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# Optical spectroscopy and upconversion luminescence in Nd<sup>3+</sup> doped Ga<sub>10</sub>Ge<sub>25</sub>S<sub>65</sub> glass

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Optical properties of a neodymium (Nd<sup>3+</sup>) doped glass having composition based on the (Ga<sub>2</sub>S<sub>3</sub>)–(GeS<sub>2</sub>) system are reported. Transition probabilities, radiative lifetimes, and branching ratios related to Nd<sup>3+</sup> levels were determined. Frequency upconversion (UC) luminescence due to nonresonant excitation at 1064 nm was observed at ≈535, ≈600, and ≈670 nm. The dependence of the UC intensity on the laser intensity and on the Nd<sup>3+</sup> concentration as well as the dynamics of the luminescence process were studied. The results indicate that two-photon absorption by isolated Nd<sup>3+</sup> ions and energy transfer among pairs of Nd<sup>3+</sup> ions contribute to the UC luminescence. © 2009 American Institute of Physics. [doi:10.1063/1.3259439]

## I. INTRODUCTION

Since the development of the first rare-earth (RE) ion laser<sup>1</sup> many crystalline and glassy systems have been investigated due to the influence of host materials on the lasing properties of the triply ionized RE ion. In particular, special glasses are being increasingly studied due to some peculiarities such as their large optical homogeneity, wide transparency from the visible to the infrared region, and simple fabrication procedures for obtaining good optical quality samples. The systems of main interest are those having low energy phonons because the quantum efficiency for RE ions luminescence is enhanced, allowing the development of more efficient lasers, optical amplifiers, and upconverters.<sup>2,3</sup> Other important characteristics are the high mechanical strength and high chemical resistance of host glasses.<sup>4–12</sup>

Materials that present ideal characteristics for photonics are the chalcogenide glasses (based on S, Se, and Te). They exhibit high refractive index, low cutoff phonon energy, and high stability against moisture and devitrification. The high linear refractive index contributes to the increase in the local field on the hosted RE ion and therefore large radiative transition probabilities may be observed. In particular, glasses based on the (Ga<sub>2</sub>S<sub>3</sub>)–(GeS<sub>2</sub>) pseudobinary system have low cutoff phonon energies (300–400 cm<sup>-1</sup>), show high RE ion solubility, and present large optical band gap. One important example is the composition Ga<sub>10</sub>Ge<sub>25</sub>S<sub>65</sub> (GGs) due to its good chemical durability, large thermal stability, high refractive index (~2.2), and broad transmission window in the 0.5–12 μm region.<sup>13–15</sup>

The aim of the present work is the study of the linear optical characteristics and the infrared-to-visible frequency

upconversion (UC) process in GGS glass doped with neodymium (Nd<sup>3+</sup>) ions. Transition probabilities, radiative lifetimes, and branching ratios associated with the Nd<sup>3+</sup> levels were determined by linear absorption spectroscopy and using the Judd–Ofelt (JO) theory.<sup>16,17</sup> UC experiments were made by exciting the samples with a laser operating at 1064 nm (out of resonance with transitions starting from the ground state). The mechanisms leading to the UC emissions in the green, orange, and red regions as well as the dynamics of the process are investigated.

