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Synthesis and properties of Ge–Sb–S: $NdCl_3$ glasses

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High purity $(GeS_2)_{80-x}(Sb_2S_3)_{20}(NdCl_3)_x$ $x = 0$, 0.01, 0.1, 0.5, glasses were prepared and their optical properties determined. The Ge–Sb–S system dissolves up to 0.5 mol.% of $NdCl_3$ and still forms stable glasses. The sturcture of these glasses is formed by interconnected GeS_4 tetrahedra and SbS_3 pyramids as it follows from the Raman spectra. The glasses are optically well transparent in the range from 15400 cm^{-1} to 1000 cm^{-1}. Doping with Nd creates new absorption bands which can be assigned to electron transfer from the $^4I_{9/2}$ level to $^2G_{5/2}$, $^2G_{7/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4F_{7/2}$, $^4S_{3/2}$, $^2H_{9/2}$, $^4F_{5/2}$, $^4F_{3/2}$, $^4I_{13/2}$ and $^4I_{11/2}$ levels. The oscillator strengths and Judd-Ofelt parameters were evaluated. Their values are close to the values of these ones of Nd^{3+} in another chalcogenide hosts. The long-wavelength absorption edge was found near 1000 cm^{-1} and is due to multiphonon Ge–S and Sb–S vibrations. In doped glasses, several broad luminescence bands, near 890, 1080, 1370 and 1540 nm, were found, which can be assigned to the transitions from $^4F_{3/2}$ to $^4I_{9/2}$, to $^4I_{11/2}$, to $^4I_{13/2}$ and $^4I_{15/2}$ electron levels. The first luminescence band was excited also by 1064 nm line and represents probably the upconversion of light.

1. Introduction

The luminescence of rare earth (RE)-doped glasses has been studied frequently for potential application in lasers, light amplifiers and light upconvertors (see, e.g. [1–7]). For such applications, the quantum efficiency, which is different for the same RE ion placed in different hosts, is important [3–5]. The non-radiative transitions to the lower electron energy state, when several lattice vibrations are generated, compete with the radiative transitions. The emission from the $^4F_{3/2}$ level of Nd^{3+} ion to the underlying $^4I_{15/2}$ level can be quenched because of the above mentioned multiphonon relaxation [6,7]. The whole quantum efficience is then reduced [3,4].

The non-radiative decay rate, ω_p, due to multiphonon relaxation, depends on the energy gap, ΔE, and phonon energy, $\hbar\omega$, and is given by Miyakawa–Dexter equations [8]

$$\omega_p = \omega_0 \exp\left(\frac{-\alpha\Delta E}{\hbar\omega}\right), \qquad \alpha = \ln(p/g) - 1, \qquad (1)$$

where $p = \hbar\omega$, g is the electron-phonon coupling strength, and ω_0 is a host dependent constant.

For glasses with a small maximum phonon energy, the number of phonons required to bridge the energy gap, is large, leading to a smaller multiphonon relaxation rate [8]. The chalcogenide glasses, because of the larger atomic weights of their constitutive elements, have smaller phonon energies than do oxide glasses and the probability of multiphonon relaxation can be less. The energy gap between $^4F_{3/2}$ and underlying $^4I_{15/2}$ level in Nd ions is relatively large ($\sim$6500 cm^{-1} [19]). Its value, in combination with low phonon energies, decreases the probability of multiphonon relaxation.

The RE compunds or elements are well soluble in oxide and halide glasses, while their solubility in chalcogenides, e.g. in Ge–S system glasses, is generally less. The achievable density of RE ions in these naterials is often too small for many possible applications [5]. A search for homogeneous chalcogenide glasses, which can dissolve larger amounts of RE elements, is, therefore, useful. From this point of view, the glasses from the system, Ge–Sb–S, similarly to the Ge–Ga–S glasses studied earlier [6], are promising because they can dissolve larger amounts of RE elements or their compounds. The justification of this suggestion is given in part 3 of this paper.

