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OPTICAL PROPERTIES AND THERMAL STABILITY OF Er-DOPED As-Se (Te, S)-Ge-Ga GLASSES FOR PHOTONICS

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We have prepared a wide range of Er_2S_3-doped As-Se(Te,S)-Ga-Ge glasses of different compositions, by melt quenching techniques. We have studied the optical and thermal properties of these glasses by IR absorption, photoluminescence, PL, and temperature modulated differential scanning calorimetry (TMDSC) measurements. The observed compositional dependences indicate the possibility of varying the optical bandgap and still maintaining a good PL signal. It is possible to include Te in the glass structure in low amounts up to about 1 at. %. Beyond this composition, the more metallic Te reduces the glass stability.

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1. Introduction

Chalcogenide host glasses for Er^{3+} possess a number of highly desirable properties: they are transparent in the infrared wavelengths of interest, have a high refractive index, low phonon energy, etc. It is relatively cheaper and easier to fabricate both bulk and film chalcogenide glass devices compared to various other technologies. Erbium doped chalcogenide glasses have shown much potential for 1550 nm optical amplifier applications [1,2,3]. Current developments in telecommunication technologies and the tendency towards integrated photonic systems have driven a need to find stable host materials to create small planar waveguide optical amplifiers. It is well known that chalcogenide glasses also exhibit various interesting and useful photoinduced phenomena [4,5]. We have prepared a range of host chalcogenide glasses with different compositions, by alloying near-stoichiometric chalcogenide glasses As_2Se_3, and $GeSe_2$, and by alloying non-stoichiometric As-Ge-Se glasses with a GaSe compound or pure Ga, in an attempt to create a host glass that has sufficient space for accommodating Er^{3+} ions. We also tried to replace Se in the glass system with Te, in order to utilize the lower phonon energy advantages of the heavier Te atom. The chalcogenide host glasses were therefore $(GaSe)_x(As_2Se_3)_{1-x}$, Ge-Se(Te)-Ga and As-Ge-Se-Ga glass systems with various amounts of Ge, Ga and Te.

2. Experimental procedure

All Er^{3+} doped and undoped $(GaSe)_x(As_2Se_3)_{(1-x)}$, Ge-Se(Te)-Ga and As-Ge-Se-Ga glass systems were prepared from As_2Se_3, GaSe or pure Ga, pure Ge and Te with Er_2S_3, using well established melt quenching techniques. The homogeneity and correct composition of all glasses

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were determined using a Kevex superdry x-ray detector connected to a scanning electron microscope. Transmission spectra in the 500 - 2500 nm region were measured using a spectrophotometer (Perkin Elmer Lambda 900). Samples were polished on both sides, down to a thickness of typically 0.15 to 1.5 mm for the optical measurements. The steady state photoluminescence spectra were excited using a fibre pigtailed laser diode operating at 980 nm. The emitted light was collected by a condenser and dispersed by an ORIEL Cornerstone 1/8m monochromator. An ORIEL cooled InGaAs photodiode was used to detect the signal.

The temperature modulated and conventional differential scanning calorimetry (TMDSC and DSC) experiments were performed as described elsewhere [6,7,8,9]. There is clearly a step-like change in the heat capacity through the glass transition region, following the typical T_g behaviour that has been reported previously for different chalcogenide glasses [6,7,8]. In contrast, in conventional DSC, the heat flow is the total flow and includes an endothermic peak associated with structural relaxations. No such peak appears in the reversing heat flow observed in TMDSC, which is one of its distinct advantages. Most importantly, the T_g measured from TMDSC shows very little dependence on thermal history [9], which allows the glass transition properties of the different glass compositions to be compared in a useful manner.

3. Results and discussion

We measured the transmission spectra over the wavelength range 700 to 1700 nm, for Er^{3+} doped $(GaSe)_3(As_2Se_3)_{97}$. These spectra (reported elsewhere) clearly identify two major strong absorption peaks around the 1550 nm region associated with the Er^{3+} ions in the glass structure, as reported previously, for example, in Er^{3+}-doped GeS_2-Ga_2S_3 chalcogenide glasses [10]. In addition, As containing chalcogenide glasses have been shown to exhibit photodarkening, which allows photoinduced waveguide gratings to be prepared [11].

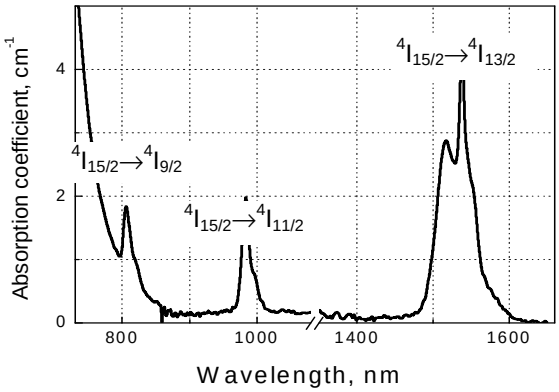

Fig. 1. A typical IR absorption spectrum of $Ge_{27}Se_{67}Ga_6$ doped with Er_2S_3 (1 at. % Er).