## II. EXPERIMENTAL DETAILS

The samples were prepared by the melting-quenching method. Three compositions were prepared for the present study: (Ga<sub>10</sub>Ge<sub>25</sub>S<sub>65</sub>)<sub>99.95</sub>–Nd<sub>0.05</sub> (sample A), (Ga<sub>10</sub>Ge<sub>25</sub>S<sub>65</sub>)<sub>99.9</sub>–Nd<sub>0.1</sub> (sample B), and (Ga<sub>10</sub>Ge<sub>25</sub>S<sub>65</sub>)<sub>99.75</sub>–Nd<sub>0.25</sub> (sample C). High purity polycrystalline germanium (5N), gallium (5N), sulfur (5N), and Nd (4N) were used for the synthesis. The elements were weighted and introduced into a silica tube having 10 mm inner diameter; vacuum of about 10<sup>-4</sup> mbar was achieved in the tube before being sealed. The ampoule was then introduced in a rocking tubular furnace and slowly heated up to 900 °C to allow thorough reaction of the starting compounds and to avoid explosion due to the high vapor pressure of sulfides. The batch was homogenized for 8 h at this temperature. Then, the rocking was stopped and the ampoule kept in the vertical position for 20 min to reduce the formation of bubbles in the glass. The ampoule was taken off the furnace, quenched in water at room temperature, and annealed at 370 °C for 3 h to reduce the internal stress caused by the quenching. Then the silica ampoule was opened; the obtained glass rod with ~4 cm length and 10 mm diameter was removed and cut into slices of 2 mm thickness. Finally,

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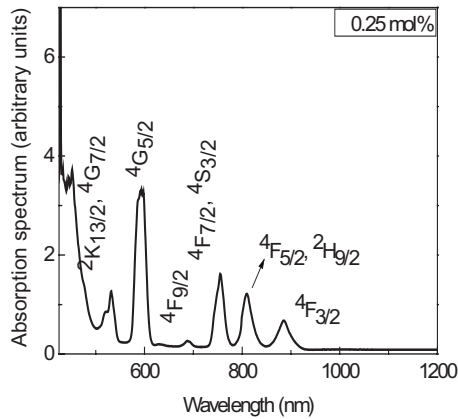


FIG. 1. Absorption spectrum of the  $(\text{Ga}_{10}\text{Ge}_{25}\text{S}_{65})_{99.75}\text{-Nd}_{0.25}$  sample.

the samples were polished to obtain two parallel and two perpendicular polished faces for the optical measurements. Samples with dimensions of  $\approx 10$  mm diameter and 2.2 mm thickness were used in the optical experiments. A more detailed description of the fabrication procedure is presented in Ref. 15.

The optical absorption experiments were made using a double-beam spectrophotometer. For the luminescence experiments a neodymium doped yttrium aluminum garnet laser operating at 1064 nm with pulses of  $\approx 7$  ns at 5 Hz was used. The linearly polarized laser beam was focused onto the sample with a 5 cm focal length lens, and the luminescence was collected in a direction perpendicular to the incident beam. The maximum intensity incident on the samples was  $\approx 100$  MW/cm<sup>2</sup>. The luminescence was analyzed by a 0.5 m spectrophotometer (resolution of 0.5 nm) attached to a photomultiplier. The signals were recorded using a digital oscilloscope connected to a computer. All measurements were made at room temperature.

### III. RESULTS AND DISCUSSION

#### A. Optical characteristics

Figure 1 shows the absorption spectrum of the Nd<sup>3+</sup> (0.25 mol %) doped chalcogenide glass sample. Absorption bands were observed at  $\approx 884$ ,  $\approx 806$ ,  $\approx 795$ ,  $\approx 750$ ,  $\approx 682$ ,  $\approx 594$ , and  $\approx 532$  nm corresponding to the transitions from the ground state ( $4I_{9/2}$ ) to the excited states  $4F_{3/2}$ ,  $4F_{5/2}$ ,  $2H_{9/2}$ ,  $4F_{7/2}$ ,  $4F_{9/2}$ ,  $4F_{5/2}$ , and  $4G_{7/2}$ , respectively. The band positions are in agreement with the values observed in the other Nd<sup>3+</sup> doped glasses.<sup>18</sup> All transitions are inhomogeneously broadened due to site-to-site variations in the crystal field. The spectra of the other samples are similar but the intensity of the absorption bands depends linearly on the concentration of the Nd<sup>3+</sup> ions.

A simplified energy level scheme of the Nd<sup>3+</sup> electronic levels is shown in Fig. 2. Oscillator strengths for different transitions on the basis of the observed absorption spectrum were determined using the JO theory. The calculated JO parameters were used to determine physical quantities such as transition probabilities, branching ratios, and radiative lifetimes associated with various Nd<sup>3+</sup> levels.

