

Broadband near-infrared emission of chromium-doped sulfide glass-ceramics containing Ga_2S_3 nanocrystals

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Upon 808 nm excitation, an intense broadband near-infrared emission from Cr^{4+} has been observed in $80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3$ chalcogenide glass-ceramics (GCs) containing Ga_2S_3 nanocrystals. The emission band peaking at 1250 nm covers the O, E, S bands (1000–1500 nm). The formation of Ga_2S_3 nanocrystals (~20 nm) increases the emission intensity of Cr^{4+} by more than three times. The quantum efficiency of the present GCs is as great as 36% at room temperature. © 2012 Optical Society of America
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Nowadays, silica glass fiber can utilize its full transmission window from 1100 to 1700 nm by using the ultradry fabrication technique [1]. Accordingly, fiber amplifiers must be capable of accessing to the whole transmission window of silica glass fibers. Transition metal (TM) ions (e.g., Cr^{4+} , Ni^{2+}) may yield broadband emission in the infrared (IR) wavelengths; however, the $d-d$ transitions of TM ions are strongly coupled to the lattice vibrations (phonons), and thus the emissions are markedly quenched in glasses of high phonon energy. One way to circumvent this problem is to encapsulate TM ions into glass-ceramics (GCs) containing crystals of low phonon energy [2].

A number of chalcogenide glasses (ChGs) are able to crystallize in a highly controllable way [3,4]. The extremely low phonon energy and improved mechanical strength of chalcogenide GCs favors applications including mid-IR lasers for medical purposes and toxic gas sensors [5]. Very recently, germanium-gallium-sulfur (Ge:Ga:S) glasses containing Ga_2S_3 nanocrystals have shown great interests owing to the following merits: (a) the refractive index of Ga_2S_3 crystal (~2.05) is close to that of the host glass (~2.00), thus the scattering due to the mismatch of the refractive indices is very low; (b) the emission efficiency of rare-earth or TM ions can be increased [6,7]; (c) the ionic radius of fourfold tetrahedrally coordinated Ga^{3+} (~0.61 Å) matches that of tetrahedrally coordinated Cr^{4+} (~0.56 Å) very well, thus Cr^{4+} may dissolve in Ga_2S_3 nanocrystals. Given the aforementioned advantages, however, there are scanty studies of the luminescence properties of TM ions doped ChGs containing Ga_2S_3 nanocrystals [8]. In this work, the IR luminescence properties of chromium-doped chalcogenide GCs are studied. We will demonstrate that the IR emission efficiency of chromium ions can be greatly enhanced by controlled crystallization. The

possible mechanism responsible for the enhancement is discussed.

The $80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3$ (GS) base glass and glass doped with 0.2 mol. % Cr (GSC) were synthesized from high purity elements (Ge, Ga, and S, 5N) and compounds (CrCl_3 , 5N). The samples were melted at 1000°C in evacuated (10^{-3} Pa) silica glass ampoules for 24 h and quenched in the water. The GCs were prepared by heating the GSC glass at 480°C for 10 h in a furnace filled with inert gas (denoted by GSC10). Both the glasses and GCs were cut to the size of $10 \times 10 \times 1$ mm and polished to good optical quality.

The x-ray diffraction (XRD) data were collected by using a D8-Advanced diffractometer ($\text{CuK}\alpha$ radiation with secondary graphite monochromator). The structure of nanoparticles was studied by using a JEM-2010 high-resolution transmission electron microscope equipped with an energy dispersive spectroscopy system.

The absorption spectra were measured by using an Fourier transform infrared spectroscopy (FTIR) spectrophotometer in transmission mode. Photoluminescence spectra were measured by using an SDL-1 double grating spectrometer. The excitation light of 808 nm continuous wave output of a semiconductor laser was used.

The chromium-doped glass (GSC) is amorphous as confirmed by XRD spectra shown in Fig. 1. Distinct diffraction peaks assigned to Ga_2S_3 crystal ($2\theta = 29^\circ$, 49.5° , and 58.6°) emerge in the GCs (GSC10). The nanoparticles are approximately 20 nm as calculated by the Scherrer formula. It is in accord with TEM measurement (inset in Fig. 1).

