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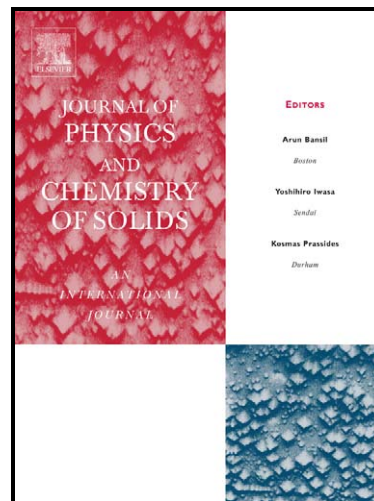
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Spectroscopic properties of Ni²⁺ and rare-earth codoped Ge-Ga-Sb-S glass

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Abstract

The infrared emission properties of rare-earth (i.e., Dy³⁺, Pr³⁺ or Sm³⁺) and nickel-codoped Ge-Ga-Sb-S glasses were investigated by photoluminescence measurements. It was found that the emission intensities of the rare-earth doped glasses were significantly weakened even with very few amount of nickel (i.e., 500 atomic ppm). On the other hand, the nickel doped glasses show larger indices of refraction, which property will be desirable in nonlinear optics. Our results, however, suggest that to obtain rare-earth doped chalcogenide glasses of better infrared emission property it is necessary to keep the nickel dopant as low as possible.

Key Words: chalcogenide; glasses; optical materials; luminescence

1 Introduction

Chalcogenide (ChG) glasses have low phonon energies due to the relatively large atomic mass of their constituent atoms. The low maximum phonon energy warrants a low probability of multiphonon relaxation between the energy levels of the rare-earth (RE) ions. Therefore, it is possible to obtain the photoluminescence of high quantum efficiency in the infrared region [1]. It also enables emission from many transition metals, which are weakly or not at all observed in other glasses, e.g., silicates and fluorides [2]. In fact, various rare-earth ions for example, erbium at 1.55 μm [3], praseodymium at 1.3 μm [4], neodymium at 1.08 μm [5], dysprosium at 1.3 μm [6], and samarium at 1.24 and 1.49 μm [7] have been shown to photoluminesce in ChG glasses so far. Fibers based on ChG glasses can also be formed with optical gain at a variety of near- and mid-infrared wavelengths [8], at which no amplification can be realized in oxide glass fibers. Of various ChG glasses, e.g., Ge-Ga-S, Ga-La-S, Ge-As-Se [6], the Ge-Ga-Sb-S (GGS) glasses are characterized by an excellent resistance to moisture, relatively high glass transition temperature, and a very weak crystallization peak upon heating [9, 10]. It has been widely used as a host glass for applications in fiber amplifiers as well as in nonlinear optics [11].

In this paper, we describe the spectroscopic properties of different RE doped GGS glasses under the influence of Ni²⁺ ions which are introduced intentionally into glass compositions. Although

recent works on the infrared emission properties of Ni²⁺-doped oxide glass-ceramics seem very promising [12, 13]. Our results, however, suggest that to obtain RE doped GGS glasses of stronger infrared luminescence it is necessary to keep the nickel dopant as low as possible.

2 Experimental

Samples based on composition Ge₂₀Ga₅Sb₁₀S₆₅ (GGS) doped with 500 atomic ppm of nickel (GGSN) or 1000 atomic ppm of RE (i.e., Dy, Sm or Pr, denoted as GGSD, GGSS and GGSP, respectively) or codoped with Ni and RE (Dy, Sm or Pr, denoted as ND, NS and NP, respectively) were synthesized from high-purity (5N) elements germanium, gallium, antimony, sulfur, nickel, dysprosium, praseodymium and samarium. The initial batches were well mixed, loaded in evacuated and sealed silica ampoules, and melted in a specially-designed rocking furnace at 950 °C for 12 hours. After synthesis, the ampoules were quenched in air, and annealed at 300 °C for 6 hours. The obtained glasses were optically homogeneous confirmed by the transmission spectra and X-ray diffraction measurement using D8-Advance diffractometer (Bruker AXS, CuK α radiation with secondary graphite monochromator).