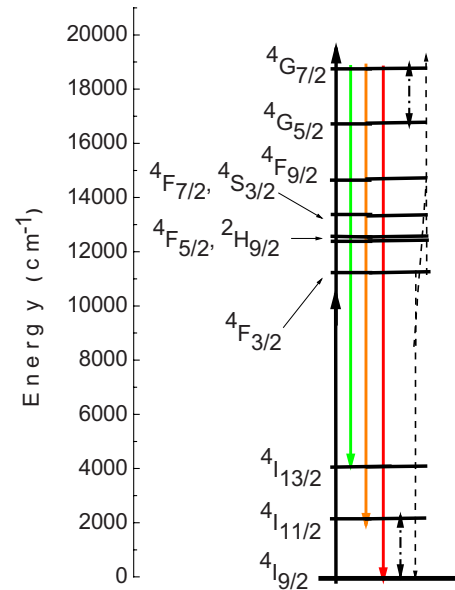


FIG. 2. (Color online) Simplified energy level scheme for the Nd<sup>3+</sup> ions. Solid lines represent radiative transitions. Dashed lines correspond to cross-relaxation involving ET processes.

The experimental oscillator strength is determined by the expression  $F_{\text{expt}} = mc^2 n^2 / \pi e^2 N \chi \int k(\nu) d\nu$ , where  $m$  is the electron mass,  $c$  is the speed of light in vacuum,  $e$  is the electron charge,  $n$  is the index of refraction,  $\chi = (n^2 + 2)^2 / 9n$  is the local field correction factor for electric-dipole transitions,  $N$  is the concentration of Nd<sup>3+</sup> ions, and  $\int k(\nu) d\nu$  is the integrated absorption coefficient.<sup>18</sup>

According to the JO theory, the oscillator strength for an electric-dipole allowed transition between the manifolds ( $S$ ,  $L$ ,  $J$ ) and ( $S'$ ,  $L'$ ,  $J'$ ) is given by

$$F_{\text{theor}} = \frac{8\pi^2 m \bar{\nu} \chi}{3h(2J+1)} \sum_{\lambda=2,4,6} \Omega_{\lambda} \langle (S, L, J) || U^{\lambda} || (S', L', J') \rangle^2,$$

where  $\bar{\nu}$  is the mean frequency between the two manifolds (in cm<sup>-1</sup>),  $J$  is the total angular momentum,  $h$  is Planck's constant, and  $\langle (S, L, J) || U^{\lambda} || (S', L', J') \rangle$  is the reduced dipole matrix element that is independent of the host environment.  $\Omega_{\lambda}$  ( $\lambda=2,3,4$ ) are the JO intensity parameters that are sensitive to the host environment, to the separation between the energy levels involved, and to the closest electronic configuration having opposite parity.

The spontaneous emission probability between the manifolds ( $S$ ,  $L$ ,  $J$ ) and ( $S'$ ,  $L'$ ,  $J'$ ) is given by  $A_{JJ'} = [64\pi^4 \chi / 3h(2J+1)\lambda^3] S_{\text{ED}}$ , where  $S_{\text{ED}}$  is the electric-dipole strength that is determined using the expression

$$S_{\text{ED}}[(S, L, J); (S', L', J')] = e^2 \sum_{\lambda=2,4,6} \Omega_{\lambda} \langle (S, L, J) || U^{\lambda} || (S', L', J') \rangle^2.$$

The magnetic-dipole strength assumes values that are two orders of magnitude smaller than  $S_{\text{ED}}$  and was neglected in the present calculations.

The  $\Omega_{\lambda}$  parameters were calculated using the experimentally observed oscillator strengths for the different transitions. The obtained values were  $\Omega_2 = 21.5 \times 10^{-21}$  cm<sup>2</sup>,  $\Omega_4$

TABLE I. Values of the theoretical and experimental oscillator strengths for Nd<sup>3+</sup> ions in the GGS glass.

