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SYNTHESIS AND LUMINESCENCE PROPERTIES OF Nd-DOPED CHALCOGENIDE GLASS $(Ge_5As_2S_{13})$ $(NdCl_3)_x$ (x = 0.3%, 0.5%)

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The synthesis of the chalcogenide glass (Ge_5As2S_{13}) doped by Nd^{3+} has been carried out. The bulk glass develops a small amount of Nd_2O_3 and As_2O_3 crystallites besides some amount of $(NdCl_3)*6H_2O$ crystalline phase initially introduced during synthesis. The optical absorption spectra demonstrate the presence of the Nd^{3+} both in the amorphous phase and in crystalline combinations. The formation of Nd_2O_3 crystallites was explained by the reaction of water with neodymium chloride. The presence of As_2O_3 is due to the oxidation of As from the glass during preparation.

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1. Introduction

The calcogenide glasses are important materials for optoelectronics [1]. Recently intense research efforts were dedicated to rare-earth doped chalcogenides. The systems $Ge_{0.25}Ga_{0.1}S_{0.65}$ and $Ge_{0.25}Ga_{0.05}As_{0.05}S_{0.65}$ doped by 0.1 and 0.3% Pr, Pr_2S_3, Pr_2O_3 and $PrCl_3$ have been studied. The photoluminescence has been observed by Raman spectroscopy[2]. In the system $(GeS_2)_{80-x}$ - $(Sb_2S_3)_{20}$ * $(NdCl_3)_x$ where x=0; 0.01; 0.1; 0.5 have been determined the optical properties and were evidenced photoluminescence bands at 890, 1080, 1370 and 1540 nm[3]. In this paper we communicate the data concerning luminescence properties of the Nd doped chalcogenide glass $(Ge_5As_2S_{13})$ $(NdCl_3)_x$ (x = 0.5).

2. Experimental

2.1 Synthesis

The synthesis of the glass have been carried out in quartz ampoules heated at 980 ^oC for 8 hours. The powders used in synthesis were of chemical purity($NdCl_3$: anhydrous, provided by Aldrich Co., 99.9% purity).

2.2 X-ray diffraction

The X-ray diagram of the glass (see Fig. 1) shows the presence of the amorphous phase (large modulation of background). Beside the amorphous phase, several narrow lines prove the presence of a crystalline phase. We have identified these lines as belonging to the minor phases of As_2O_3 and Nd_2O_3 and $NdCl_3*6H_2O$.

