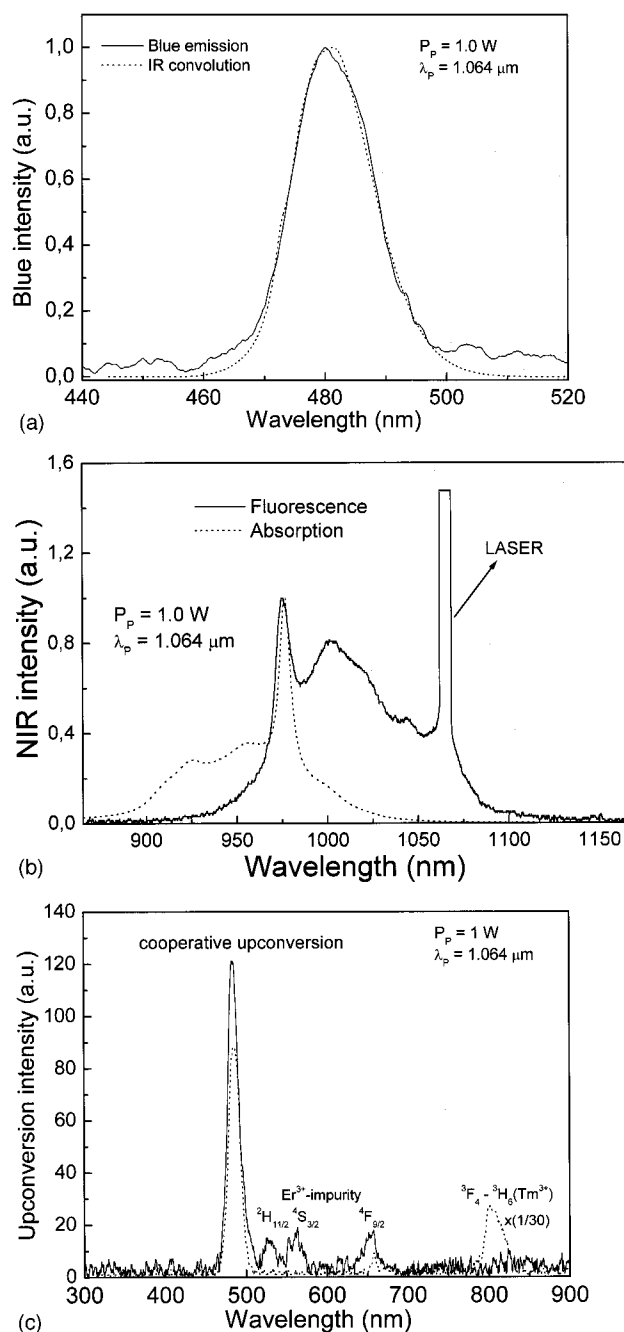


FIG. 2. Room-temperature cooperative blue emission and convolution of the infrared emission (a), NIR absorption and fluorescence emission (b), and violet-NIR luminescence emission (c) spectra for the Yb^{3+} -doped samples under 1.0 W excitation power at $1.064 \mu\text{m}$ launched onto it. The dotted line in (c) stands for the upconversion emission of a test low concentration Tm/Yb -codoped sample.

version fluorescence emission in the region of 530–560 nm (${}^2H_{11/2}$ and ${}^4S_{3/2}$) and a red signal around 660 nm (${}^4F_{9/2}$), and Tm^{3+} yields intense 480 nm blue (1G_4 , 800 nm near-infrared (3F_4), and also weak 655 nm red (${}^1G_4 + {}^3F_{2,3}$) signals in glasses sensitized by Yb^{3+} ions and excited at $1.064 \mu\text{m}$. In both rare-earth codoped systems the upconversion excitation process of the activated ions is accomplished by means of sequential energy-transfer from the ytterbium-sensitizer.^{12,13} In Refs. 6–9, upconversion emission originating from contamination levels of a few ppm/wt

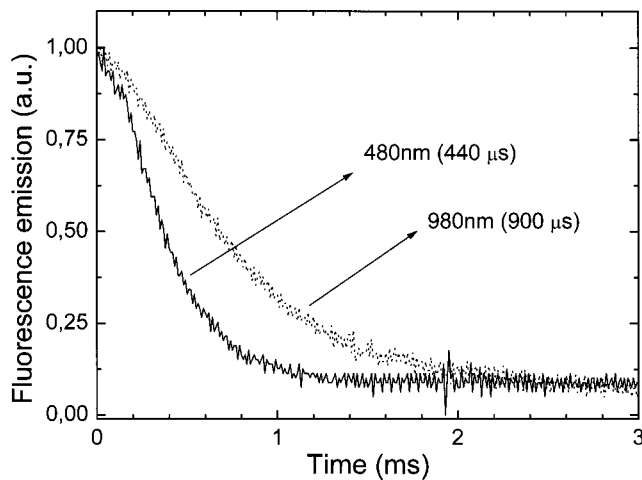


FIG. 3. Oscilloscope traces of the decay times for the blue and NIR emission signals.