The absorption spectra and the indices of refraction were measured by a Jasco V-570 spectrophotometer and by VASE (Variable Angle Spectroscopic Ellipsometry) J.A. Woollam Co., Inc. ellipsometry with rotating analyzer and angles of incident 55°, 60° and 65°, respectively. A Cauchy model was used to fit the refractive index dispersions. Photoluminescence spectra were obtained in the region of 1000–1600 nm. The excitation lights of 808, 980 and 1050 nm continuous wave output of a semiconductor laser (SL) were used for the samples doped with Dy³⁺, Sm³⁺ and Pr³⁺, respectively. A double grating 0.5 m monochromator with a reciprocal dispersion 3.2 nm/mm of a slit was used to analyse the emitted light, which was detected by a Ge detector. All the experiments were carried out at room temperature.

3 Results

Figure 1 shows the Vis-NIR absorption spectra of Ni-doped, RE (Dy, Sm and Pr, respectively)-doped and Ni/RE codoped glasses. The ascription of various absorption bands due to Ni²⁺ and RE³⁺ ions can be found in table I. Several common features are shared by Fig. 1 (a), (b) and (c). First, as compared to RE doped glasses (GGSD, GGSS and GGSP), the absorption edges of Ni doped (GGSN) and Ni/RE codoped (ND, NS and NP) glasses are shifted to longer wavelengths and the absorption coefficients are increased considerably; second, on top of the gross increase in the

absorption coefficients, the characteristic absorption bands of RE ions in Ni/RE codoped glasses are centered at the same wavelengths as those of RE-doped glasses. By close inspection, it is found that the absorption bands of Ni ions centered at 1168 nm disappear in Ni/Dy and Ni/Sm codoped glasses, but it is still perceptible in Ni/Pr codoped glass.

Figure 2 shows the refractive indices of host glass (GGS), and Ni-doped (GGSN) glasses. The indices of glasses are increased upon addition of nickel ions.

Figure 3 shows the emission spectra of Ni-doped (GGSN, inset in (a)) and RE doped (GGSD (a), GGSS (b) and GGSP (c)) and Ni/RE codoped (ND (a), NS (b) and NP (c), dashed lines) glasses excited by SL of appropriate wavelengths according to different RE ions. A broadband infrared emission from 1100 to 1600 nm was observed in Ni-doped glass (GGSN, inset in Fig. 3 (a)). It is the first report, as far as we know, on the infrared emission of Ni^{2+} ions in ChG glasses. The emission peak of Ni^{2+} ions is centered at 1327 nm, which is longer than that has been found in oxide glass-ceramics [13]. On the other hand, the emission intensities of Ni/RE codoped glasses are reduced to half of RE doped glasses.

Figure 4 shows the fluorescence decay curves of Dy-doped ((a), GGSD) and Ni/Dy codoped ((b), ND) glass samples at 1320 nm. The decay curves can be well fitted by the first-order exponential decay as indicated by the red curves. The emission lifetimes were then extracted from the fitting curves. It was decreased from 64.48 μs of Dy-doped sample to 60.05 μs of Ni/Dy codoped sample. The lifetimes of Dy-doped and Ni/Dy codoped glasses were larger than that was measured in Ge-As-S glass (29 μs , [14]).