The aim of this work is:

a) the determination fo the glass-forming ability in the system, Ge–Sb–S–$NdCl_3$; b) the preparation of homogeneous glasses; c) the determination of basic properties of these glasses, such as optical transmissivity and luminescence.

2. Experimental

Samples were prepared from high purity elements (Ge, Sb, S, all of 5N-purity) and from neodymium chloride ($NdCl_3$ per analysis, p.a.) in evacuated silica ampoules ($T \sim 960°C$, 40 hrs) in a rocking furnace. After the synthesis, the ampoules were annealed at 800°C for 8 hrs and then the ampoules with the melt were water quenched. The homogeneity of the samples was confirmed by optical and electron microscopy and by X-ray diffraction. The composition and its uniformity was also checked by an energy dispersive X-ray analyzer (EDAX).

The optical spectra of cut and polished planparallel plates were measured using spectrophotometer (Perkin–Elmer Lambda 12, JASCO V-570 (VIS, NIR)) and FT spectrophotometer (BIO–RAD FTS 45 (R)).

The Raman spectra were measured at room temperature by FT Bruker IFS 55/FRA 106 spectrophotometer, the YAG:Nd line (1064 nm) was used for excitation of Raman spectra. The Ar^+ ion laser lines (476.5, 488 nm) and YAG : Nd laser line (1064 nm) were used for luminescence excitation.

3. Results

The samples $(GeS_2)_{80-x}(Sb_2S_3)_{20}(NdCl_3)_x$ ($x = 0$, 0.01, 0.1, 0.5) were orange in color. The glasses were optically homogeneous to the eyes and to the methods given above. Their X-ray diffraction patterns did not contain any peaks attributable to crystals. Several broad bands typical of the amorphous state were observed. The densities of samples were increasing a little with increasing Nd^{3+} content ($\rho = 3.22 - 3.26\,g/cm^3$).

The short-wavelength absorption edge lies between 500 and 600 nm in the visible region of the spectrum.

Doping of the samples with $NdCl_3$ (Fig. 1) creates new absorption bands near 16 892, 16 447, 14 493, 13 333, 12 315, 11 312 cm^{-1} (Fig. 1), which are similar to the bands of Nd^{3+} in fluoride glasses [10,11] and in GeS_2–Ga_2S_3 glasses [6]. In the spectra of glasses with higher Nd content (~ 0.5 mol%) can be seen a weak absorption band near 1950 cm^{-1} which can be assigned to electronic transitions between the level $^4I_{9/2}$ and $^4I_{11/2}$ of Nd^{3+} ion.

In the infrared (IR) spectra, there were found weak absorption bands near 1120 and 1310 cm^{-1}, weak bands in the region 1500–1700, 2510, 3240 and 3600–3800 cm^{-1}. The bands in the region 1500–1700 and 3600–3800 cm^{-1} can be assigned to the valence vibrations of OH groups of water sorbed on the surface of the glass. The weak band near 1600 cm^{-1} corresponds to the breathing vibration of OH groups of sorbed water (see, e. g. [5,12,13]). Weak absorption bands near 1120 and 1320 cm^{-1} can be assigned to the vibrations of Sb–O and Ge–O bonds, respectively. Vibrations of S–H bonds probably cause the absorption near 2510 and 3240 cm^{-1}.

