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Upconversion processes in Nd^{3+}-doped fluoroarsenate glasses

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Abstract

In this work we have studied the infrared to visible upconversion luminescence of Nd^{3+}-doped fluoroarsenate glasses with different neodymium concentrations (0.1, 0.5, 2, 3, 4, and 5 mol%) under continuous wave and pulsed laser excitation. Green, orange, and red emissions are observed with excitation at 802 and 874 nm within the $^4F_{5/2}$ and $^4F_{3/2}$ levels. In addition, a weak blue emission appears under continuous wave (cw) laser excitation which under pulsed laser excitation only occurs for the most concentrated sample at 77 K. The green, orange, and red emissions can be attributed to transitions from the $^4G_{7/2}$ excited state. The pump power dependencies of these upconverted emissions together with the shape of the upconverted excitation spectra which are similar to the one-photon absorption spectrum and the temporal behavior of the decays, indicate that an ETU process seems to be responsible for the observed visible luminescence, though other possible mechanisms cannot be disregarded.

Keywords: Optical properties; Luminescence; Non-linear optics; Time-resolved optical spectroscopies; Amorphous materials

1. Introduction

Frequency upconversion of infrared light to visible and ultraviolet light in rare-earth (RE) doped solids has attracted much interest in recent years because of its large number of potential applications [1]. One of these is the operation of short-wavelength upconversion lasers pumped with commercially available lasers. From a fundamental point of view, the study of frequency upconversion processes is also important to understand the mechanisms of interaction between the RE ions in different hosts. In addition, it is a very useful tool for studying the higher energy states of the optically active centers in solids [2].

The upconverted emissions are in general attained by different mechanisms: (i) sequential absorption of pump photons in one ion involving excited state absorption (ESA), (ii) photon avalanche, and (iii) energy transfer upconversion (ETU). In two-step excitation, a single photon is absorbed, followed by relaxation to an excited metastable energy level. This is followed by either radiative or non-radiative relaxation. ETU is a process in which two nearby excited ions interact simultaneously, causing one of the pair to be excited to an even higher level while the other one relaxes to a lower state. These two processes can coexist, thus contributing to the population of higher excited states.

This paper deals with upconversion processes in Nd^{3+}-doped fluoroarsenate glasses. Recently new glasses were discovered in the $Na_4As_2O_7$, BaF_2, YF_3 system which are parent materials with fluorophosphate glasses of the $NaPO_3$, BaF_2, YF_3 system. Whereas optical properties of some active ions have already been investigated in fluorophosphate glasses [3–5], the behavior of rare-earth ions in fluoroarsenate glasses is practically unknown. In a previous work [6], we have investigated the optical properties of Nd^{3+} ions in these glasses by using time-resolved laser spectroscopy. In this work we report a study of conversion

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of infrared excitation light into blue, green, orange, and red emission light.

2. Experimental techniques

The raw materials are commercial BaF_2, Y_2O_3, and $Na_2HAsO_4 \cdot 7H_2O$. The yttrium and neodymium oxides are fluorinated by a classical reaction with ammonium bifluoride NH_4F,HF at 300°C in an open platinum crucible. The arsenate compound is obtained by dehydration of $Na_2HAsO_4 \cdot 7H_2O$ in a vitreous carbon crucible heated at 300°C for 3 h under nitrogen flow. A thermal gravimetric analysis confirms the dehydration. After this stage, the arsenate compound is introduced into a dry glove box where the various compounds are weighed.

The use of a vitreous carbon crucible for glass melting is not possible because reduction of As^{V} into As^{III}, and even As^{0}, occurs. Thus, melting of fluoroarsenate glasses must take place in a platinum crucible heated at 900°C for 15 min in air. The risk of reaction between platinum and arsenic is real, but only in reducing conditions, which is not the case in the present experiment. Then, the melt is cast into a brass mould, either at room temperature for vitreous domain investigations, or preheated at a temperature close to the glass transition (T_g) to obtain bulk pieces. Finally, the samples are annealed at T_g and cooled down to room temperature before being cut and polished for optical measurements. Neodymium doped glasses are prepared by substituting NdF_3 for YF_3 in the initial batch. Glasses containing 0.1, 0.5, 2, 3, 4, and 5 mol% NdF_3 were synthesized.