The addition of chromium changes the color of $80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3$ (GS) base glass from yellow to deep red. Subsequent thermal treatment turns the color to a mixture of red and green [inset photos in Fig. 2(a)]. The absorption spectra of the chromium-doped glass (GSC)

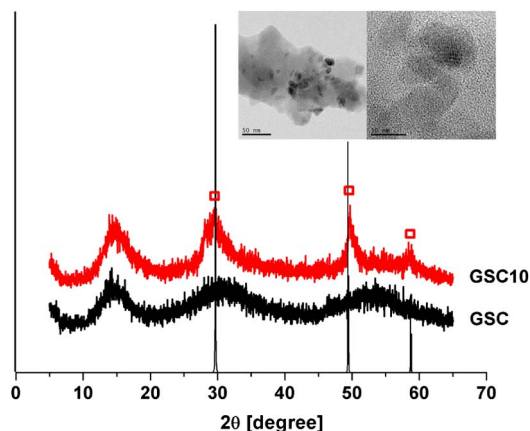


Fig. 1. (Color online) XRD spectra of the glass (GSC) and GCs (GSC10). The sharp lines are XRD data for standard Ga_2S_3 crystal. Inset, TEM image of the GCs.

show a broad band in $\sim 600\text{--}900\text{ nm}$ (with a peak at 687 nm). Calas *et al.* have found the same 687 nm absorption band in chromium-doped sodium silicate glasses [9]. They attributed the band to the spin-allowed $^4\text{A}_{2g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{F})$ transition of octahedrally coordinated Cr^{3+} . However, the $^3\text{T}_1$ absorption of tetrahedrally coordinated Cr^{4+} may overlap with the $^4\text{T}_2$ absorption of Cr^{3+} in the $600\text{--}900\text{ nm}$ range. For example, Aronson *et al.* have found a similar 690 nm absorption band in chromium-doped GeSi and As_2S_3 sulfide glasses [10]. They assigned the absorption to the $^3\text{A}_2 \rightarrow ^3\text{T}_1$ transition of Cr^{4+} .

To distinguish the absorption caused by Cr^{4+} , the background absorption was subtracted from the spectra of the chromium-doped glass and GCs. The resulted differential spectra [Fig. 2(b)] were fitted to several Gaussian peaks. The results are shown in Fig. 2(c). The GCs (GSC10) show a broad but rather weak band in

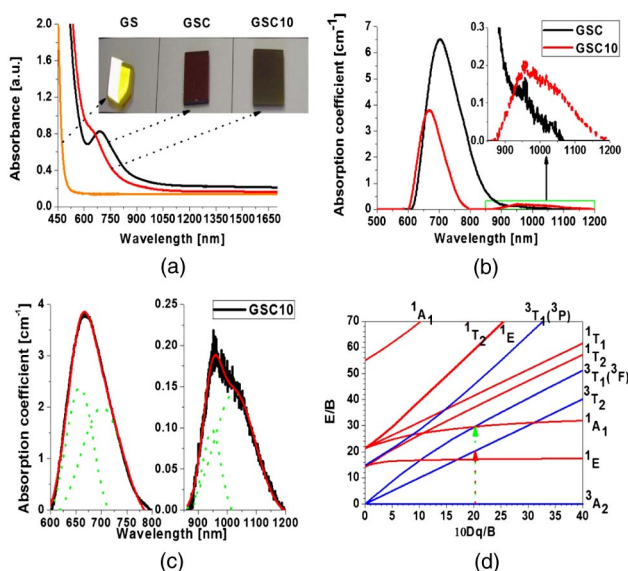


Fig. 2. (Color online) (a) Absorption spectra of the base glass (GS), chromium-doped glass (GSC) and GCs (GSC10). Inset: photos of the glasses and GCs. (b) Differential absorption spectra obtained by subtraction of the background absorption. (c) Multiple peaks fit to the differential absorption spectra of the GCs. (d) Tanabe–Sugano (TS) diagram for tetrahedrally coordinated Cr^{4+} (d^2 metal).

