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Silver metal enhanced photoluminescence of Tm^{3+} doped GeS_2–Ga_2S_3–CsCl glasses

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ABSTRACT

We report silver metal enhanced near-IR and infrared-to-visible upconversion luminescence in Tm^{3+} doped $70GeS_2$–$10Ga_2S_3$–20CsCl (in mol. %) glasses. The metal embedded glasses are prepared under controlled crystallization. Upon 808 nm excitation three fold enhancement of emissions is observed in the visible (446 nm, 496 nm, and 532 nm) and near infrared (1230 nm, 1450 nm and 1480 nm) regions. The possible mechanism responsible for the enhanced luminescence is discussed.

1. Introduction

Engineering the spectral properties of rare earth (RE) ions, such as the enhancement of luminescence intensity, can be achieved through coupling with surface plasmon resonance (SPR) in metallic nanoparticles (NPs). This process, referred to as metal-enhanced fluorescence, offers promise for a range of applications, including LEDs, sensor technology and solar cells [1–4]. Metal-enhanced photoluminescence has been intensively studied for a variety of RE ions doped glasses [5–7]. An important progress was made by Malta et al. who reported the drastically enhanced Eu^{3+} emission in borate glasses containing silver NPs [6]. Luciana et al. also reported a growth of ~1000% of Eu^{3+} 614 nm emission in GeO_2–Bi_2O_3 glasses containing gold NPs [8]. Other work on the luminescence enhancement of RE ions includes silver or gold NPs embedded heavy metal oxide glasses and chalcogenide glasses (ChGs) [7–11]. For example, Pan et al. observed the enhanced Er^{3+} 550 nm emission upon the excitation at 488 nm, which is in proximity to the SPR of silver NPs in $Ga_{10}Ge_{25}S_{65}$ glass [7]. Rai et al. found that the upconverted (UC) luminescence of Pr^{3+} 500 nm emission was enhanced in $Ga_{10}Ge_{25}S_{65}$ glass containing silver NPs [11].

In principle, when excitation or emission bands of RE ions are in vicinity of SPR of metal NPs, metal-enhanced luminescence is likely to occur. Since the SPR is located in the 400–600 nm range as found in most silver or gold NPs embedded glasses, metal-enhanced visible emission has been well established. However, studies on metal-enhanced near-IR luminescence are rather limited. As an excellent near-IR emitting material, the CsCl modified ChGs have the following merits including good glass-forming ability, high solubility of RE ions and extended transparency into the visible range [12,13]. Recently Tm^{3+} doped ChGs have received considerable attention due to the relatively large absorption cross-section of Tm^{3+} at 0.8 μm; thus one may use a commercial GaAlAs laser diode as the pump source for both near-IR and visible UC emissions of Tm^{3+} [14–17]. In this paper, we study the silver metal enhanced near infrared and UC luminescence of Tm^{3+} doped GeS_2–Ga_2S_3–CsCl chalcohalide glasses. The possible mechanism responsible for the enhanced luminescence is discussed.

2. Experimental

The GeS_2–Ga_2S_3–CsCl (GGSC) glass samples studied have the compositions of $70GeS_2$–$10Ga_2S_3$–20CsCl: $0.125Tm_2S_3$, x Ag ($x=0$, 1.5 mol. %, denoted as T and 1.5AT, respectively). Bulk glass samples were synthesized by conventional melt-quenching method employing the high-purity elements (Ge, Ga and S, 5N; Ag, 3N) and compounds (CsCl, Tm_2S_3, 3N). Each mixed batch (about 6 g) was sealed in a silica ampoule under vacuum. The ampoules were heated to 950 °C in a rocking furnace for 12 h, and then quenched vertically in the water. The obtained glass samples were annealed at the temperature around T_g for 2 h. Samples of the $Ø10\times2$ mm^2 size were cut and well polished for optical characterizations. Subsequently, the samples were submitted to heat treatments at temperatures determined by differential scanning calorimeter (DSC). The DSC data were recorded by a Sapphire DSC from room temperature to 500 °C with a heating rate of 10 °C/min. The absorption spectra of the samples were performed by a Jasco V-570 spectrophotometer (JASCO Ltd., Great Dunmow, U.K.). The vis–NIR emission spectra were recorded in 850–1600 nm range using a Zolix SBP300 spectrofluorometer (Zolix Corp., Beijing, China) with InGaAs as the