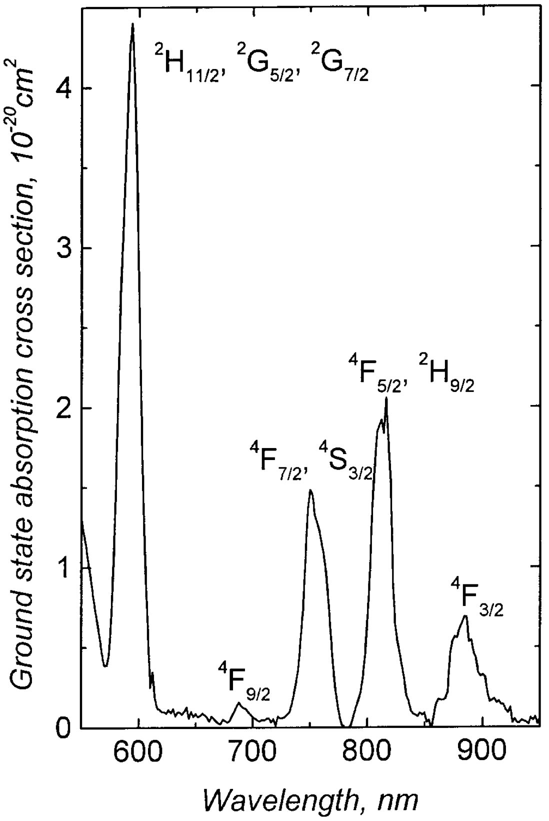

Figure 1. Ground state absorption cross section of Nd^{3+} ions in $(GeS_2)_{79.5}(Sb_2S_3)_{20}(NdCl_3)_{0.5}$ glass.

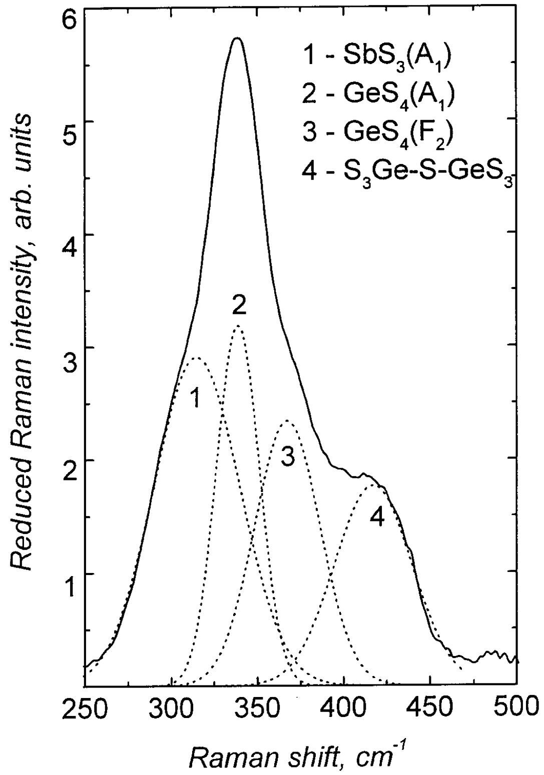

Figure 2. Raman spectrum of $(GeS_2)_{80}(Sb_2S_3)_{20}$. Deconvoluted individual bands are given by dotted lines. *1* — the band corresponds to the vibrations of SbS_3 pyramids (A_1); *2,3* — the bands correspond to the vibrations of GeS_4 tetrahedra (A_1, F_2); *4* — the band corresponds to the vibrations of S_3Ge–S–GeS_3 structural units. The Raman spectra of doped (GeS_2)–(Sb_2S_3)–$(NdCl_3)$ glasses were identical with the spectra of undoped glasses.

The long-wavelength absorption edge of the samples was found near 1000 cm^{-1} and its position can be assigned to the multiphonon Ge–S and Sb–S vibrations. The absorption in the far IR region, behind this absroption edge, is strong. The amplitudes and band positions in this region are identical with the undoped samples.