$\sim 850\text{--}1200\text{ nm}$, which owns its origin to the symmetry forbidden $^3\text{A}_2 \rightarrow ^3\text{T}_2$ transition of Cr^{4+} , and can be fitted into two Gaussian peaks at 947 and 1025 nm . Similar bands have been reported in Cr^{4+} -doped LiAlO_2 , LiGaO_2 , and $\text{Li}_2\text{TiGeO}_5$ crystals [11,12]. The absorption band in the $600\text{--}900\text{ nm}$ range can be also fitted into two Gaussian peaks at 657 and 700 nm . The former is tentatively ascribed to Cr^{3+} [9], and the latter is assigned to the symmetry allowed $^3\text{A}_2 \rightarrow ^3\text{T}_1$ transition of Cr^{4+} . The existence of Cr^{3+} in the glass and GCs has been confirmed by electron paramagnetic resonance (EPR) (results are not shown here).

The Racah parameter (B) and crystal field strength (Dq) can be obtained by using the Tanabe–Sugano (TS) diagram [Fig. 2(d)]. Two transitions at 700 (14286 cm^{-1}) and 1025 (9756 cm^{-1}) nm observed experimentally in the GCs are indicated by a green and a red arrow, respectively. The ratio of Dq to B (Dq/B) is ~ 2.0 , which is above the crossing point of $^3\text{T}_2$ and ^1E levels. It implies that Cr^{4+} occupies “strong field” sites. The following values are obtained: $B = 480\text{ cm}^{-1}$ and $Dq = 1426\text{ cm}^{-1}$.

A broadband IR emission with a full-width at half-maximum (FWHM) more than 250 nm is observed in the chromium-doped glass and GCs [Fig. 3(a)]. This emission peaking at 1250 nm covers the O, E, and S bands, and can be fitted into five Gaussian peaks [Fig. 3(a)]. The FWHM values of the fitted bands are less than 100 nm except for the 1400 nm one [inset table in Fig. 3(a)]. The sharp feature of the emission bands is reminiscent of Cr^{4+} ions occupying “strong field” sites. The emission profile of the GCs looks similar to that of the glass but the intensity is greatly enhanced by more than three times. In solids the laser-active Cr^{4+} occupies tetrahedral sites, which are available in Ga_2S_3 crystals [13]. The $[\text{GaS}_4]$ tetrahedron has one negative charge since Ga is in the $+3$ state. Thus, charge compensation by Cr^{3+} transforming into Cr^{4+} and substituting for Ga^{3+} becomes possible [14]. As demonstrated in Raman spectra (Fig. 4), the Ga_2S_3 nanocrystals formed in the GCs (GSC10) have a much lower phonon energy ($\sim 235\text{ cm}^{-1}$) than that of

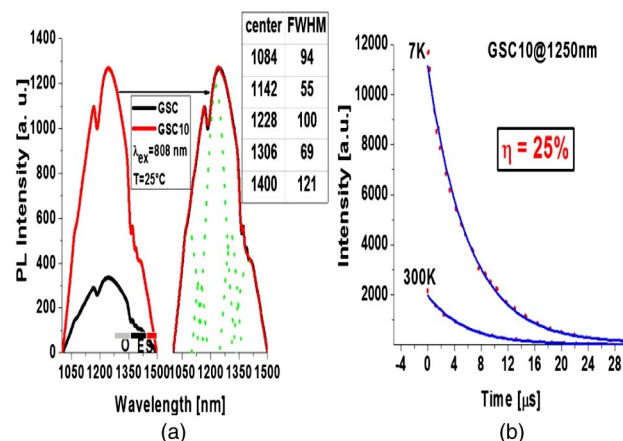


Fig. 3. (Color online) (a) Left: Emission spectra of the glass (GSC) and GCs (GSC10). Right: Multiple peaks fit to the emission spectra of the GCs. (b) Decay of the 1250 nm emission monitored at room temperature and 7 K , respectively. The dotted curves are experimental data and the solid curves are single exponential fitting curves.