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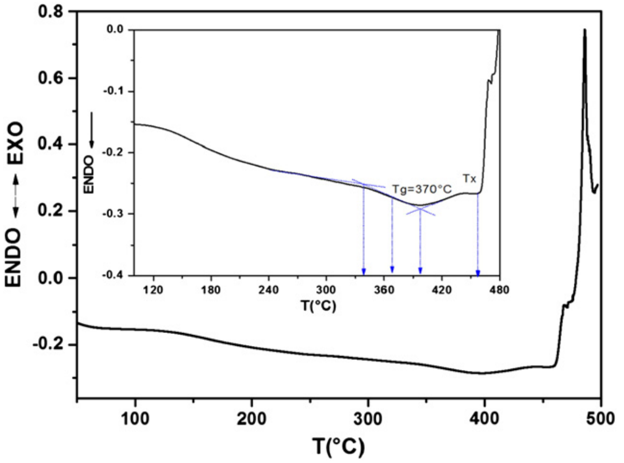

Fig. 1. DSC curve of the 1.5 mol. % Ag and 0.25 mol. % Tm^{3+} codoped sample (1.5AT).

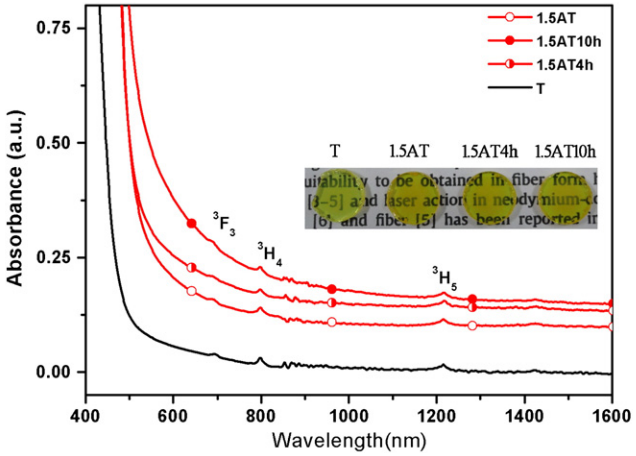

Fig. 3. Absorption spectra of the silver free sample (T), sample containing 1.5 mol. % silver (1.5AT), and the silver containing sample heated at 330 °C for 4 (1.5AT4h) and 10 (1.5AT10h) h.

detector. The excitation light was provided by an 808 nm laser diode. The absorbed photon numbers were determined by collecting the emission spectra under different pumping laser power. X-ray diffraction (XRD) data were collected using a Bruker AXS D8 Advance diffractometer (Voltage 50 kV, current 40 mA, Cu Ka) with a step width of 0.02°. All spectroscopic measurements were carried out at room temperature.

3. Results and discussion

Controlled crystallization is crucial to obtain transparent glass samples. As the crystallization is very sensitive to temperature, the glass transition (T_g) and crystallization temperatures (T_x) are analyzed from DSC. Fig. 1 shows the DSC result for the 1.5 mol. % Ag and 0.25 mol. % Tm^{3+} codoped sample (1.5AT).