The reduced Raman spectrum of $(GeS_2)_{80}(Sb_2S_3)_{20}$ glass in given in Fig. 2. The broad band with maximum near 340 cm^{-1} can be apparently deconvoluted into four subbands with maxima near 314 cm^{-1}, 340 cm^{-1}, 367 cm^{-1} and at 416 cm^{-1}. They can be, in accordance with [14], assigned to the vibrations of SbS_3 pyramids (A_1), to the

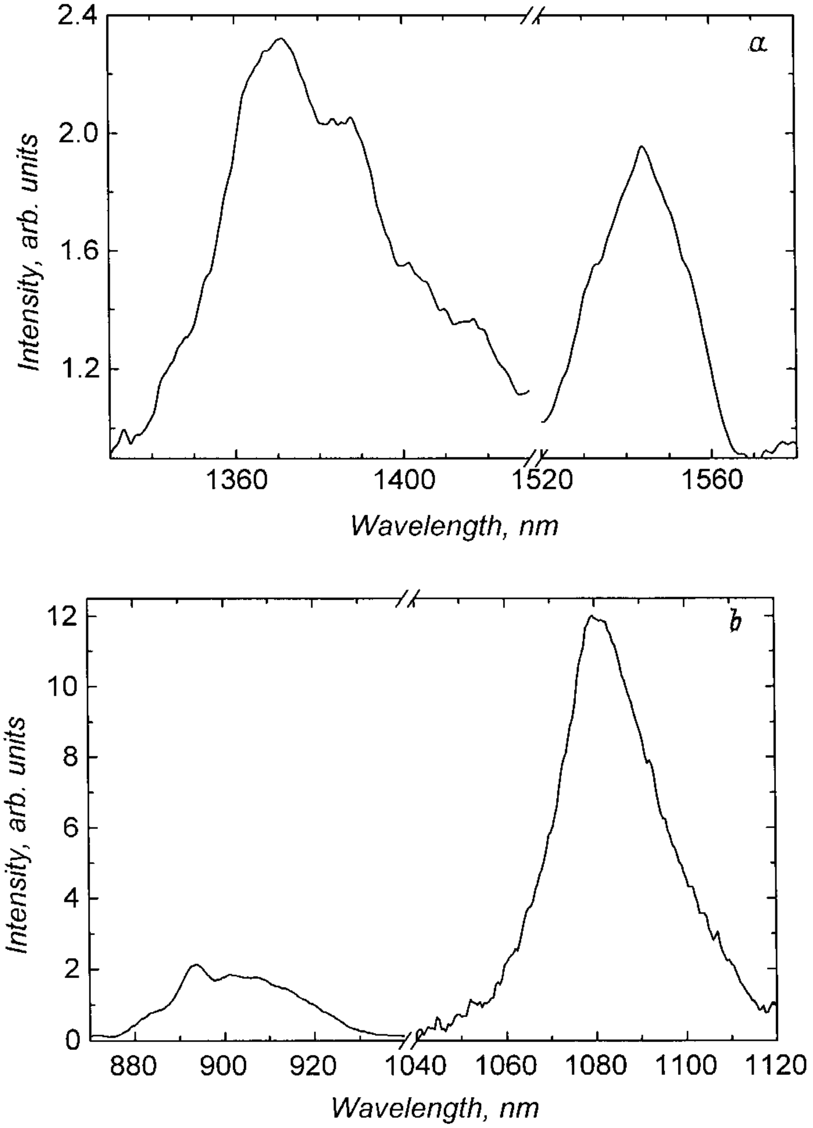

Figure 3. Luminescence spectrum of the glass $(GeS_2)_{79.9}(Sb_2S_3)_{20}(NdCl_3)_{0.1}$. *a* — the bands with maxima near 1370 and 1540 nm (excitation line 1064 nm); *b* — the bands with maxima near 890 and 1080 nm. The band with maximum near 890 nm was excited by 1064 nm laser line and corresponds apparently to the upconversion. The luminescence band near 1080 nm was excited by Ar^+ laser lines (476.5 or 488 nm). The intensity of excitation light for both bands was different.

vibrations of GeS_4 tetrahedra (A_1, F_2) and to vibrations of S_3Ge–S–GeS_3 structural units, respectively. It does mean that the structure of host glass is fromed mainly by the "lattice" of GeS_4 tetrahedra and SbS_3 pyramids, which are interconnected by bridging sulfur atoms. An identical result was obtained also from the analysis of IR reflectivity spectra. As the Me–S–Me bonds angle in germanium dichalcogenides is $\sim 90-110°$ [15] and similar angle can be found in antimony sulfides, the GeS_4 tetrahedra and SbS_3 pyraminds are vibrating independently and can be considered as isolated oscillators.