of Tm^{3+} and/or Er^{3+} in highly ytterbium-doped samples were detectable. For Tm^{3+} impurities, one would expect strong upconversion emission around 800 nm. As can be seen from data of Fig. 2(c), we have indeed recorded upconversion signals associated with the Er^{3+} contaminant, but found no evidence whatsoever of emission originated from Tm^{3+} impurities. In order to stress that point we have performed the same experiment using a sample containing the pair Tm/Yb with very low concentration (a few ppm/wt), and the observation of the spectrum depicted in the dotted curve of Fig. 2(c) allows one discarding Tm contamination as responsible for the blue emission in the high purity Yb^{3+} -doped samples. Besides, the power dependence for the double-doped sample showed clearly a three-photon process for the 485 nm emission which was not the case for the cooperative luminescence signal, as will be shown later on in this paper.

The luminescence decay times of both the blue cooperative signal and the ${}^2F_{5/2}$ manifold was investigated and the results produced time constants of 440 and 900 μs , respectively, as illustrated in the scope traces of Fig. 3. The 900 μs luminescence decay time of the ${}^2F_{5/2}$ manifold, measured at room temperature for the samples with 1000 and 5000 ppm/wt, can be considered as solely radiative owing to the relatively low maximum phonon-energy of $\sim 850 \text{ cm}^{-1}$ associated with tellurite glasses in addition to the relatively low Yb^{3+} concentration of the samples. The results also indicated that both signals decay times curves are fitted by single-exponential decay functions, with very little deviation in the tails. However, for the sample with 30 000 ppm/wt we have estimated a fluorescence decay time for the ${}^2F_{5/2}$ manifold and found approximately 570 μs . This value has been calculated considering energy migration² between Yb^{3+} - Yb^{3+} pair which is an effect assigned to Yb^{3+} clustering formed in high concentration samples. The dependence of the cooperative luminescence signal upon the excitation power was examined and the results are presented in the log-log plot of Fig. 4. The results revealed that the slope of the curve is 1.85 which is approximately equal to the quadratic power law behavior, expected for a mechanism involving the participa-

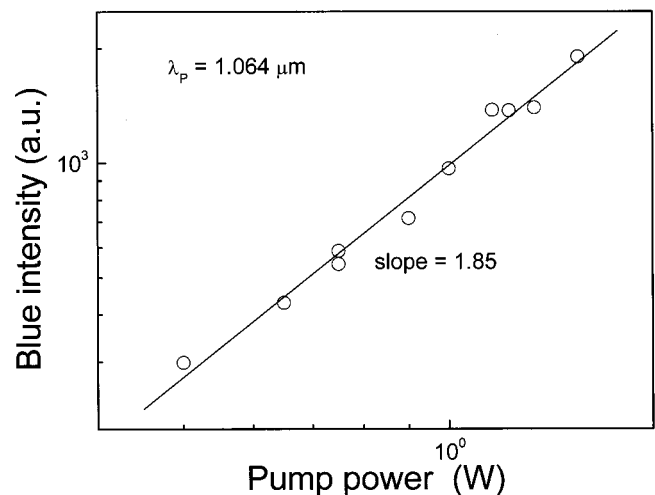


FIG. 4. Log-log plot of the blue upconversion emission intensity as a function of the excitation power at 1.064 μm at room temperature.

tion of two pump photons in the excitation of the Yb^{3+} - Yb^{3+} pair. The results presented in Fig. 4 have shown no indication of saturation in the cooperative upconverted signal. The behavior of the blue signal with several pump intensity levels and the measured upconversion emission decay time and wavelength, corroborate the proposed upconversion emission mechanism herein reported and elsewhere by many in crystals and glasses doped with trivalent ytterbium.²⁻¹¹ Moreover, in our measurements the blue emission intensity has shown a quadratic dependence upon the Yb^{3+} concentration. The dependence of the blue emission upon excitation power and the relation between decay times of the near-infrared and cooperative blue emissions can be described by the rate equation for the energy levels of the Yb^{3+} ions, which has the following form:

$$\dot{n}_e = \phi\sigma(T)n_g - \frac{n_e}{\tau_e} - Xn_e^2, \quad (1)$$

where n_g and n_e represent, respectively, the population density of the ground-state and excited-state, τ_e is the infrared decay time, ϕ is the excitation power flux, and X is the cooperative luminescence rate parameter. In the rate equation, $\sigma(T)$ stands for the temperature dependent effective absorption cross-section for the ytterbium, which takes into account the multiphonon-assisted anti-Stokes excitation process.¹⁴ The near-infrared luminescence is proportional to the population of the excited-state n_e and the cooperative upconversion process has a very low efficiency such that, one may assume that there is no depletion of the ground-state. Accordingly, for low concentration, the decay times of the luminescent signals can be expressed as

$$I_{\text{NIR}} \propto n_e \propto \exp(-t/\tau_e)$$

and

$$I_{\text{coop}} \propto n_e^2 \propto \exp(-2t/\tau_e).$$

As can be inferred from data depicted in Fig. 3, the experimental results for the decay times agree very well with theory with the blue luminescence signal decay time being