4 Discussion

As shown in Fig. 1, only one absorption band of Ni^{2+} ions centered at 1168 nm has been observed in GGSN glass, which comes from the ${}^3\text{A}_{2g}({}^3\text{F}) \rightarrow {}^3\text{T}_{2g}({}^3\text{F})$ transition of Ni^{2+} ions occupying octahedral sites. It is known that this band can be detected in oxide glasses centered around 1100 nm only after heating, i.e., only observed in glasses containing nanocrystals, the so-called “glass-ceramics, (GCs)” [18]. Another absorption band of Ni^{2+} centered at 620 nm, which can also be found in oxide GCs, however, is not seen here. This is due to the intense absorption of host glass. It is believed that only octahedral Ni^{2+} ions are active in the infrared emission [12-13, 18]. Considering the fact that the broadband infrared emission does occur in our glass samples (inset in Fig. 3(a)), we assume Ni^{2+} ions reside in octahedral sites. It should be mentioned that, we did not apply any heat treatment on the Ni-doped glasses. In fact, there is no indication of the formation of nanoparticles in GGSN glass as confirmed by XRD measurement. However, since no infrared luminescence has been observed in Ni^{2+} doped glasses, we cannot rule it out that there may be small amount of nanocrystals containing

Ni^{2+} ions precipitate in the ChG glasses during preparation. Transition metal ions are very sensitive to their local chemical environment. According to ligand field theory, the energy splitting of d orbitals in an octahedral crystal field are varied in terms of the so-called “strong-field” and “weak-field” ligand series [19]. Generally, ChG glasses offer weaker ligands than do oxide glasses. Therefore, the energy splitting is narrower in ChG glasses, which explains the fact that the ${}^3\text{A}_{2g}({}^3\text{F}) \rightarrow {}^3\text{T}_{2g}({}^3\text{F})$ transition of Ni^{2+} ions centered at longer wavelength in ChG glasses.

Glasses containing metal ions often display high absorption coefficients and refractive indices (Fig. 2). The absorption in the transparent regime is related to the concentration of free electrons, and the refractive index is subjected to the concentration of free electrons as well as the polarizability of constituent atoms. Ni ions have high polarizabilities and when added to glasses the concentration of electrons is also increased. The high refractive index of Ni-doped glasses will be desirable for application in nonlinear optics.

As seen from Fig. 3, the infrared emission intensities of Ni/RE codoped glasses are much lower than RE doped glasses. In view of the rather close emission peaks of Dy^{3+} (1323 nm), Sm^{3+} (1335 nm) and Pr^{3+} (1337 nm) ions to that of Ni^{2+} ions (1327 nm), strong excited absorption of Ni^{2+} ions at room temperature is likely to happen in Ni/RE codoped glasses, and this is also the reason why it is not easy to realize optical amplification and lasing in Ni^{2+} doped glasses and crystals [13]. However, enhanced infrared emission of Ni^{2+} in oxide GCs has been observed with proper chosen of sensitizer, such as Yb^{3+} ions [20]. Presumably, the energy transfer between Yb^{3+} and Ni^{2+} ions is from a “forbidden” absorption band of Yb^{3+} ions to an “allowed” broad absorption band of Ni^{2+} ions, thus high rate of energy transfer is possible.

5 Conclusion

A broad infrared emission from 1100 nm to 1600 nm is first observed in Ni^{2+} -doped Ge-Ga-Sb-S glass. The addition of Ni^{2+} ions in different rare-earth (Dy^{3+} , Sm^{3+} and Pr^{3+}) doped GGS glasses is detrimental to the infrared emission properties. The index of refraction, on the other hand, is increased. Our results, however, suggest that to obtain RE doped ChG glasses of good infrared emission property especially at 1.3 μm , it is necessary to keep the nickel dopant as low as possible

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Figure option:

Fig. 1 The Vis-NIR absorption spectra of (a) Ni-doped (GGSN), Dy-doped (GGSD) and Ni/Dy codoped (ND, dashed line) glasses (b) Ni-doped (GGSN), Sm-doped (GGSS) and Ni/Sm codoped (NS, dashed line) glasses (c) Ni-doped (GGSN), Pr-doped (GGSP) and Ni/Pr codoped (NP, dashed line) glasses.

Fig. 2 The refractive indices of, from the bottom, GGS, and Ni-doped (GGSN) glasses.