Transitions	$\Delta E$ (cm <sup>-1</sup> )	$F_{\text{expt}}$ ( $\times 10^{-6}$ )	$F_{\text{theor}}$ ( $\times 10^{-6}$ )
<sup>4</sup> I <sub>9/2</sub> → <sup>4</sup> F <sub>3/2</sub>	11 315	5.86	4.83
<sup>4</sup> I <sub>9/2</sub> → <sup>4</sup> F <sub>5/2</sub> ; <sup>2</sup> H <sub>9/2</sub>	12 576	12.58	15.56
<sup>4</sup> I <sub>9/2</sub> → <sup>4</sup> F <sub>7/2</sub>	13 331	1.50	1.06
<sup>4</sup> I <sub>9/2</sub> → <sup>4</sup> F <sub>9/2</sub>	14 663	5.10	4.78
<sup>4</sup> I <sub>9/2</sub> → <sup>4</sup> G <sub>5/2</sub>	16 832	4.38	10.10
<sup>4</sup> I <sub>9/2</sub> → <sup>4</sup> G <sub>7/2</sub> ; <sup>2</sup> K <sub>13/2</sub>	18 797	3.64	3.30

= 35.6 × 10<sup>-21</sup> cm<sup>2</sup>, and  $\Omega_6 = 59.2 \times 10^{-21}$  cm<sup>2</sup> with a root-mean-square deviation  $\delta_{\text{rms}} = \pm 3.79 \times 10^{-6}$ . The theoretical values determined for the oscillator strengths using the values obtained for  $\Omega_\lambda$  ( $\lambda = 2, 4, 6$ ) are in reasonable agreement with the experimental results, as shown in Table I.

The radiative lifetimes of the excited states were calculated by  $\tau_R = (\sum_{J'} A_{JJ'})^{-1}$ , and the branching ratios for emission from level  $J$  to  $J'$  were calculated by  $\beta_{JJ'} = A_{JJ'} \tau_R$ . The calculated values are given in Table II.

## B. Infrared-to-visible frequency UC

The UC spectrum observed under infrared excitation at 1064 nm is shown in Fig. 3. Three luminescence bands are observed at  $\approx 535$ ,  $\approx 600$ , and  $\approx 670$  nm corresponding to transitions <sup>4</sup>G<sub>7/2</sub> → <sup>4</sup>I<sub>9/2</sub>, [<sup>4</sup>G<sub>7/2</sub> → <sup>4</sup>I<sub>11/2</sub>; <sup>4</sup>G<sub>5/2</sub> → <sup>4</sup>I<sub>9/2</sub>], and [<sup>4</sup>G<sub>7/2</sub> → <sup>4</sup>I<sub>13/2</sub>; <sup>4</sup>G<sub>5/2</sub> → <sup>4</sup>I<sub>11/2</sub>], respectively.

To determine the number of photons and ions participating in the UC process, the UC intensity was measured as a function of the laser power and as a function of the Nd<sup>3+</sup> concentration. In Fig. 4(a) a quadratic dependence of the UC intensity on the pump power can be observed, indicating that two laser photons contribute to the emission of each UC photon. On the other hand, the log-log plot of the UC intensity as a function of the Nd<sup>3+</sup> concentration, shown in Fig. 4(b), presents a slope that varies from 1.59 to 1.75. This shows that more than one Nd<sup>3+</sup> ion is involved in the excitation process of the UC emissions.