The temperature of the samples was varied between 4.2 and 300 K in a continuous flow cryostat. Conventional absorption spectra were performed with a Cary 5 spectrophotometer. The emission measurements were made by using a Ti-Sapphire ring laser (0.4-cm^{-1} linewidth) in the 780–920-nm range. The fluorescence was analyzed with a 0.22-m SPEX monochromator, and the signal was detected by a Hamamatsu R928 photomultiplier and finally amplified by a standard lock-in technique.

Lifetime measurements were performed by exciting the samples with a a Ti-Sapphire laser, pumped by a pulsed frequency doubled Nd:YAG laser (9-ns pulse width), and detecting the emission with a Hamamatsu R928 photomultiplier. Data were processed by a boxcar integrator.

3. Results

Visible upconversion has been observed at room temperature and low temperature in this glass doped with 0.1, 0.5, 2, 3, 4, and 5 mol% of Nd^{3+} under cw and pulsed IR laser excitation. The steady-state emission and excitation spectra were obtained by exciting the samples in the 780–920-nm spectral range by using a cw Ti-Sapphire ring laser (0.4-cm^{-1} linewidth). Cut-off filters were used to remove both the pumping radiation and the infrared luminescence from the samples. As an example, Fig. 1 shows the upconversion fluorescence in the 400–750-nm region at 295 and 77 K for the glass doped with 4 mol% (3.74×10^{20} ions/cm^3) obtained by exciting at 802 nm (cw) in resonance with the $^4I_{9/2} \rightarrow {}^4F_{5/2}$ transition. The spectra show three main bands located at 535, 596 and 663 nm, and in addition, there are also weak blue emissions at 417 and 451 nm. As shown in Fig. 1(a), at room temperature these bands present a high energy component which disappears at 77 K. These features demonstrate that the transitions originate from two closely-spaced levels, the higher-energy level being populated through thermalization processes. Similar spectra are obtained by pumping at 874 nm in resonance with the $^4F_{3/2}$ level.

The excitation spectrum of the visible emissions was investigated in the 780–920-nm range (by using the Ti-Sapphire tunability). Similar excitation spectra were ob-

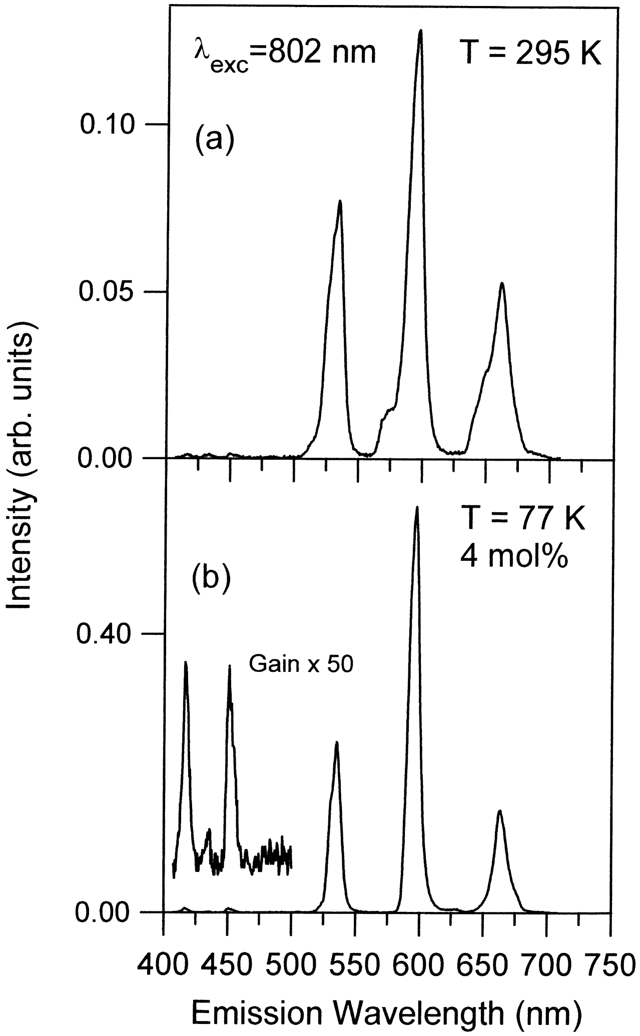

Fig. 1. Upconversion emission spectra for the sample doped with 4 mol% of Nd^{3+} obtained by exciting the sample at 802 nm at 295 and 77 K.

tained by collecting the luminescence at 535, 596, and 663 nm. As an example, the room temperature excitation spectrum of the upconverted emission at 596 nm is presented in Fig. 2 together with the one-photon absorption spectrum in this spectral range (in the inset) for comparison. As can be observed the excitation spectrum shows the peaks corresponding to the $^4I_{9/2}\rightarrow{}^4F_{5/2},{}^4F_{3/2}$ absorption bands, with no significant differences with the absorption spectrum.

