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Thermal and optical properties of erbium doped $(GeS_2)_{75}(Ga_2S_3)_{25}$ glasses

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We have studied the thermal stability, in terms of the glass transition and crystallization, of $(GeS_2)_{75}(Ga_2S_3)_{25}$ glasses doped with high amounts of Er_2S_3 (1.8 to 2.4 mol. %). These bulk glasses were synthesized from the sulphides of Ge, Ga and Er by conventional rapid quenching of the melts in ice-water. The Er^{3+} photoluminescence spectrum is a broad emission band at ~1540 nm. The PL lineshape does not show any dependence on the Er^{3+} content. The PL decay times are in the 1.13 – 1.55 ms range, and decrease with the rare earth content.

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1. Introduction

There has been considerable interest in chalcogenide glasses doped with rare-earth (RE) elements. Among the chalcogenides, germanium-sulphide glasses have been the subject of close studies, because of potential applications in different photonic devices [1]. These chalcogenide glasses (ChGs) have low phonon energies and small non-radiative losses compared to various other glasses. Sulphides and other similar chalcogenide glasses (e.g. germanium selenium glasses) have good transparency in the infrared region. Their high refractive index leads to large emission and absorption cross-sections for radiative electron transitions between the discrete energy levels of the RE ions [2,3].

Recently, Ge-S-Ga glasses with different compositions have been closely studied, because of the enhanced RE solubility [4,5] in this glass system. As is well known, erbium doped glasses are attractive for use in all-optical devices and integrated optoelectronics, because of the Er^{3+} intra-4f emissions at the telecommunications wavelength of 1540 nm.

The purpose of this work is to study the thermal stability and some optical properties (the PL emission and PL lifetime) of a matrix of composition $(GeS_2)_{75}(Ga_2S_3)_{25}$ at this wavelength under host excitation and under direct excitation of Er^{3+} ions, in which the Ge and Ga concentrations are approximately 21and 14 at.% respectively.

2. Experimental

Bulk glasses with compositions $(GeS_2)_{75}$ $(Ga_2S_3)_{25}$: $x Er_2S_3$, where x = 1.8, 2.1 and 2.4 mol % (e.g. 1.8 mol % Er_2S_3 corresponds to 1.05 at % Er, etc.) were synthesized from the sulphides of Ge, Ga and Er by conventional rapid quenching of the melts in ice-water. The material was heated to about 1000 ^oC with a rate of 2-4 ^oC min^{-1} in an evacuated (~10^{-3} Pa) silica ampoule in a rocking furnace.

A stepwise heating regime (at 250, 550 and 750 ^oC for 2h) was chosen for the preparation of glassy GeS_2. The synthesis of Ga_2S_3 was much more complicated, due to the high vapour pressure of S at the melting point of this compound. The Er_2S_3 (99.9 % pure) was received as an Er salt from Alfa Aesar (a Johnson Matthey Company).

Differential scanning calorimetry (DSC) experiments were performed using a TM (Temperature Modulated) DSC (TMDSC) with a refrigerated cooling system and a nitrogen gas DSC cell purge. The DSC 2910 and DSC Q100 systems allow both heating and cooling scans in the modulated or non-modulated DSC regime. DSC Q100, with the novel *T*-zero technology, minimizes the thermal lag problem in DSC experiments. The instrument was calibrated for enthalpy and temperature readings, using standard high purity elemental indium. The instrument was also calibrated for the specific heat capacity (C_p) with a standard sample of sapphire using the same heating rate, oscillation period and amplitude in the temperature range of interest. The reference value for sapphire was obtained from the manufacturer (TA Instruments).

The samples were first heated from an initial temperature of 30 ^oC at a rate of 5 ^oC min^{-1} in a conventional DSC mode, to a temperature of 580 ^oC in the DSC Q100 module. The glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) observed during the heating scan are operationally defined as follows. The T_g measurement was based on the onset point definition, as applied to the observed heat flow vs. temperature behaviour in the DSC scan. T_c represents the temperature at which the crystallization exothermic heat flow reaches its maximum rate. T_m corresponds to the onset of the endothermic heat flow upon melting.