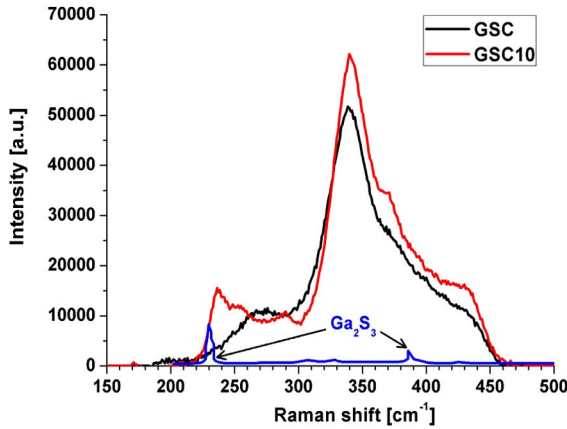


Fig. 4. (Color online) Raman spectra of the glass (GSC) and GCs (GSC10). The bottom curve is the Raman data for standard Ga_2S_3 crystal.

the host glass ($\sim 340 \text{ cm}^{-1}$), thus Cr^{4+} embedded in Ga_2S_3 nanocrystals may experience reduced phonon energy, giving rise to the enhanced IR emissions. It is likely that Cr^{4+} occupy similar coordination environments both in the glass and GCs. This is because: (a) Ga^{3+} is also fourfold tetrahedrally coordinated with S^{2-} in the base glass, and (b) the crystal structures of Ga_2S_3 appear to be not very different from its amorphous counterpart at least within the first coordination shell. Consequently, the emission profile of the GCs seems alike to that of the glass.

The decay of the 1250 nm emission can be fitted by a single exponential function, as shown in Fig. 3(b). The lifetimes are about 4 and 16 μs for the GCs measured at room temperature (300 K) and low temperature (7 K), respectively. The internal quantum efficiency (η) determined by $\eta = \tau_{300 \text{ K}} / \tau_{50 \text{ K}}$ is approximately 25%, and should be considered as an upper limit. It is much higher than those of V^{3+} -doped gallium lanthanum sulfide glasses (4.2%), Cr^{4+} -doped $\text{Li}_2\text{TiGeO}_5$ (10%), and YAG (14%) crystals [8,11].

To estimate the feasibility of the present GCs as a laser material, we calculated the product of measured lifetime (τ_{mea}) and emission cross section (σ_e). This product is a measure of the laser threshold. The emission cross section (σ_e) is calculated according to McCumber formula:

$$\sigma_e(\lambda) = \sqrt{\frac{\ln 2}{\pi}} \frac{A}{4\pi cn^2} \frac{\lambda^4}{\Delta\lambda_{\text{eff}}}, \quad (1)$$

where λ is the peak wavelength, $\Delta\lambda_{\text{eff}}$ is the effective bandwidth, n is the refractive index, c is the speed of

light, and A is the Einstein coefficient obtained from η/τ_{mea} . The product ($\sim 0.62 \times 10^{-24} \text{ cm}^2 \text{ s}$) is comparable to the Cr^{4+} -doped YAG crystal ($\sim 1.35 \times 10^{-24} \text{ cm}^2 \text{ s}$) and much larger than that of the V^{3+} doped GaLaS glass ($\sim 0.1 \times 10^{-24} \text{ cm}^2 \text{ s}$) [8]. The present GCs, which are highly reproducible, could be a promising candidate for fiber amplifiers and lasers.

In summary, enhanced broadband IR emission from Cr^{4+} can be observed in sulfide GCs via the controlled crystallization. Cr^{4+} substituting for Ga^{3+} in the Ga_2S_3 nanocrystals may experience reduced phonon energy, which leads to the enhanced IR emission. The possibility of using 808 nm as a pump source suggests that the present GCs could be a candidate for a broadband fiber amplifier and tunable laser covering from the O to S bands.

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