The upconversion emission intensity (I_{em}) depends on the incident pump power (P_{pump}) according to the following equation:

$$I_{em}\propto(P_{pump})^n, \qquad (1)$$

where n is the number of photons involved in the pumping mechanism. In our case, the dependence of the intensity of the three visible lines (535, 596 and 663 nm) on the pump power gives a value of 1.6±0.05 for n, which indicates a two-photon upconversion process. Fig. 3 shows a logarithmic plot of the integrated emission intensity of the upconverted fluorescence at 596 nm as a function of the pump laser intensity. The same behavior was observed by exciting at the $^4I_{9/2}\rightarrow{}^4F_{5/2}$ transition.

The temporal evolution of the upconverted emissions was obtained by exciting the samples at 874 nm in resonance with the $^4F_{3/2}$ level with a Ti-Sapphire laser pumped by a doubled pulsed Nd:YAG laser. All the experimental decays present a rapid initial decay followed by a longer non-exponential decay. As an example, the logarithmic plot of the experimental decay of the 596-nm emission for the samples doped with 2, 4, and 5 mol% obtained at 77 K is shown in Fig. 4. Similar temporal evolutions are observed for the green and red emissions. The decay curves of the upconverted emission are not single exponentials and the lifetimes are much longer than that of the $^4G_{7/2}$ state under direct excitation (the long time upconverted luminescence decays with an average lifetime ranging between 89 and 53 μs as concentration increases from 2 to 5 mol%). The lifetime values of the $^4G_{7/2}$ and $^4G_{5/2}$ levels obtained under direct excitation are too short to be measured with our equipment. These lifetimes have been measured to be less than 10 ns in fluoride crystals [7]. The same behavior was observed at room temperature. The upconverted emission for the samples doped with 0.1 and 0.5 mol% is too weak for an accurate measurement of the decays.

Under pulsed excitation in resonance with the $^4F_{3/2}$ level, the weak blue emissions are only observed at 77 K for the sample doped with 5 mol%.

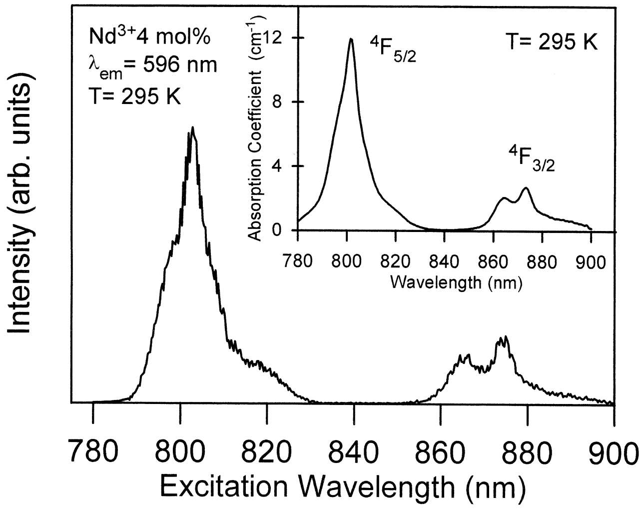

Fig. 2. Excitation spectrum of the 596-nm line for the sample doped with 4 mol% of Nd^{3+}, corrected for the spectral variation of the laser intensity. Measurements correspond to 295 K.

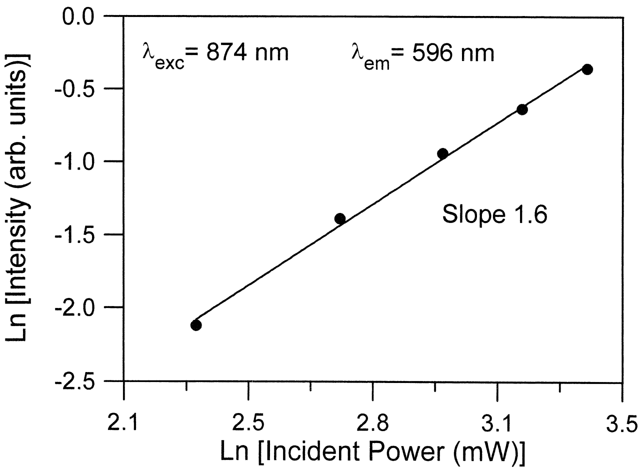

Fig. 3. Logarithmic plot of the integrated intensity of the upconverted orange emission (596 nm) as a function of the pump laser intensity. Data correspond to 77 K and 4 mol% of Nd^{3+}.