TMDSC requires the control of three experimental parameters, *i.e.* the underlying heating rate, oscillation amplitude and oscillation period. In order to obtain accurate reproducible results, the underlying heating rate

was set to 1°C min^{-1}, the oscillation amplitude was +/–1.0 °C, and the oscillation period was 60 seconds. A typical heating TMDSC consisted of a modulated heating scan from a temperature of 20 °C to 580 °C. The specific heat capacity was extracted from the reversing heat flow, using TA Instruments thermal analysis software. The values of the heat capacity and T_g were established from the step transition of the heat capacity (C_p) vs. T curve, in the glass transition region.

The steady state photoluminescence spectra were measured on the same samples using an ORIEL Cornerstone 1/8m monochromator and an ORIEL cooled InGaAs photodiode. The PL excitation was carried out by laser diodes operating at 532, 644, 770 and 982 nm. The PL decay time (τ) was measured using mechanically chopped excitation at a wavelength of 818 nm. The PL exiting the sample was filtered using a bare Si wafer to remove any of the residual pump wavelengths. The filtered signal was detected using Ge and InGaAs detectors.

The absences of crystallinity and homogeneity of the samples were checked by X-ray diffraction and electron microscopy.

3. Results

Thermal analysis data of the glasses studied are shown in Figures 1, 2 and 3.

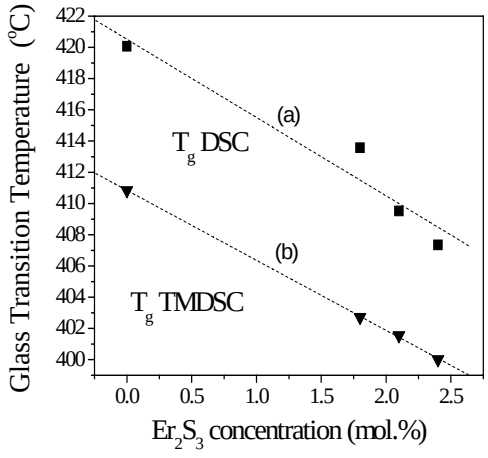

Fig. 1. Glass transition temperature of Er-doped $(GeS_2)_{75}(Ga_2S_3)_{25}$ glasses evaluated from two different experiments: (a) heat flow curve (DSC) and (b) heat capacity curve (TMDSC).

Fig. 1 shows that T_g decreases only slightly with the Er_2S_3 content. The absolute decrease from the undoped to the heaviest doped sample is around 10°C, which is a small overall temperature change for these materials with high glass transition temperatures. From a practical point of view, a lower T_g is more desirable, provided that the glass stability is maintained. The decrease in T_g with the Er-content is related to the effect of Er^{3+} in opening up the structure through ionic bonding. The DSC thermograms (not shown in the paper) evince two distinct crystallization exotherms, which indicate two phases separating out from the matrix by crystallization. Figure 2 shows the compositional dependence of the two crystallization peaks observed in the DSC scans. While the higher T_c one decreases with the composition, the lower T_c one increases. There is a seeming tendency for these two peaks to meet for a large amount of Er_2S_3 addition, but such large amounts of Er_2S_3 are obviously impossible to dissolve in these glasses.

Initially, all samples were heated to 580 °C without reaching the melting temperature, following which the samples were gradually cooled. In order to check the glass stability, DSC runs were repeated for all heat-treated samples. It was observed that the non-doped glass fully crystallized (no glass transition and crystallization transformations were observed) whereas the doped-samples showed clear T_g, T_c and T_m peaks with values that exhibit very little dependence on the composition, as shown in Fig. 3.

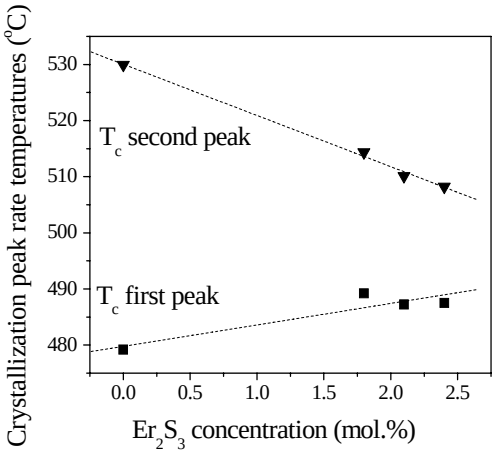

Fig. 2 Crystallization peak rate temperatures of erbium doped $(GeS_2)_{75}(Ga_2S_3)_{25}$ glasses (DSC).