To obtain more information about the UC process the temporal evolution of the <sup>4</sup>G<sub>7/2</sub> → <sup>4</sup>I<sub>9/2</sub> transition peaking at  $\approx 535$  nm was studied. The luminescence signal shows decay times of  $53.4 \pm 0.4$ ,  $32.6 \pm 0.3$ , and  $18.0 \pm 0.1$   $\mu\text{s}$  for Nd<sup>3+</sup> concentrations of 0.05, 0.10, and 0.25 mol %, respectively, as shown in Figs. 5(a)–5(c). Since the radiative lifetime  $\tau_R$  of the <sup>4</sup>G<sub>7/2</sub> level is 81.23  $\mu\text{s}$  (Table II) the measured decay times indicate a strong interaction among the Nd<sup>3+</sup> ions. We note that the energy difference [ $E(^4\text{G}_{7/2}) - E(^4\text{G}_{5/2})$ ] has about the same value as [ $E(^4\text{I}_{11/2}) - E(^4\text{I}_{9/2})$ ]. Then the decrease in the lifetime of the <sup>4</sup>G<sub>7/2</sub> level is attributed to the cross-relaxation process (<sup>4</sup>G<sub>7/2</sub>; <sup>4</sup>I<sub>9/2</sub>) → (<sup>4</sup>G<sub>5/2</sub>; <sup>4</sup>I<sub>11/2</sub>). The actual lifetime is related to the cross-relaxation rate by  $\tau = \tau_R / (1 + W_{\text{CR}} \tau_R)$  with  $W_{\text{CR}}$  being equal to  $6.4 \times 10^3$  s<sup>-1</sup> (sample A),  $18 \times 10^3$  s<sup>-1</sup> (sample B), and  $43 \times 10^3$  s<sup>-1</sup> (sample C).

In order to understand the origin of the UC luminescence we analyze three possible excitation pathways. We first note that the laser frequency  $\omega_L$  is off resonance for a Nd<sup>3+</sup> tran-

TABLE II. Energy difference ( $\Delta E$ ), radiative transition probability ( $A_{JJ'}$ ), and branching ratio ( $\beta_{JJ'}$ ) between multiplets and radiative lifetime ( $\tau_R$ ) for each state of Nd<sup>3+</sup> ions.