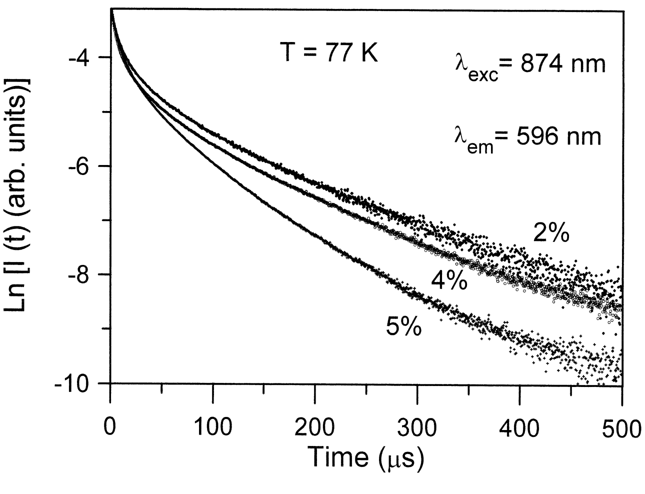

Fig. 4. Logarithmic plot of the experimental decay curve of the 596-nm emission obtained under excitation in resonance with the $^4F_{3/2}$ level for the samples doped with 2, 4 and 5 mol% of Nd^{3+}. Data correspond to 77 K.

3.1. Discussion

In order to identify each upconverted emission band, we have used the low temperature emission spectrum given in Fig. 1 and the energy level diagram of Nd^{3+} in this glass shown in Fig. 5. The three main bands observed in the emission spectrum have been reported in other Nd-doped materials, and attributed to transitions from the $^4G_{7/2}$ and $^4G_{5/2}$ levels [8–10]. An analysis of the energy level diagram and the upconverted emission spectrum suggests that these bands can be originated from the $^4G_{7/2}$ level. In addition, decay measurements yielded similar lifetimes for these emissions, which show they originate from the same level or group of levels. Thus, the possibility of emission from ($^4G_{5/2}$, $^2G_{7/2}$), the energy of which is too low for allowing green emission at 535 nm, can be discarded. So the bands can be attributed to radiative transitions $^4G_{7/2}\rightarrow{}^4I_{9/2}$ (535 nm), $^4G_{7/2}\rightarrow{}^4I_{11/2}$ (596 nm) and $^4G_{7/2}\rightarrow{}^4I_{13/2}$ (663 nm).

The excited $^4G_{7/2}$ state can be populated by two possible mechanisms, excited state absorption (ESA), and/or energy transfer (ETU) (Fig. 5). In the first process (ESA), one Nd^{3+} ion, initially in the ground state, absorbs one IR photon and is excited to the $^4F_{5/2}$ state from where the $^4F_{3/2}$ state is populated by fast non-radiative relaxation. This is followed by absorption of a second IR photon from the $^4F_{3/2}$ excited state to the $^2D_{5/2}$ state, from which it can decay non-radiatively to the $^4G_{7/2}$ state. In the second process (ETU), when two Nd^{3+} ions are excited to the $^4F_{3/2}$ state, a transfer occurs by which one ion loses energy and goes to the $^4I_{13/2}$ state while the other one gains energy and goes to the $^4G_{7/2}$ state. These processes can coexist, contributing to the excitation into higher levels. As can be observed the excitation spectrum shows the peaks corresponding to the $^4I_{9/2}\rightarrow{}^4F_{5/2},{}^4F_{3/2}$ absorption bands, with no significant differences with the absorption spectrum. This is in contrast to other Nd^{3+}-doped materials [11] in which differences were observed between one-photon absorption and upconversion excitation spectra, indicating that resonant absorption of the pump radiation took place at particular wavelengths. Consequently, peaks in the one-photon absorption spectrum may not appear in the excitation spectrum of the upconverted luminescence. In our case, the excitation spectra of the upconverted luminescence indicates that resonant absorption of pump radiation is not produced from the metastable $^4F_{3/2}$ state. This behavior suggests that an ETU process seems to be more likely for the observed visible luminescence, though other possible mechanisms cannot be disregarded. In addition, the intensity of the upconverted emission shows a quadratic dependence on Nd^{3+} concentration, whereas in the case of excited state absorption, the upconverted fluorescence should have a linear dependence on concentration.