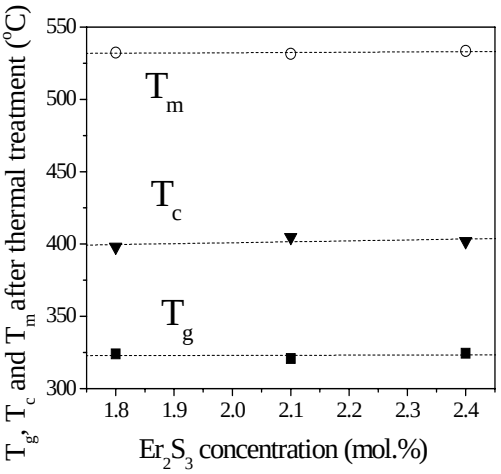

Fig. 3 Thermal properties of erbium doped $GeS_2)_{75}(Ga_2S_3)_{25}$ glasses after heat treatment at 580 °C (DSC experiments).

The photoluminescence properties of the glasses are presented in Figs. 4, 5 and 6. As was expected, all the Er_2S_3 doped $(GeS_2)_{75}(Ga_2S_3)_{25}$ samples contained optically active Er^{3+} ions which exhibited a characteristic PL spectrum centred around 1540 nm, as shown in Figure 4. It can be clearly seen that the PL line-shape is virtually independent of the doping level, with minor variations which can be attributed to self-absorption effects, as discussed in [6]. Figure 5 demonstrates that the PL line can be decomposed into four Gaussians, which are normally associated with the corresponding Stark components and optical transitions between the lower sublevels of the $^4I_{15/2}$ and $^4I_{13/2}$ manifolds.

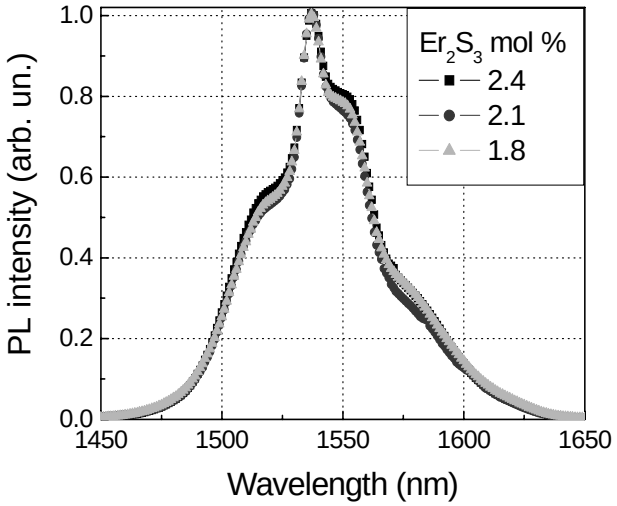

Fig.4 Photoluminescence spectra of erbium doped $(GeS_2)_{75}(Ga_2S_3)_{25}$ glasses.

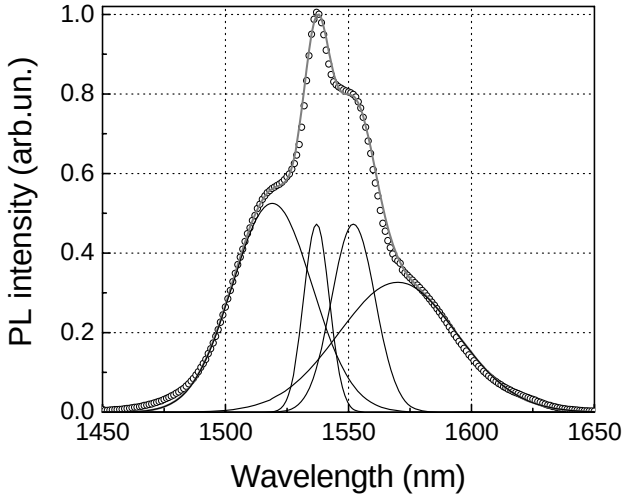

Fig. 5 Line decomposition for the PL spectrum at 2.4 mol % Er_2S_3 doping.