Transition	$\Delta E$ (cm <sup>-1</sup> )	$A_{JJ'}$ (s <sup>-1</sup> )	$\beta_{JJ'}$	$\tau_R$ ( $\mu\text{s}$ )
<sup>4</sup> I <sub>11/2</sub> → <sup>4</sup> I <sub>9/2</sub>	2 110	43.43	1.0000	23 025.5
<sup>4</sup> I <sub>13/2</sub> → <sup>4</sup> I <sub>11/2</sub>	1 954	11.08	0.099	9 022.83
<sup>4</sup> I <sub>13/2</sub> → <sup>4</sup> I <sub>9/2</sub>	4 064	99.75	0.900	
<sup>4</sup> F <sub>3/2</sub> → <sup>4</sup> I <sub>13/2</sub>	7 251	822.89	0.146	177.51
<sup>4</sup> F <sub>3/2</sub> → <sup>4</sup> I <sub>11/2</sub>	9 205	1 683.54	0.299	
<sup>4</sup> F <sub>3/2</sub> → <sup>4</sup> I <sub>9/2</sub>	11 315	3 126.91	0.555	
<sup>4</sup> F <sub>5/2</sub> → <sup>4</sup> F <sub>3/2</sub>	1 095	5.26	0.0003	69.54
<sup>4</sup> F <sub>5/2</sub> → <sup>4</sup> I <sub>13/2</sub>	8 346	2 330.91	0.162	
<sup>4</sup> F <sub>5/2</sub> → <sup>4</sup> I <sub>11/2</sub>	10 300	4 381.28	0.305	
<sup>4</sup> F <sub>5/2</sub> → <sup>4</sup> I <sub>9/2</sub>	12 410	7 663.11	0.533	
<sup>2</sup> H <sub>9/2</sub> → <sup>4</sup> F <sub>5/2</sub>	166	0.0025	0.0000	480.22
<sup>2</sup> H <sub>9/2</sub> → <sup>4</sup> F <sub>3/2</sub>	1 261	1.11	0.0005	
<sup>2</sup> H <sub>9/2</sub> → <sup>4</sup> I <sub>13/2</sub>	8 512	342.09	0.164	
<sup>2</sup> H <sub>9/2</sub> → <sup>4</sup> I <sub>11/2</sub>	10 466	635.91	0.305	
<sup>2</sup> H <sub>9/2</sub> → <sup>4</sup> I <sub>9/2</sub>	12 576	1 103.26	0.529	
<sup>4</sup> F <sub>7/2</sub> → <sup>2</sup> H <sub>9/2</sub>	754	0.57	0.00009	163.18
<sup>4</sup> F <sub>7/2</sub> → <sup>4</sup> F <sub>5/2</sub>	920	1.04	0.00016	
<sup>4</sup> F <sub>7/2</sub> → <sup>4</sup> F <sub>3/2</sub>	2 015	10.93	0.0018	
<sup>4</sup> F <sub>7/2</sub> → <sup>4</sup> I <sub>13/2</sub>	9 266	1 063.11	0.173	
<sup>4</sup> F <sub>7/2</sub> → <sup>4</sup> I <sub>11/2</sub>	11 220	1 887.48	0.308	
<sup>4</sup> F <sub>7/2</sub> → <sup>4</sup> I <sub>9/2</sub>	13 330	3 165.15	0.516	
<sup>4</sup> F <sub>9/2</sub> → <sup>2</sup> H <sub>9/2</sub>	1 333	0.54	0.0003	691.65
<sup>4</sup> F <sub>9/2</sub> → <sup>4</sup> F <sub>7/2</sub>	2 087	2.07	0.0014	
<sup>4</sup> F <sub>9/2</sub> → <sup>4</sup> F <sub>5/2</sub>	2 253	2.59	0.0018	
<sup>4</sup> F <sub>9/2</sub> → <sup>4</sup> F <sub>3/2</sub>	3 348	8.50	0.0058	
<sup>4</sup> F <sub>9/2</sub> → <sup>4</sup> I <sub>13/2</sub>	10 599	269.75	0.186	
<sup>4</sup> F <sub>9/2</sub> → <sup>4</sup> I <sub>11/2</sub>	12 553	448.14	0.309	
<sup>4</sup> F <sub>9/2</sub> → <sup>4</sup> I <sub>9/2</sub>	14 663	714.23	0.493	
<sup>4</sup> G <sub>5/2</sub> → <sup>2</sup> H <sub>9/2</sub>	2 169	46.51	0.0009	21.05
<sup>4</sup> G <sub>5/2</sub> → <sup>4</sup> F <sub>9/2</sub>	3 502	195.74	0.004	
<sup>4</sup> G <sub>5/2</sub> → <sup>4</sup> F <sub>7/2</sub>	4 256	351.35	0.007	
<sup>4</sup> G <sub>5/2</sub> → <sup>4</sup> F <sub>5/2</sub>	4 422	394.08	0.008	
<sup>4</sup> G <sub>5/2</sub> → <sup>4</sup> F <sub>3/2</sub>	5 517	765.32	0.016	
<sup>4</sup> G <sub>5/2</sub> → <sup>4</sup> I <sub>13/2</sub>	12 768	9 486.40	0.199	
<sup>4</sup> G <sub>5/2</sub> → <sup>4</sup> I <sub>11/2</sub>	14 722	14 542.31	0.306	
<sup>4</sup> G <sub>5/2</sub> → <sup>4</sup> I <sub>9/2</sub>	16 832	21 734.02	0.457	
<sup>4</sup> G <sub>7/2</sub> → <sup>4</sup> G <sub>5/2</sub>	1 965	5.96	0.0005	81.23
<sup>4</sup> G <sub>7/2</sub> → <sup>2</sup> H <sub>9/2</sub>	4 134	55.58	0.0045	
<sup>4</sup> G <sub>7/2</sub> → <sup>4</sup> F <sub>9/2</sub>	5 467	128.54	0.0104	
<sup>4</sup> G <sub>7/2</sub> → <sup>4</sup> F <sub>7/2</sub>	6 221	189.39	0.0154	
<sup>4</sup> G <sub>7/2</sub> → <sup>4</sup> F <sub>5/2</sub>	6 387	204.96	0.0166	
<sup>4</sup> G <sub>7/2</sub> → <sup>4</sup> F <sub>3/2</sub>	7 482	329.49	0.0267	
<sup>4</sup> G <sub>7/2</sub> → <sup>4</sup> I <sub>13/2</sub>	14 733	2 515.72	0.2043	
<sup>4</sup> G <sub>7/2</sub> → <sup>4</sup> I <sub>11/2</sub>	16 687	3 655.66	0.2969	
<sup>4</sup> G <sub>7/2</sub> → <sup>4</sup> I <sub>9/2</sub>	18 797	5 224.61	0.4244	