The doping of Ge–Sb–S glass by Nd does not influence the IR and Raman specta as can be expected, because the density of $NdCl_3$ dissolved molecules in glassy matrix is low.

The luminescence spectra of Nd-activated glasses are given in Figs. 3, *a,b*. Four broad luminescence bands are observed, which can be assigned to the transitions between the discrete electron levels of Nd^{3+} ions.

4. Discussion

In analogy with Ref. [6,7,10,11], the absorption bands introduced by Nd doping in visible (VIS) and near infrared (NIR) region of spectrum can be assigned to the electron transitions from the ground $^4I_{9/2}$ level to the $^2G_{5/2}$, $^2G_{7/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4F_{7/2}$, $^4S_{3/2}$, $^2H_{9/2}$, $^4F_{5/2}$ and $^4F_{3/2}$ higher energy levels. The transitions from the $^4I_{9/2}$ level to ($^4G_{7/2}$, Experimental (f_{exp}) and calculated (f_{calc}) oscillator strengths for transitions from $^4I_{9/2}$ level of Nd^{3+} ion to the level given in the table

Level	Wavenumber, cm^{-1}	f_{exp}, 10^{-8}	f_{calc}, 10^{-8}
$^4F_{3/2}$	11 312	281	286
$^4F_{5/2}$, $^2H_{9/2}$	12 315	711	705
$^4F_{7/2}$, $^4S_{3/2}$	13 333	619	624
$^4F_{9/2}$	14 493	59	54
$^2H_{11/2}$, $^2G_{5/2}$, $^2G_{7/2}$	16 447, 16 892	2548	2550

$^4G_{9/2}$, $^2K_{13/2}$) are hidden in short wavelength absorption edge, the transition to ($^2H_{11/2}$, $^2G_{5/2}$, $^2F_{7/2}$), to ($^4F_{7/2}$, $^4S_{3/2}$) and to ($^2H_{9/2}$, $^4F_{5/2}$) levels are forming absorption with overlapping of individual bands (Fig. 1).

The oscillator strength f depends on the intensity of absorption bands and can be calculated from

$$f = \frac{mc}{\pi e^2 N}\int \sigma(\nu)\,d\nu; \tag{2}$$

where m and e are electron mass and charge, respectively, $\sigma(\nu)$ is absroption cross-section, N is the density of Nd^{3+} ions. The absorption cross-section is given by $\sigma(\nu) = \alpha(\nu)/N$, where α is absorption coefficient and N is the density of Nd^{3+} ions (cm^{-3}). The obtained values of oscillator strengths are given in the Table.

A set of f_{exp} data served as the basis for calculation of the Judd-Ofelt parameters [16,17], Ω_t, using Eq. (3)

$$f_{\text{exp}}(aJ, a'J') \cong f_{\text{calc}}(aJ, a'J') = \frac{8\pi^2 m v}{3h(2J+1)} \times \left[\frac{(n^2+2)^2}{9n}\sum_{t=2,4,6}\Omega_t\left|\langle aJ\|U^{(t)}\|a'J'\rangle\right|^2\right], \tag{3}$$

where f_{exp} and f_{calc} are experimental and calculated oscillator strengths, respectively. The h is Planck's constant, m is electron mass, v is mean wavenumber of the absroption band, J is the ground-state total angular momentum of Nd^{3+} ($J = 9/2$), n is the refractive index of the material, Ω_t are the Judd-Ofelt phenomenological intensity parameters and the $\langle aJ\|U^{(t)}\|a'J'\rangle$ are the reduced matrix elements of the tensor operator, $U^{(t)}$ of rank t, which have been taken from [16,17]. The obtained values of the Judd-Ofelt parameters are $\Omega_2 = (3.1 \pm 0.07) \times 10^{-20}\,\text{cm}^2$, $\Omega_4 = (3.2 \pm 0.1) \times 10^{-20}\,\text{cm}^2$, $\Omega_6 = (7 \pm 3) \times 10^{-20}\,\text{cm}^2$. The Ω_i parameters obtained are similar to these ones for Nd^{3+} in Ga–Ge–As–S glasses [7].