Fig. 3 The emission spectra of (a) Dy-doped (GGSD) and Ni/Dy codoped (ND, dashed line) glasses excited by 808 nm SL (b) Sm-doped (GGSS) and Ni/Sm codoped (NS, dashed line) glasses excited by 980 nm SL (c) Pr-doped (GGSP) and Ni/Pr codoped (NP, dashed line) glasses excited by 1050 nm SL. Inset in (a) is the emission spectrum of Ni-doped glass (GGSN) excited by 980 nm SL.

Fig. 4 Fluorescence decay curves of (a) Dy-doped (GGSD) and (b) Ni/Dy codoped (ND) glasses at 1320 nm.

Table I

The ascription of various absorption bands due to Ni^{2+} and RE^{3+} (Dy^{3+} , Sm^{3+} and Pr^{3+} , respectively) ions.

Ni^{2+}	1168 nm: ${}^3\text{A}_{2g}({}^3\text{F}) \rightarrow {}^3\text{T}_{2g}({}^3\text{F})$ [15]
Dy^{3+} [16]	1108 nm: ${}^6\text{H}_{15/2} \rightarrow ({}^6\text{H}_{5/2}, {}^6\text{F}_{7/2})$; 1294 nm: ${}^6\text{H}_{15/2} \rightarrow ({}^6\text{H}_{7/2}, {}^6\text{F}_{9/2})$
Sm^{3+} [17]	1096 nm: ${}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{9/2}$ 1250 nm: ${}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{7/2}$ 1402 nm: ${}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{5/2}$ 1516 nm: ${}^6\text{H}_{5/2} \rightarrow ({}^6\text{F}_{5/2} + {}^6\text{H}_{15/2})$
Pr^{3+}	1538 nm: ${}^6\text{H}_4 \rightarrow ({}^3\text{F}_3, {}^3\text{F}_4)$ [1]

Fig 1a

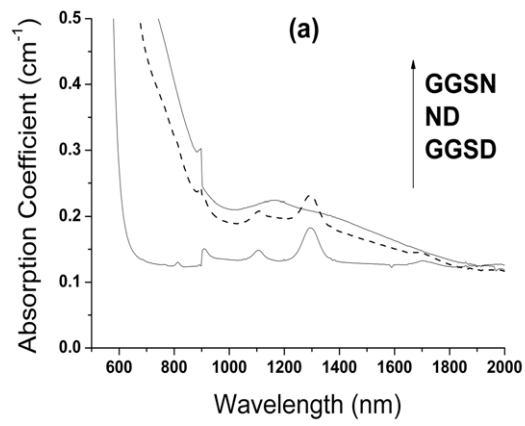


Fig 1b

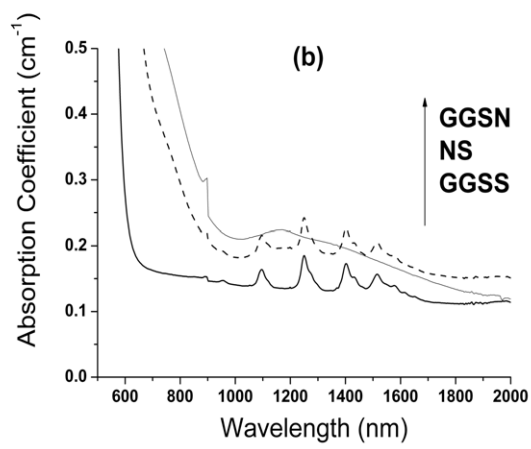
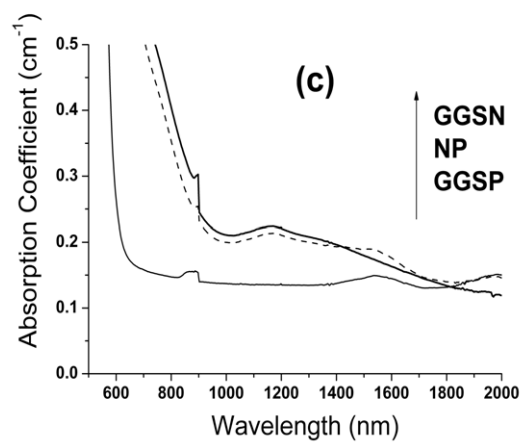