sition starting from the ground state (<sup>4</sup>I<sub>9/2</sub>). However, two-photon absorption (TPA) is resonant for a transition from the ground state to the <sup>4</sup>G<sub>7/2</sub> level. The UC luminescence intensity in this case would be quadratic with the laser intensity and would vary linearly with the Nd<sup>3+</sup> concentration.

Another possibility would be due to a one-photon transition to level <sup>4</sup>F<sub>3/2</sub> followed by energy transfer (ET) between pairs of excited Nd<sup>3+</sup> ions. As a result of this process two ions excited to the <sup>4</sup>F<sub>3/2</sub> level may interact and exchange energy in such a way that one ion decays to the ground state

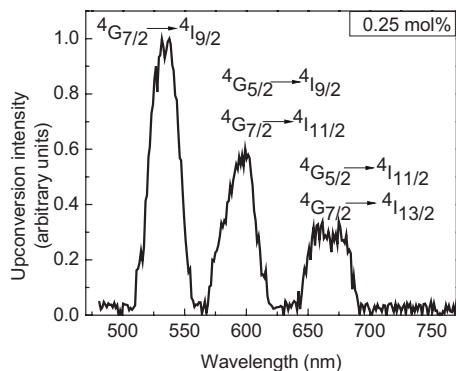


FIG. 3. Frequency UC spectrum for excitation using a laser operating at 1064 nm. Concentration of  $\text{Nd}^{3+}$  ions: 0.25 mol %.

and the other is promoted to the  ${}^4G_{7/2}$  level from where it decays radiatively to lower lying levels. However, although this process of ET has been observed in other glasses<sup>14,19</sup> in the present case this process is not expected to be more efficient than the TPA process discussed above because the one-photon frequency detuning for the electronic transition  ${}^4I_{9/2} \rightarrow {}^4F_{3/2}$  is  $\approx 1500 \text{ cm}^{-1}$ . The one-photon transition has to be phonon assisted requiring the participation of at least four phonons, and the corresponding probability is small. Another possibility to excite level  ${}^4F_{3/2}$  would be a resonant one-photon transition originating from level  ${}^4I_{11/2}$ . However, the population in level  ${}^4I_{11/2}$  is small at 300 K. In both cases the UC luminescence intensity would present a quadratic dependence on the laser intensity (as in the TPA case) but the dependence on the  $\text{Nd}^{3+}$  concentration should be quadratic.