The luminescence spectrum of Nd-activated glasses (Figs. 3, *a*, *b*) consists of several broad luminescence bands which we assign to the transitions between discrete electron levels of Nd^{3+} ions: $^4F_{3/2} - {}^4I_{9/2}$ or $^4F_{7/2} - {}^4I_{11/2}$ (890 nm); $^4F_{3/2} - {}^4I_{11/2}$ (1080 nm); $^4F_{3/2} - {}^4I_{13/2}$ (1370 nm); and $^4F_{3/2} - {}^4I_{15/2}$ (1540 nm). The different shape of individual luminescence bands of NdCl$_3$ doped glasses may be caused by difference in the coordination sphere of Nd^{3+} ions.

The luminescence band with maximum near 890 nm has higher energy than the exitation light (1064 nm) and it is probably caused by an upconversion effect. The exciting light can transfer electrons of Nd^{3+} ions from fundamental level $^4I_{9/2}$ to the excited level $^4F_{3/2}$ or to the $^4F_{7/2}$($^4S_{3/2}$) level in two steps. The difference of energy between $^4F_{3/2}$ and $^4I_{9/2}$ level is higher (Fig. 4) than the energy of

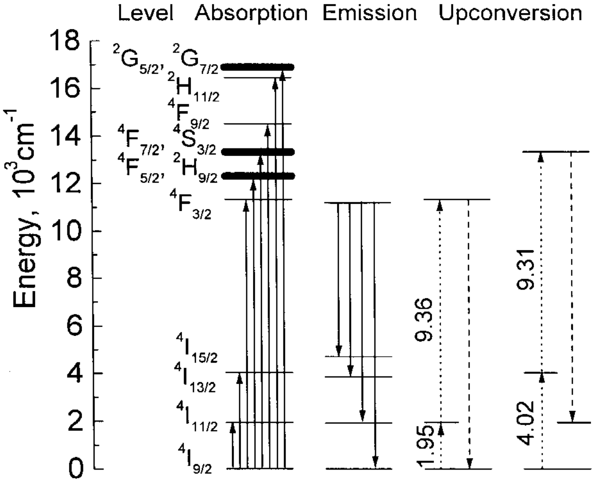

Figure 4. Energy scheme of electron transitions in Nd^{3+} ion in (GeS$_2$)$_{79.9}$(Sb$_2$S$_3$)$_{20}$(NdCl$_3$)$_{0.5}$ glass. Possible upconversion transitions are given by dotted lines, corresponding luminescence transitions by dashed lines.

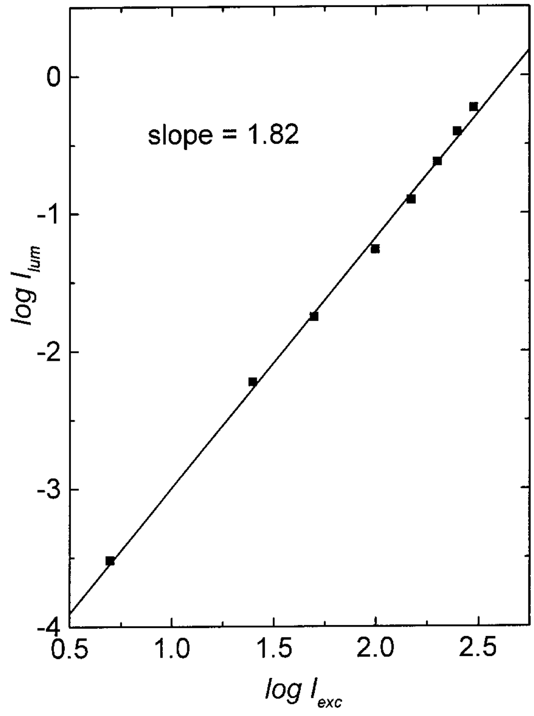

Figure 5. The dependence of luminescence intensity of the band near 890 nm on intensity of excitation light (1064 nm).

