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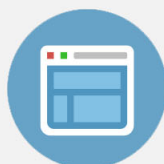
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Thermally enhanced frequency upconversion in Nd³⁺-doped fluoroindate glass

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Multiphonon assisted frequency upconversion was observed in a Nd³⁺-doped fluoroindate glass pumped at 866 nm. A near-infrared upconverted emission at 750 nm with a peculiar linear dependence with the laser intensity was observed and explained. The intensity of the upconverted emission experienced a 40-fold enhancement when the sample's temperature was varied from 298 to 498 K. A rate equation model that includes light pumping and multiphonon absorption via thermally coupled electronic excited states of Nd³⁺ was used, describing quite well the experimental results. © 2001 American Institute of Physics. [DOI: 10.1063/1.1410326]

I. INTRODUCTION

The study of multiphonon (MP) assisted processes in rare-earth (RE) doped materials has been the subject of much interest. In the past, luminescence and frequency upconversion (UPC) mediated by phonons have been analyzed by Auzel *et al.*¹⁻³ and Pellé and Auzel.⁴ They demonstrated that it is possible to induce luminescence in solids doped with RE ions even when the difference between the excitation frequency and the electronic transition frequency is larger than the maximum phonon frequency of the host material. This was observed both for transitions involving creation or annihilation of phonons. Furthermore, contrary to what was generally thought, Auzel *et al.*¹⁻³ and Pellé and Auzel⁴ also showed that MP assisted processes should be described in terms of an effective phonon mode (EPM) (or “promoting mode”), with a frequency smaller than the phonon cutoff frequency of the host material. Recently, it was demonstrated that besides scientific interest, studies of phonon assisted processes are useful to photonic applications such as phase conjugation,⁵ lasers,⁶ avalanche UPC,⁷ laser cooling of solids,^{8,9} and temperature sensors.^{10,11}

The choice of an appropriate material doped with a particular RE ion is an essential step for each application. For instance, the use of fluoride glasses doped with RE ions [Yb³⁺ (Ref. 8); Tm³⁺ (Ref. 9)] was important for obtaining laser cooling of solids in a process where one phonon is annihilated for each absorbed photon. Another interesting example is that by increasing the temperature of a codoped Yb³⁺-Er³⁺ silica fiber from 296 to 423 K, it was observed that a reduction of the fiber laser threshold by a factor of 4 due to the annihilation of at least one phonon for each absorbed pump photon took place.¹²

The exploitation of MP assisted processes is promising to increase the UPC efficiency of a system and these studies may lead to the operation of temperature sensors^{10,11} or effi-

cient incoherent light sources emitting from the infrared to the ultraviolet (UV). For example, a study of UPC enhanced by heating a fluoroindate glass (FIG) sample codoped with Yb³⁺ and Pr³⁺ was reported in Ref. 13. In this case it was verified that by using Yb³⁺ as a sensitizer, it is possible to enhance the UPC efficiency via a nonresonant excitation of the sensitizer in a process involving absorption of two phonons. Subsequent energy transfer to Pr³⁺ occurs followed by an excitation process in Pr³⁺, which involves one photon absorption and annihilation of two further phonons. Finally, upconverted blue light is emitted by the excited Pr³⁺ ions. The UPC intensity was shown to increase by a 20-fold factor when the sample's temperature was varied from 293 to 533 K. The choice of the sample was motivated by the large UPC efficiency of RE doped FIG as previously reported (see for instance Refs. 14–19). In fact, InF₃-based glasses have been the subject of increasing interest due to their relatively large transparency window from 0.25 to 8 μm, their ability to incorporate large RE concentrations (up to 10 mol %), their large stability, and resistance to moisture. Our previous investigations of Nd³⁺-doped FIG at room temperature have shown that this system is a good frequency upconverter from visible to UV^{17,18} and from infrared to the UV.¹⁹ Furthermore, besides the possible use of Nd³⁺-doped FIG for operation of conventional lasers,²⁰ optical amplification in the blue and in the violet region was recently demonstrated.²¹

In this article we show that UPC processes assisted by MP absorption can be highly efficient if optical transitions and thermal coupling between electronic levels are conveniently exploited. Here our studies were mainly concentrated in the investigation of a continuous wave (cw) MP assisted UPC process from 866 to 750 nm. A 40-fold enhancement of the UPC emission intensity was observed when the temperature of the sample was varied from 298 to 498 K. This result represents the largest thermally induced enhancement observed in a UPC process assisted by MP absorption.