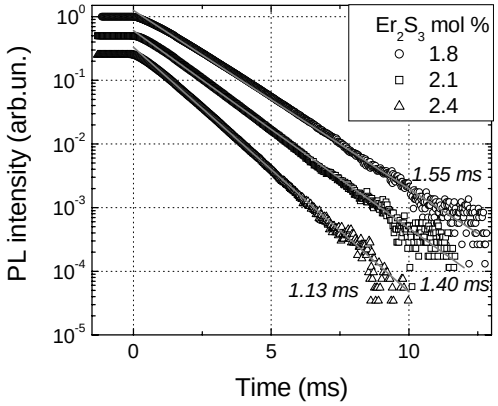

Fig. 6. PL decay from the steady-state after the cessation of illumination in erbium-doped $(GeS_2)_{75}(Ga_2S_3)_{25}$ glasses. The curves are shifted vertically to facilitate the comparison.

One of the most important parameters for rare-earth activated optical glasses is the lifetime of the excited $^4I_{13/2}$ level, which can be estimated by measuring the PL decay time. Figure 6 shows that all samples exhibit a decay time longer than 1 ms, which indicates their potential suitability for optical amplifiers operating in the third telecommunication window around 1540 nm. We observed that the decay time becomes shorter in more heavily doped samples, which is probably due to a self-quenching effect.

4. Discussion

Germanium glass compositions with double crystallization peaks are commonly used for different applications, such as in optical recording media (e.g. $Ge_2Sb_2Te_5$ etc.). They do not necessarily imply that the glass is inhomogeneous and unstable. The Ge-S-Ga glasses in this work have been prepared by experimentally implementing the formula $(GeS_2)_{75}(Ga_2S_3)_{25}$ by first preparing the GeS_2 and Ga_2S_3 *stoichiometric* compounds and then mixing them in a 75/25 ratio. The manifestation of two crystallization peaks does not necessarily represent the two portions in these two compounds. The first crystallization peak has about 25 % larger enthalpy than the second one, and the second is sharper than the first. Non-doped glass is unstable, does not survive high temperatures, and crystallizes. The introduction of Er_2S_3 prevents the glass from fast crystallization and helps render a more uniform single-phase glass system. The exact mechanism of this effect is not clear, but it is likely to be similar to the proposed structure for Er-doped $(GeSe_2)_{1-y}(Ga_2Se_3)_y$ glasses, in which Er becomes Er^{3+} and balances the negatively charged $(GaSe_4)^-$ units in a more stable structure [8]. Without the pseudo-ionic bonding of the type Er^{3+}–$(GaSe_4)^-$, the glass structure is more disrupted and more strained, and hence less resistant to crystallization. It should be emphasized that, in the case of Ge-Se-Ga glasses, we have found Er-doped glasses to be

more stable than non Er-doped glasses, and furthermore stocihiometric glasses to be more stable than non-stoichiometric glasses [7]. The present results are qualitatively consistent with these and other observations on Ge-Se-Ga glasses [8].

The Er^{3+} PL line shape is relatively stable and the sub-bands do not differ significantly between glasses with different proportions of GeS_2 and Ga_2S_3.

5. Conclusions

The addition of high concentrations of Er_2S_3 (1.8 – 2.4 mol %) to $(GeS_2)_{75}(Ga_2S_3)_{25}$ glasses resulted in a relatively more stable structure. An additional stabilization effect after thermal treatment was also observed. These erbium doped glasses had a glass transition of about 325 °C, followed by crystallization that starts near 400 °C and melting at about 580 °C.

The Er^{3+} photoluminescence spectrum of these glasses was a broad emission band at ~1540 nm. The PL lineshape did not show any dependence on the Er^{3+} content, and could be decomposed into four Gaussian components that correspond to optical transitions between the lower sublevels of the $^4I_{15/2}$ and $^4I_{13/2}$ manifolds. The positions of the observed sub-bands were close to those reported previously for Ge-Ga-S glasses with smaller levels of erbium doping

The PL decay times were in the 1.13 – 1.55 ms range, and decreased slightly with the Er content. These long decay times indicate that the present Er-doped glasses are suitable for potential applications in optical amplifiers operating at ~1540 nm.

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