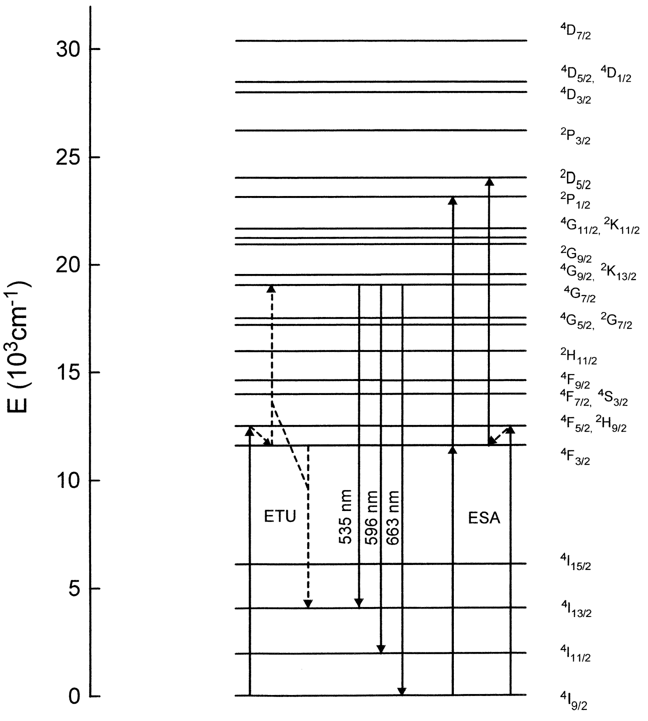

Fig. 5. Energy level diagram of Nd^{3+} ions in fluoroarsenate glasses obtained from the room temperature absorption spectrum. Possible upconversion mechanisms and assignments of the main upconverted emission bands observed with 802- and 874-nm excitations are also indicated.

A further support to this hypothesis is given by the results obtained under IR pulsed laser excitation. Lifetime measurements provide an invaluable tool in discerning which is the operative mechanism. The radiative ESA process occurs within the excitation pulse width, leading to an immediate decay of the upconversion luminescence after excitation. Upconversion by energy transfer leads to a decay curve for the anti-Stokes emission which shows a rise time after the laser pulse, followed by a decay and a lifetime longer than the one of level $^4G_{7/2}$ under direct excitation. This distinction is possible when the pulse width is much shorter than the time constant of the relevant energy transfer step. As we mentioned in Section 3, the temporal evolution of the decays of the visible luminescence shows a rapid initial decay followed by a longer non-exponential decay with an average lifetime much longer than the lifetime of $^4G_{7/2}$ obtained under direct excitation. This behavior has also been observed in Nd:YLF crystal and attributed to a combination of static ETU and migration assisted ETU. The rapid initial stage observed in Fig. 4 is interpreted as a static ETU, whereas the long-term dynamics is attributed to migration assisted ETU [7]. As a matter of fact, energy migration on the $^4F_{3/2}$ manifold has been observed in a previous work in this glass for concentrations higher than 1 mol% [6].

The observed weak blue emission corresponds to levels with higher energies ($^4D_{5/2}$, $^4D_{3/2}$ or $^2P_{3/2}$) than that of two infrared photons (see the energy level diagram in Fig.

5); therefore higher order ETU processes that involve at least three $^4F_{3/2}$ excitations are required. These processes have not been considered in detail in this paper.

4. Conclusions

The study of upconversion processes has shown that infrared excitation at 802 nm in level $^4F_{5/2}$ or at 874 nm in level $^4F_{3/2}$ lead to green, orange, and red emissions from the $^4G_{7/2}$ level. Under cw excitation in $^4F_{5/2}$ or $^4F_{3/2}$ multiplets additional blue emissions are also observed. The temporal dependence of the decays from the upconverted green, orange and red emissions, together with the characteristics of the excitation spectra suggest that an energy transfer upconversion is the dominant mechanism for such emissions in this glass.

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