The T_g and T_x values derived from the DSC curve (inset in Fig. 1) are 370 °C and 460 °C, respectively. A series of try-and-error shows that glasses of good transparency can be obtained only when the heating temperature is no higher than 330 °C. Otherwise, thermal treatment will lead to devitrification due to bulk crystallization (Fig. 2(a)). Having identified the suitable temperature at 330 °C, the glass containing 1.5 mol. % silver (1.5AT) is heated for different duration of time. The degree of crystallization after the thermal treatment is check by XRD as shown in Fig. 2(b). No obvious crystallization peak appears until the heating time increases up to 30 h. Then several sharp peaks corresponding to Ga_2S_3 and GeS_2 crystals emerge. However, the low content of silver precludes the identification of silver NPs by SEM and TEM. Their presence has to be confirmed optically as discussed below.

Transparent glasses are obtained after the controlled crystallization as illustrated in the inset in Fig. 3. According to the absorption spectra (Fig. 3), the introduction of silver induces a shift in the absorption edge towards the longer wavelength. Subsequent heating of the silver containing sample (1.5AT) leads to further red-shift in the absorption edge.

Enlarged absorption spectra related to SPR of silver NPs are shown in Fig. 4(a). The absorption band is around 520 nm, which is not related to Tm^{3+} and cannot be distinguished in the silver-free samples when heated under the same conditions taken for the silver-containing ones. This band suffers an obvious red shift compared to that observed

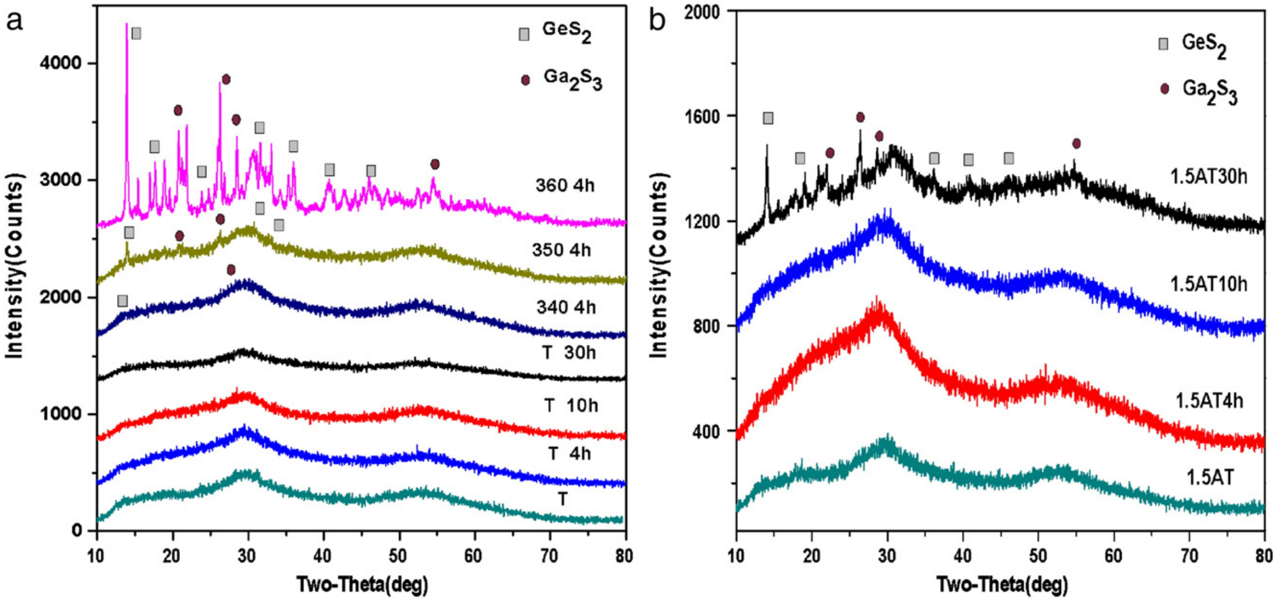

Fig. 2. XRD patterns of (a) the silver free sample (T) heated at different temperature and time; (b) the sample containing 1.5 mol. % silver (1.5AT) heated at 330 °C for different time.