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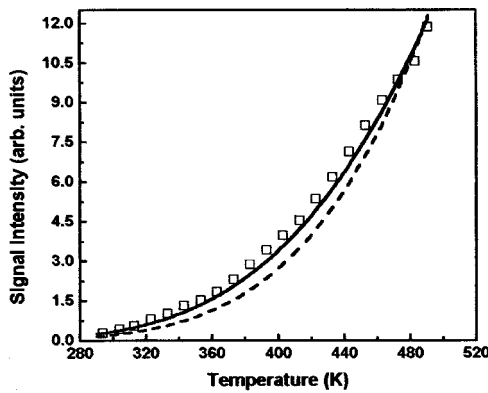


FIG. 4. Temperature dependence of the integrated UPC intensity for the emission centered at 750 nm. Pump power: 160 mW. The solid (dashed) line represents Eq. (5) with the parameters and with the effective phonon mode of 310 cm^{-1} (maximum phonon energy of 507 cm^{-1}). The error bars are smaller than the squared points.

(level 4) and following the approach described below. A rate equation system written for the population densities n_i ($i = 1, 2, 3$) assumes the form:

$$dn_1/dt = \sigma_0 \Phi n_0 - \Lambda_{12}(T)n_1 - \gamma_1(T)n_1 - \sigma_1(T)\Phi n_1, \quad (1)$$

$$dn_2/dt = \Lambda_{12}(T)n_1 - \Lambda_{23}(T)n_2 - \gamma_2(T)n_2, \quad (2)$$

$$dn_3/dt = \Lambda_{23}(T)n_2 - \gamma_3(T)n_3, \quad (3)$$

where Φ is the photon flux, σ_0 is the absorption cross section corresponding to transition ${}^4I_{9/2} \rightarrow {}^4F_{3/2}$ ($5.0 \times 10^{-20} \text{ cm}^2$), and $\sigma_1(T)$ is the phonon assisted one-photon absorption cross section between states 1 and 4, from which other transitions occur contributing to UPC emissions in the visible and UV. The absorption cross sections for excited state transitions from levels ${}^4F_{5/2}(\sigma_2(T))$ and ${}^4F_{7/2}(\sigma_3(T))$ to higher lying levels were not included in our model, since their resonant parts, calculated with basis on the Judd–Ofelt theory (JOT),^{24,25} have values that are considerably less than the resonant part of $\sigma_1(T)$, which according to the JOT is equal to $\sigma_1^0 = 1.5 \times 10^{-22} \text{ cm}^2$. The MP excitation rates are given by $\Lambda_{ij}(T) = C_{ij}^{\text{ep}} P_{ij}(T)$, where C_{ij}^{ep} is a parameter proportional to the electron–phonon coupling strength and $P_{ij}(T)$ are the phonon occupancy numbers given by²⁶

$$P_{ij}(T) = (\exp(\hbar\omega/kT) - 1)^{-q_{ij}}, \quad (4)$$

where q_{ij} is the number of effective phonons with energy $\hbar\omega$ involved in the MP excitation from level i to level j , k is the Boltzmann constant, and T is the absolute temperature of the sample. The temperature-dependent absorption cross section is given by¹³

$$\sigma_1(T) = \sigma_1^0 [\exp(\hbar\omega/kT) - 1]^{-q}, \quad (5)$$

where the exponent q accounts for the number of effective phonons participating in the absorption process. The population relaxation rates are given by $\gamma_i(T) = \gamma_i^{\text{rad}} + W_i^{\text{NR}}(T)$, with $(\gamma_i^{\text{rad}})^{-1}$ being the radiative decay time. $W_i^{\text{NR}}(T)$ is the nonradiative relaxation rate from level i due to MP relaxation processes.