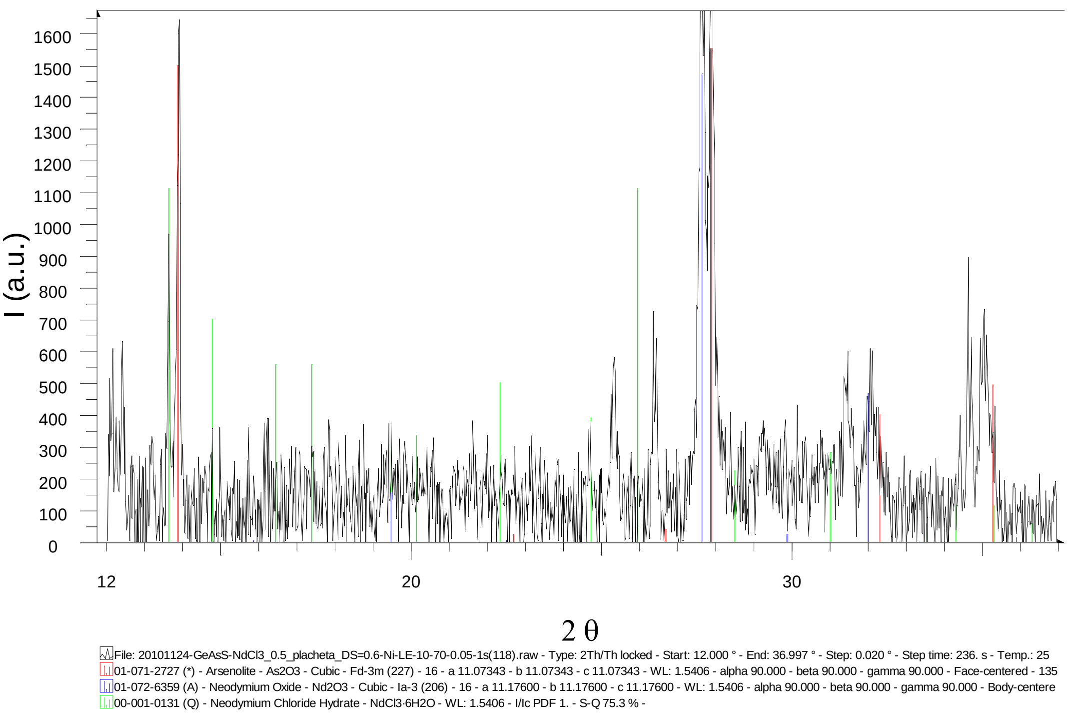

Fig. 1 X-ray diagram of $(Ge_5As_2S_{13})$ $(NdCl_3)_x$ (x = 0.5%) :
Red line - As_2O_3 (ASTM File No.01-071-2727);
Blue line - Nd_2O_3 (ASTM File No.01-072-6359);
Green line - $NdCl_3$ - 6 H_2O (ASTM File No.00-001-0131).

2.3 Optical spectroscopy

The experimental apparatus used to record the absorption and luminescence spectra was composed from an 1 m Jarrell Ash monochromator whose grating was blazed at 1 μm, a Ge (111) detector, and a lock in amplifier () online with a computer. The Nd^{3+} luminescence was excited with the laser diode (FAP SYSTEM) at 808 nm. All the measurements were performed at room temperature.

3. Results and discussion

The absorption spectrum of the $(Ge_5As_2S_{13})$ $(NdCl_3)_x$ (x = 0.5%) glass is shown in Fig. 2. In the transparency domain of this glass, only three absorption bands can be recorded: $^4I_{9/2} \rightarrow {}^4F_{7/2}$, $^4S_{3/2}$ (740 - 775 nm); $^4I_{9/2} \rightarrow {}^4F_{5/2}$, $^2H_{9/2}$ (780 - 850 nm), and $^4I_{9/2} \rightarrow {}^4F_{3/2}$ (870 - 960 nm).

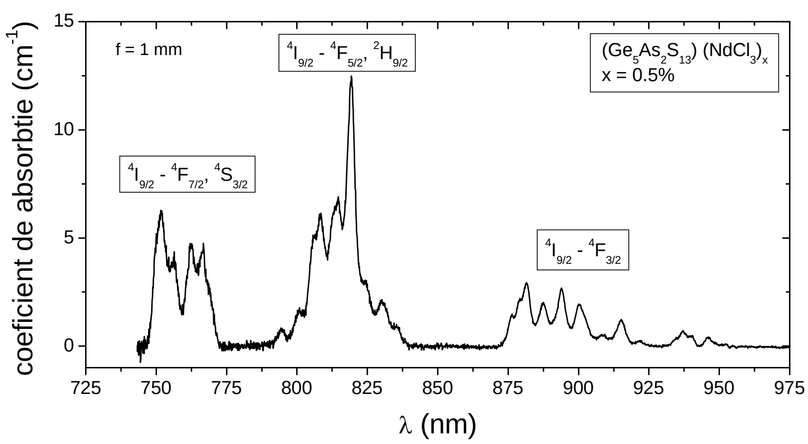

Fig. 2. Absorption spectrum of the $(Ge_5As_2S_{13})$ $(NdCl_3)_x$, x = 0.5% glass.

Because only three absorption band are accessible, we could try a Judd-Ofelt analysis [4, 5]. According to the Judd-Ofelt theory, the area of the absorption line and the linestrength S is given by [6]:

$$\int_{band} k(\lambda)d\lambda = \rho \frac{8\pi^3 e^2 \widetilde{\lambda}}{3ch(2J+1)} \frac{1}{n} \left[\frac{(n^2+2)^2}{9} \right] S \tag{1}$$

where $k(\lambda)$ is the absorption coefficient at the wavelength λ, ρ is the concentration of the Nd^{3+} ions, J is the quantum number for the initial state ($J = 9/2$ for Nd^{3+}), and $n = n(\lambda)$ is the bulk index of refraction at wavelength λ. The factor in the brackets represents the local field correction for the ion in a dielectric medium under the tight binding approximation [7]. For the our chalcogenide glass, n = 2.36. In the following, we will neglect the wavelength dependence of the refraction index.