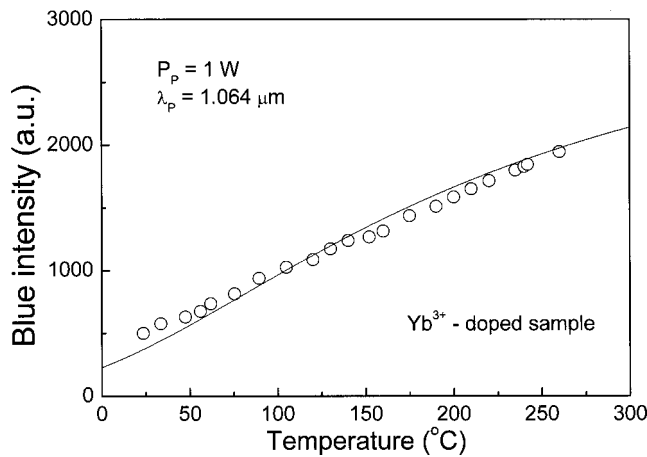


FIG. 5. Blue upconversion emission intensity as a function of the sample temperature at a fixed excitation power of 1.0 W. Symbols stand for experimental data and solid line is the theoretical fit.

half of the NIR emission signal. The dependence of the cooperative upconversion process upon the sample temperature was inspected for the sample with a concentration of 30 000 ppm/wt and the results have shown a fourfold enhancement in the blue emission when the sample was heated in the temperature range of 20–260 °C for a fixed launched power, as illustrated in Fig. 5. The temperature-induced enhancement in Yb^{3+} -sensitized systems pumped off-resonance has already been described in detail for Er^{3+} - and Pr^{3+} -doped glasses sensitized by Yb^{3+} and pumped at 1.064 μm ,^{15–17} and it suffices to mention here that the excitation of the Yb^{3+} from the ${}^2F_{7/2}$ ground-state to the ${}^2F_{5/2}$ excited-state, requires the participation of optical phonons in order to compensate for the energy mismatch of ($\sim 800\text{ cm}^{-1}$) between the incident excitation photon at 1.064 μm (9398 cm^{-1}) and the energy connecting the ${}^2F_{7/2}$ – ${}^2F_{5/2}$ transition of the ytterbium ions which is $\sim 10\,200\text{ cm}^{-1}$. Therefore, the effective pumping of the Yb^{3+} ions excited-state relies upon the phonon population in the host material. This mechanism is accounted for by introducing a temperature dependent effective absorption cross-section for the Yb^{3+} , such that $\sigma(T) = \sigma_Y^0 F(T)$, where σ_Y^0 is the Yb^{3+} absorption cross section at resonance peaked around 975 nm ($\sim 10\,200\text{ cm}^{-1}$) and $F(T) = [\exp(h\nu_{\text{phonon}}/k_B T) - 1]^{-p}$ accounts for the phonon population in the host material. The exponent p is associated with the number of optical phonons involved in the Yb^{3+} excitation process, $h\nu_{\text{phonon}}$ is the phonon energy, k_B is the Boltzmann constant, and T the absolute temperature. For the TeO_2 -based glasses, we may assume $p=1$ since the energy mismatch between the pump photon and the ytterbium transition ($\sim 800\text{ cm}^{-1}$) corresponds approximately to the value of the cutoff phonon energy for tellurite glasses.

In order to obtain the theoretical fit (solid line) for the experimental data depicted in Fig. 5 we have solved the rate Eq. (1) for steady-state regime and have obtained the following expression for cooperative emission intensity:

$$I_{\text{coop}} = XN_Y^2 \tau_e^2 \phi^2 (\sigma(T))^2, \quad (2)$$

where $N_Y(n_g + n_e = N_Y)$ is the ytterbium concentration. It is

interesting to emphasize the quadratic dependence of the blue intensity on both the pump power and concentration. The decay time τ_e can be written as