Fig 1c



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Fig 2

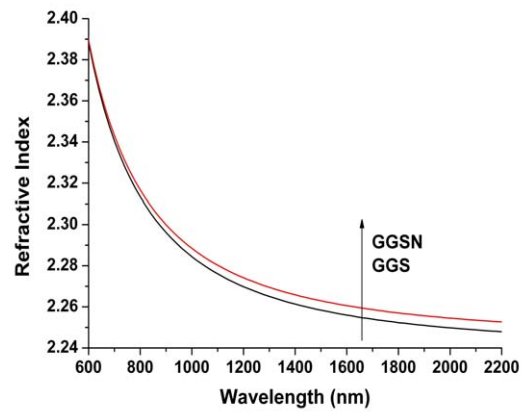


Fig 3a

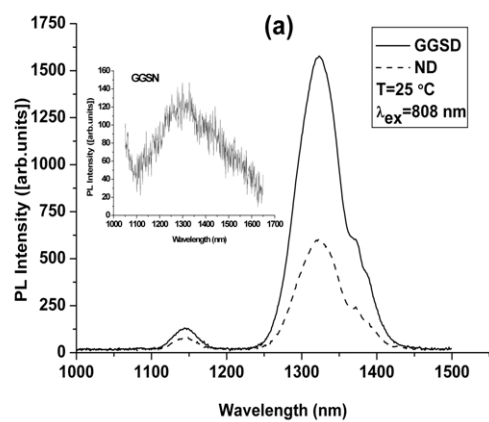


Fig 3b

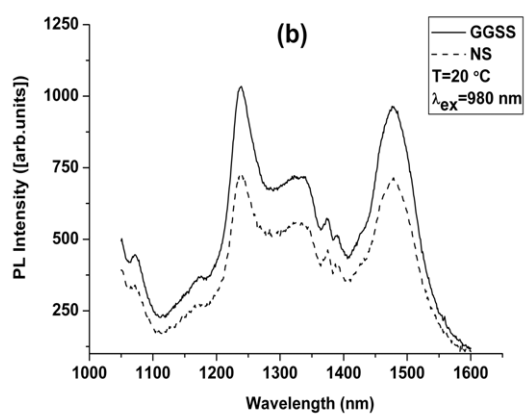


Fig 3c

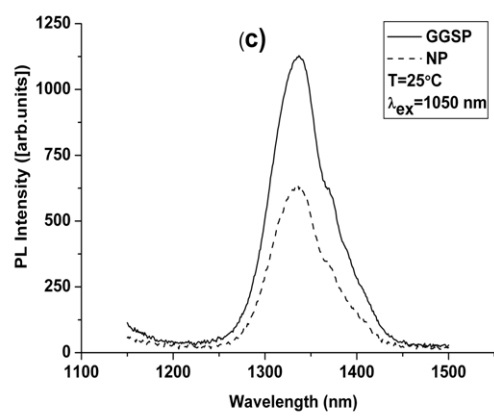


Fig 4a

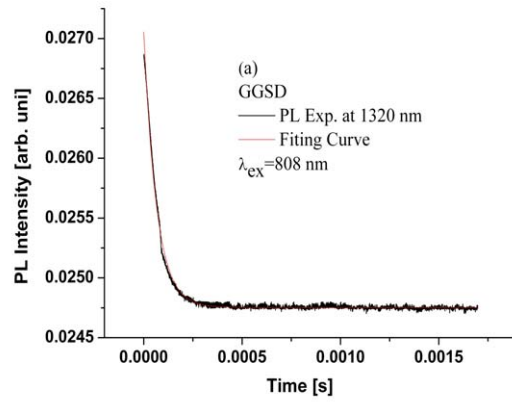


Fig 4b