According to the Judd-Ofelt theory, the linestrength S of a electric-dipole transition can be expressed as [8]:

$$S = \sum_{t=2,4,6} \Omega_t \left| \left\langle [S,L]J \left\| U^{(t)} \right\| [S',L']J' \right\rangle \right|^2 \tag{2}$$

where $\left| \left\langle \left\| U^{(t)} \right\| \right\rangle \right|^2$ are the double reduced matrix elements of the unitary operators $U^{(t)}$ in intermediate coupling. Their values can be found in Ref. [9]. For the absorption transitions shown in Fig. 1, the necessary $\left| \left\langle \left\| U^{(t)} \right\| \right\rangle \right|^2$ are given in Table. 1. Ω_2, Ω_4 and Ω_6 are phenomenological parameters which characterize the transition probabilities within the ground configuration of Nd^{3+} ($4f^3$).

Table 1. Doubly reduced unit tensor operators calculated in the intermediate-coupling approximation for Nd^{3+} [9].

Transition	$\left\|\left\langle\left\|U^{(2)}\right\|\right\rangle\right\|^2$	$\left\|\left\langle\left\|U^{(4)}\right\|\right\rangle\right\|^2$	$\left\|\left\langle\left\|U^{(6)}\right\|\right\rangle\right\|^2$
$^4I_{9/2} \rightarrow {}^4F_{3/2}$	0	0.2293	0.0549
$^4I_{9/2} \rightarrow {}^4F_{5/2}$	0.0010	0.2371	0.3970
$^4I_{9/2} \rightarrow {}^2H_{9/2}$	0.0092	0.0080	0.1154
$^4I_{9/2} \rightarrow {}^4F_{7/2}$	0	0.0027	0.2352
$^4I_{9/2} \rightarrow {}^4S_{3/2}$	0.0010	0.0422	0.4245

The electric dipole transition probability between the initial $\left|[S',L']J'\right\rangle$ final $\left|[S'',L'']J''\right\rangle$ states is given by [6]:

$$A([S',L']J',[S'',L'']J'') = \frac{64\pi^4 e^2}{3h(2J'+1)\widetilde{\lambda}^3} n \left[\frac{(n^2+2)^2}{9} \right] \sum_{t=2,4,6} \Omega_t \left| \left\langle [S',L']J' \left\| U^{(t)} \right\| [S'',L'']J'' \right\rangle \right| \tag{3}$$

For Nd^{3+}, the initial state is $^4F_{3/2}$.

The neodymium activated materials are characterized by the figure of merit Ω_4 / Ω_6.

We apply Eqs. (1) and (2) for the three absorption bands shown in Fig. 1. In absence of the Nd^{3+} ions concentration, the values of the Judd-Ofelt parameters can not be determined. Instead, we can obtain the ratio Ω_4 / Ω_6 In our case, this ratio is 1.86. Knowing this ratio, we can calculate with Eq. (3) the ratio of the transition probabilities:

$$\frac{A\left({}^4F_{3/2}\rightarrow{}^4I_{11/2}\right)}{A\left({}^4F_{3/2}\rightarrow{}^4I_{9/2}\right)}=\frac{(0.89)^3}{(1.06)^3}\times\frac{0.142\times\Omega_4+0.407\times\Omega_6}{0.2293\times\Omega_4+0.0549\times\Omega_6}=\frac{(0.89)^3}{(1.06)^3}\times\frac{0.142\times\Omega_4/\Omega_6+0.407}{0.2293\times\Omega_4/\Omega_6+0.0549}\cong 0.83$$

where 0.89 μm and 1.06 μm are, respectively, the average wavelengths on the transitions $^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{9/2}$. In Eq. (3), the double reduced matrix elements for the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition are taken from Ref. 3.

The complex line spectra from Fig.2 suggest the presence of part of Neodymium atoms incorporated into the crystalline phase of Nd_2O_3. Neodymium Chloride, which is rather hygroscopic, is responsible for the significant amount of oxygen in the material by the intermediate of OH groups absorbed from air after dosing of raw powders before synthesis. This leads to the formation of crystalline clusters in the glass network as evidenced by X-ray diffraction.

4. Conclusions

We have shown that the Ge-As-S glass doped by Nd^{3+} include Nd_2O_3 and $NdCl_3*6H_2O$ crystallites. The optical absorption spectra shows that Nd^{3+} ions enter into the glass matrix. Nd is present in the crystallites of Nd_2O_3 and $NdCl_3.6H_2O$. Nd_2O_3 is developed during synthesis, as a consequence of the interaction of neodymium chloride with the water present in the ampoule.

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