From Eqs. (1)–(3) the steady-state population of the ${}^4F_{7/2}$ level can be found and it is given by

$$n_3(T) = \frac{\sigma_0 \Phi \Lambda_{12}(T) \Lambda_{23}(T) n_0}{\gamma_3(T) [\Lambda_{12}(T) + \gamma_1(T) + \sigma_1(T) \Phi] \cdot [\Lambda_{23}(T) + \gamma_2(T)]}. \quad (6)$$

The signal intensity shown in Fig. 4 is proportional to $n_3(T)$. Thus, in order to compare Eq. (6) with the data of Fig. 4 the following procedure was used. First, to obtain the temperature dependence of n_3 a reference temperature ($T_0 = 300 \text{ K}$) was chosen and $W_i^{\text{NR}}(T)$ was determined through the following expression obtained from Ref. 1:

$$W_i^{\text{NR}}(T) = W_i^{\text{NR}}(T_0) \left[\frac{1 - \exp(-\hbar\omega/kT)}{1 - \exp(-\hbar\omega/kT_0)} \right]^{-q_i}, \quad (7)$$

where q_i represents the number of effective phonons involved in the relaxation of level i to the closest low energy level. The other relaxation parameters in Eq. (6) were obtained using the measured lifetimes of states ${}^4F_{3/2}$ ($\sim 186 \mu\text{s}$), ${}^4F_{5/2}$ ($\sim 5 \mu\text{s}$), and ${}^4F_{7/2}$ ($\sim 47 \mu\text{s}$) at room temperature,²³ as well as their nonradiative emission rates, $W_i^{\text{NR}}(T_0)$, determined through the energy-gap law²⁷ as 0.5, 1×10^8 , and 1.5×10^8 Hz, respectively.

The comparison of Eq. (6) to the experimental results shown in Fig. 4 was made and the best agreement is observed when EPMs are assumed to participate in all MP processes, as proposed in Refs. 1–4. The parameters obtained from the fitting were $q = 1$, $q_{12} = q_{23} = 3$, and $\omega = 310 \text{ cm}^{-1}$. Also shown in Fig. 4 is a curve (dashed line) obtained from Eq. (6) for $\omega = 507 \text{ cm}^{-1}$. We recall that the energy of the most energetic phonons in the FIG matrix is $\sim 507 \text{ cm}^{-1}$, as determined by Raman scattering and infrared absorption experiments.²⁸ The mismatch of the dashed line with the experimental points obviates that the most energetic phonons do not dominate the MP absorption processes. In fact, several phonon modes contribute in a way that is determined by the phonon distribution density of states (PDDS) and the description in terms of EPM represents a kind of statistical average, which takes into account the characteristics of the PDDS. The value of $\omega = 310 \text{ cm}^{-1}$ obtained from Eq. (6) corresponds to the EPM frequency of the glassy matrix. A comparison of this result with the result of Ref. 2 for ZBLAN glass (phonon cutoff frequency: $\sim 580 \text{ cm}^{-1}$, EPM frequency: 325 cm^{-1}) indicates a similar energy dependence of the PDDS in both materials.

IV. CONCLUSIONS

The present results, together with the previous ones reported in Refs. 12 and 13, provide a clear indication that the exploitation of multiphonon processes may increase the efficiency of rare-earth doped systems for particular applications. While in the case of $\text{Pr}^{3+}/\text{Yb}^{3+}$ codoped fluorindate glass¹³ a 20-fold upconversion emission enhancement was obtained through thermal effects, in the present work we demonstrated a 40-fold enhancement of cw upconverted light obtained when MP absorption due to thermally coupled elec-

tronic levels was exploited in an appropriate excitation scheme. Here, the resonant absorption of phonons among electronic energy levels is responsible for the large enhancement observed. As it was already demonstrated for the $\text{Er}^{3+}/\text{Yb}^{3+}$ system,¹² further application of these ideas may improve the performance of rare-earth doped upconversion lasers reducing their pumping threshold and increasing their output intensity. Of course in all cases one must work in temperatures far below the onset of crystallization of the glass.²⁹

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