A typical absorption spectrum of an Er^{3+} doped Ge-Se-Ga glass is shown in Fig. 1. This figure shows several absorption peaks corresponding to the main electron transitions in Er^{3+} (at about 820 nm ($^4I_{15/2}$-$^4I_{9/2}$), and about 980 nm ($^4I_{15/2}$-$^4I_{11/2}$) used mostly as laser pumping wavelengths) and the main working transition for the second telecommunications window at 1555 nm ($^4I_{15/2}$-$^4I_{13/2}$). The Judd-Ofelt parameters were calculated using optical absorption spectra similar to that in Fig. 1. The lower value of the optical band gap meant that we could only detect four Er^{3+} absorption peaks, which therefore puts a limit on the accuracy of the calculated Judd-Ofelt parameters: $\Omega_2 = (13 \pm 2)\times10^{-20}$ cm^2, $\Omega_4 = (3.4 \pm 0.2)\times10^{-20}$ cm^2 and $\Omega_6 = (1.3 \pm 0.1)\times10^{-20}$ cm^2 for the best Ge-Ga-Se-S:Er glass, in a good agreement with values for similar materials [6]. Fig. 2 shows typical experimental optical and PL emission spectra for Er^{3+} doped Ge-Se(S)-Ga glasses with and without As, in good agreement with the spectrum calculated from the McCumber theory [12]. Therefore, both the PL emission spectra and the IR optical absorption can be used to detect the Er^{3+} activity in the glass. Fig. 2 also illustrates that Er is more homogenously dispersed in Ge-based glasses than in As-based glasses; compare (a), (b) and (c).

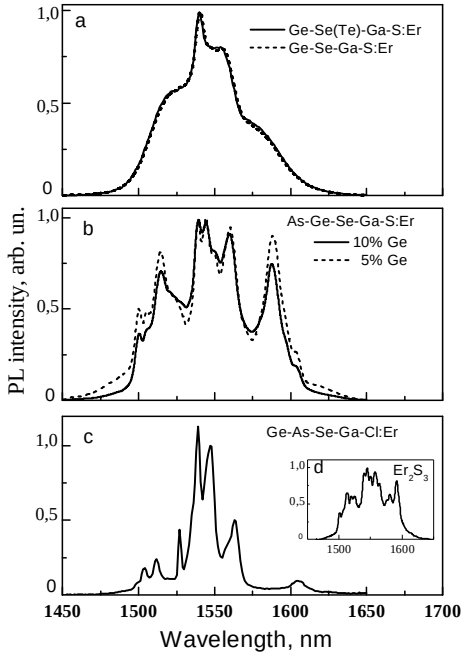

Fig. 2. Photoluminescence spectra of the studied glasses.

Fig. 3 shows the dependence of the glass transition T_g at the inflection point on the Te content in the Te containing glasses (active when Er^{3+} doped). There is also a crystallization exothermic peak (not shown) with a crystallisation onset temperature T_c. Germanium based chalcogenide glasses appear to be the most stable ones in the range of we have studied. However, they exhibit smaller light induced effects for near-bandgap illumination. Te alloying in amounts greater than 1 at. %, as shown in Fig. 3, leads to a drop in the glass transition and crystallization temperatures T_g and T_c; that is, a lower stability. Although Te alloying actually increases the glass transition temperature in the Se-Te binary system, in the cross linked structures such as $Ge_{30}(Se,Te)_{70}$ glasses, Te reduces the glass transition temperature, and hence the stability.

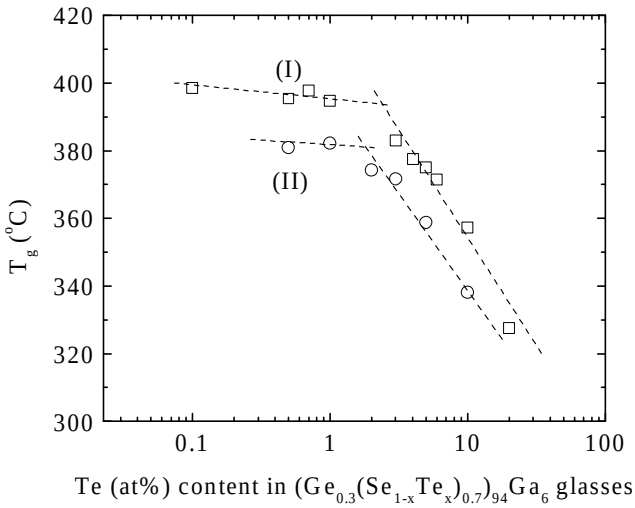

Fig. 3. Semilogarithmic plot of the glass transition temperature dependence on the Te concentration (I - composition prepared in Canada and II – composition prepared in Japan).

4. Conclusions

We have studied the optical and thermal properties of a series of Er_2S_3-doped As-Se (Te,S)-Ga-Ge glasses with different compositions. We have calculated typical Judd-Ofelt parameters for these glasses. McComber theory can explain the observed PL emission spectra for those glasses in which Er^{3+} is well dissolved (dispersed), such as the Ge-based glasses. As-based glasses showed limited Er^{3+} solubility. We were able to substitute Te for Se up to about 1 at% Te, without affecting the stability of the glass. Beyond 1 at.% Te, both T_g and T_c decreased with the Te content, making these Te alloyed glasses less stable.

Acknowledgements

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