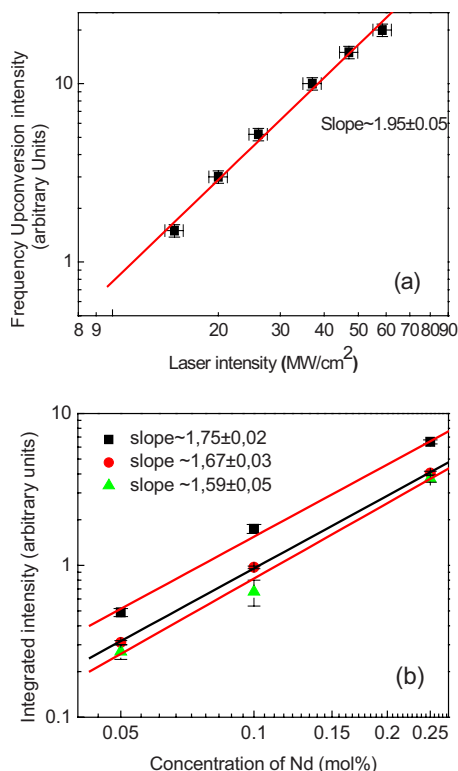


FIG. 4. (Color online) Dependence of the frequency UC signal on the laser intensity corresponding to the  ${}^4G_{7/2} \rightarrow {}^4I_{9/2}$  transition for 0.25 mol % (a) and on the  $\text{Nd}^{3+}$  concentration (b). Transitions:  ${}^4G_{7/2} \rightarrow {}^4I_{9/2}$  (squares),  ${}^4G_{7/2} \rightarrow {}^4I_{11/2}$  (solid circles), and  ${}^4G_{7/2} \rightarrow {}^4I_{13/2}$  (triangles).

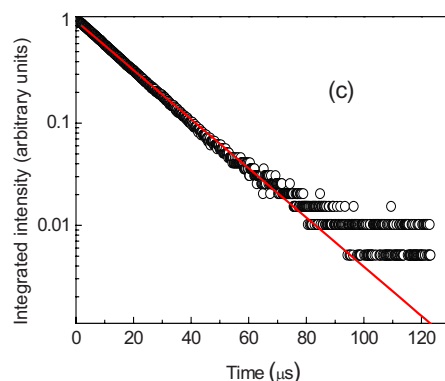
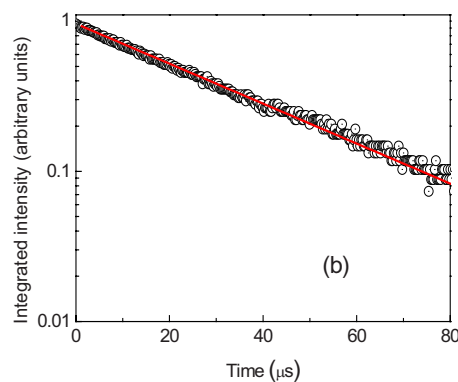
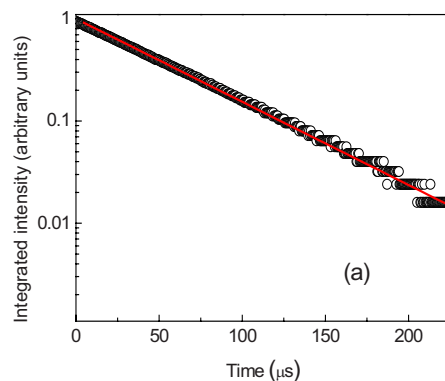


FIG. 5. (Color online) Temporal evolution of the UC signal due to the  ${}^4G_{7/2} \rightarrow {}^4I_{9/2}$  transition. Samples with different values of  $\text{Nd}^{3+}$  concentration: (a) 0.05 mol %, (b) 0.10 mol %, and (c) 0.25 mol %.

Therefore the three UC pathways may originate a luminescence signal that presents quadratic dependence with the laser intensity in agreement with the results of Fig. 4(a). Concerning the dependence on the  $\text{Nd}^{3+}$  concentration, the simultaneous contribution of the three processes leads to a slope between 1 and 2 being in accord with Fig. 4(b). Therefore we conclude that the three processes discussed contribute to the UC luminescence.

#### IV. SUMMARY

Radiative parameters of  $\text{Nd}^{3+}$  doped GGS glasses were determined from the optical absorption spectrum using the JO theory. The excitation of the samples at 1064 nm produced frequency UC in the visible region. The experiments indicate that possible mechanisms contributing to the upconverted emissions are TPA from the ground state  ${}^4I_{9/2}$  to the

$^4G_{7/2}$  level involving isolated  $Nd^{3+}$  ions and one-photon absorption to the  $^4F_{3/2}$  level followed by ET among pairs of  $Nd^{3+}$  excited to the  $^4F_{3/2}$  level.

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