$$\tau_e = \frac{1}{(1/\tau_R) + W_{MP} + W_{EM}}, \quad (3)$$

where τ_R is the radiative lifetime of the ${}^2F_{5/2}$ manifold, W_{MP} is multiphonon decay-rate, and W_{EM} is the rate of energy migration between Yb – Yb pair. In Eq. (3), W_{MP} can be neglected, because of the relatively low maximum phonon energy associated with tellurite glasses as already mentioned above. With the assumption that the dipole–dipole interaction is the dominant effect, the energy migration-rate term W_{EM} is given by¹⁸

$$W_{EM} = \frac{3\hbar^4 c^4}{4\pi^4 \tau_R} \left(\frac{1}{R_{YY}} \right)^6 Q_Y \int \frac{F_e(E)F_a(E)dE}{E^4}, \quad (4)$$

where R_{YY} is the ytterbium–ytterbium distance, Q_Y is the integrated absorption cross section $\int \sigma(T)dE$, $F_e(E)$, and $F_a(E)$ are the normalized shapes of the absorption and fluorescence spectra as function of the photon energy E . Using $\sigma(T)$, the measured absorption and fluorescence spectra [Fig. 2(b)], $(R_{YY})^6 = N^{-2}$ and combining Eqs. (3) and (4) into the rate Eq. (2), we have obtained the theoretical fit (solid line) for the experimental data depicted in Fig. 5. It is clear that the theoretical results, based upon the temperature dependent effective absorption cross-section of the Yb^{3+} ions and taking into account the energy migration effect, agree very well with experimental data.

IV. CONCLUSIONS

In summary, we have demonstrated the generation of blue upconversion emission around 480 nm in Yb^{3+} -doped tellurite glasses excited by cw radiation at 1.064 μm . The frequency upconversion mechanism responsible for the blue emission signal is ascribed to the cooperative luminescence from pairs of ytterbium ions. A fourfold temperature-induced enhancement in the cooperative luminescence process was also observed and was assigned to the temperature dependent effective absorption cross section of the ytterbium ions which relies upon the phonon population number in the host matrix.

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- ¹F. E. Auzel, Proc. IEEE **61**, 758 (1973).
- ²E. Nakazawa and S. Shionoya, Phys. Rev. Lett. **25**, 1710 (1970).
- ³M. P. Hehlen and H. U. Güdel, J. Chem. Phys. **98**, 1768 (1993).
- ⁴F. E. Auzel, D. Meichenin, F. Pellé, and P. Goldner, Opt. Mater. **4**, 35 (1994).
- ⁵R. T. Wegh and A. Meijerink, Chem. Phys. Lett. **246**, 495 (1995).
- ⁶P. Goldner, F. Pellé, D. Meichenin, and F. E. Auzel, J. Lumin. **71**, 137 (1997).
- ⁷B. Schaudel, P. Goldner, M. Prassas, and F. Auzel, J. Alloys Compd. **300-301**, 443 (2000).
- ⁸P. Goldner, B. Schaudel, M. Prassas, and F. Auzel, J. Lumin. **87-89**, 688 (2000).
- ⁹F. Auzel and P. Goldner, Opt. Mater. **16**, 93 (2001).
- ¹⁰G. S. Maciel, A. Biswas, R. Kapoor, and P. N. Prasad, Appl. Phys. Lett. **76**, 1978 (2000).
- ¹¹G. C. Maciel, A. Biswas, and P. N. Prasad, Opt. Commun. **178**, 65 (2000).
- ¹²A. S. Oliveira, M. T. de Araujo, A. S. Gouveia-Neto, J. A. Medeiros Neto, A. S. B. Sombra, and Y. Messaddeq, Appl. Phys. Lett. **72**, 753 (1998).
- ¹³I. R. Martin, V. D. Rodriguez, V. Lavin, and U. R. Rodriguez-Mendoza, Spectrochim. Acta, Part A **55**, 941 (1999).
- ¹⁴F. Auzel, Phys. Rev. B **13**, 2809 (1976).
- ¹⁵P. V. dos Santos, E. A. Gouveia, M. T. de Araujo, A. S. Gouveia-Neto, A. S. B. Sombra, and J. A. Medeiros Neto, Appl. Phys. Lett. **74**, 3607 (1999); C. J. da Silva, M. T. de Araujo, E. A. Gouveia, and A. S. Gouveia-Neto, Appl. Phys. B: Lasers Opt. **70**, 185 (2000).
- ¹⁶A. S. Oliveira, E. A. Gouveia, M. T. de Araujo, A. S. Gouveia-Neto, C. B. de Araújo, and Y. Messaddeq, J. Appl. Phys. **87**, 4274 (2000).
- ¹⁷P. V. dos Santos, E. A. Gouveia, M. T. de Araujo, A. S. Gouveia-Neto, S. J. L. Ribeiro, and S. H. S. Benedicto, J. Phys.: Condens. Matter **12**, 10003 (2000).
- ¹⁸D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).