excitation ligth ($1064\,\text{nm} = 9398\,\text{cm}^{-1}$ and the process of excitation can not proceed by absorption of one photon only. The suggestion of two step model of mechanisms of absorption is in accordance with logarithmic dependence of intensity of luminescence of the intensity of excitation (Fig. 5). The slope of this line, $k = 1.82$, strongly suggests two-photons upconversion process. The value of k is rather less than 2, which can be expected, because the downward electron transitions tend to equalize the populations of the pumped initial and final states. Such an effect is commonly observed in two-photon upconversion processes [18]. We suppose that excited states produced by upconversion are $^4F_{3/2}$ or $^4F_{7/2}(^4S_{3/2})$ (Fig. 4). These states are accessible by excitaiton of 1064 nm ($9398\,\text{cm}^{-1}$) photon from $^4I_{11/2}$ to $^4F_{3/2}$ electron level or from the $^4I_{13/2}$ to $^4F_{7/2}$ level. Transitions from the basic $^4I_{9/2}$ to the $^4I_{11/2}$ and to the $^4I_{13/2}$ levels demand lower energy than the excitation light ($\sim 9400\,\text{cm}^{-1}$), and are, therefore, less efficient. This fact probably lowers the whole luminescence intensity of "upconverted" light. As the $^4F_{3/2}$ level of Nd^{3+} is generally relatively long lived [18], the upconversion via this level is more probable.

It is also possible to explain the presence of luminescence band with maximum near 890 nm (when excited by 1064 nm light) as an anti-Stokes band excited with contribution of several phonons. The energy difference between the excitation and luminescence light maxima is $\sim 1950\,\text{cm}^{-1}$, the highest energy of phonons in this type of glasses can be evaluated as $\sim 400\,\text{cm}^{-1}$ [5]. It does mean that ~ 5 phonons should be absorbed for such luminescence excitation, which seems to be less probable.

The relatively small intensity of the luminescence transitions may be due to several reasons: The wavelength used for excitation (476.5, 488 nm) was not optimal for Nd $^4F_{3/2}$ level excitation. This excitation is strongly absorbed due to fundamental absorption and the penetration depth of excitation light is very low. Contrary to it, the 1064 nm excitation light is not practically absorbed in studied glasses. The efficiency of excitation is, therefore, very small, too. A relatively low intensity of luminescence could be also caused by the presence of small amounts of OH groups, which were identified by IR spectroscopy. It is known that OH groups can be effective quenchers of the radiation at 1070 nm ($\sim 930\,\text{cm}^{-1}$) [9]. The intensity of luminescence can be also decreased by multiphonon relaxation. Since the energy gap between $^4F_{3/2}$ level and the next lower level ($^4I_{15/2}$) of Nd is relatively high and energy of phonons is chalcogenide glasses is low, the probability of such multiphonon relaxation is low as we have mentioned above.

5. Conclusion

The GeS_2–Sb_2S_3 glasses dissolve relatively large amounts of Nd^{3+} and form stable and homogeneous glasses. Their properties are similar to Nd-doped Ge–Ga–S and Ge–Ga–As–S glasses [6,7]. Due to lower phonon frequencies in sulfide glasses than in oxide or halide glasses, the Nd doped chalcogenides may be good candidates for high efficiency light amplifiers, up-convertors, lasers and other optoelectronic devices.

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