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Short communication

Distribution of Tm^{3+} and Ni^{2+} in chalcogenide glass ceramics containing Ga_2S_3 nanocrystals: Influence on photoluminescence properties

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ABSTRACT

The distribution of Tm^{3+} and Ni^{2+} ions is unambiguously exhibited in $80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3$ chalcogenide glass ceramics (GCs) containing Ga_2S_3 nanocrystals (NCs) by using advanced analytical transmission electron microscopy. Distinctively different distribution patterns of Tm^{3+} and Ni^{2+} ions are observed in the GCs obtained by controlled crystallization. The distribution of the dopants imposes strong influence on their optical properties which are revealed by absorption and photoluminescence (PL) spectra. Detailed discussions are given of the mechanisms of the crystallization-induced PL enhancement and quenching of the Tm^{3+} mid-infrared and Ni^{2+} near-infrared emissions, respectively.

1. Introduction

Chalcogenide glasses (ChGs), thanks to their excellent mid-infrared (MIR) transparency and unique low phonon energy, are promising hosts to yield MIR emissions at wavelengths ($> 3.0 \mu\text{m}$) which are, weakly if not absolutely impossibly, observable in other hosts including famous fluoride glasses [1]. So far, MIR emissions from rare earth (RE) ions (e.g., Pr^{3+} , Nd^{3+} , Sm^{3+} , Tb^{3+} , Dy^{3+} , Tm^{3+} etc.) doped ChGs and fibers have been extended up to $8.0 \mu\text{m}$ [2–5] and theoretical modelings have illustrated the lasing feasibility within $4.2\text{--}5.3 \mu\text{m}$ from Dy^{3+} , Pr^{3+} or Tb^{3+} doped optical fibers based on ChGs [6–8]. However, the lasing performance of ChGs is strongly hampered by their poor RE-ion-solubility among other factors [1]. This problem can be overcome by compounding gallium or indium metal in ChGs such as Ge-Ga-S(Se) and Ge-Sb-Ga-S(Se) systems [9]. Moreover, it is possible, with a controlled thermal treatment, to obtain highly transparent chalcogenide glass ceramics (GCs) with limited scattering-related losses [10]. Because of the wide glass forming region as well as rich crystallization behaviors, chalcogenide GCs based on the $\text{GeS}_2\text{-Ga}_2\text{S}_3$ system have been extensively studied for potential applications in fiber amplifiers and nonlinear optics. Recently, significantly enhanced (by an order of

magnitude) upconversion, near-infrared (NIR) and MIR emissions were reported in such glass system upon the controlled crystallization of Ga_2S_3 nanocrystals (NCs) [11–16].

However, the mechanisms behind the enhanced emissions remain extremely controversy [10], mainly because the distribution of RE ions in GCs containing the Ga_2S_3 NCs is still open to discussion. There have been studies suggesting that RE ions were entering into the Ga_2S_3 NCs because of the narrowing [11] and splitting of RE ions emission bands due to the crystallization [12]. However, much more evidence that the profiles of emission bands barely changed after the crystallization implied that RE ions were most likely located in the residual glass matrix [13,17]. A recent study also suggested the accumulation of RE ions on the surface of the Ga_2S_3 NCs according to the results of transmission electron microscopy (TEM) measurement [16]. Accordingly, the origins of the enhanced emissions induced by the crystallization have been ascribed to different causes: multi-reflection between the NCs [18], variation of local chemical composition and thus environment around the RE ions [13,14], and bonding of the RE ions to Ga^{3+} on the NCs surface [16]. There has existed a similar divergence of opinions concerning the distribution of RE ions in oxide GCs containing Ga_2O_3 NCs. It is not until recently has the ambiguity been cleared away by some of

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the authors of this article using advanced analytical TEM [19].

Being an equally important lasing candidate as RE ions doped ChGs, transition metal (TM) ions (Cr^{2+} , Co^{2+} , Fe^{2+} etc.) doped chalcogenide GCs and crystals have made breathtaking progress in the development of solid state MIR lasers in the last two decades [20,21]. However, compared with RE ions, the emission properties of TM ions are much more strongly influenced by their surrounding chemical environment. For example, the emissions of Ni^{2+} can be either in the NIR (1100–1700 nm) or the MIR wavelength region depending on whether Ni^{2+} ions occupy octahedral or tetrahedral sites in GCs, respectively [20]. Therefore, the knowledge of dopants distribution in GCs may secure a rational design of materials for targeted optical functions [22]. Although substantially enhanced emissions (by an order of magnitude) have been shown of the TM ions (Mn^{2+} , Cr^{4+} etc.) doped chalcogenide GCs containing Ga_2S_3 NCs [15,23], the distribution of the TM ions in such kind of GCs is largely left unknown.

In this letter, using advanced high-resolution TEM analyses, we provide, for the first time, the straightforward evidence of how Tm^{3+} and Ni^{2+} ions are distributed in the chalcogenide GCs containing the Ga_2S_3 NCs. The results may shed new light on understanding the enhancement/quenching mechanisms of RE and TM ions emissions in chalcogenide GCs.

2. Experimental section

The composition of $80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3$ was chosen to generate the Ga_2S_3 NCs because of its controlled crystallization. Tm_2S_3 (0.2, 1.0 mol %) and NiCl_2 (0.15 mol, 0.5 mol%) were added as the dopants. The low and high concentrations of the dopants were used for optical properties study, and for reliable TEM measurement, respectively. Base glasses (BGs) were prepared by traditional melt quenching method. The BGs were further heat treated in vacuum at 460°C for 10 h to obtain GCs. The crystal phase of the thermally grown NCs in the GCs was identified for the powdered GCs using an X-ray diffractometer (D/MAX 2550VB/PC, Rigaku Corporation, Japan) with the $\text{Cu-K}\alpha$ irradiation. The microscopic phase, particle size and distribution of the NCs were examined by high angle annular dark field STEM (HAADF-STEM) using FEI Talos F200x, USA, operating at 200 kV and equipped with an energy-dispersive spectrometer (EDS) system. The elemental mapping and sub-nanometer linescan were measured in the STEM-EDS mode. In the STEM-EDS measurements, the probing electron beam size was 0.13 nm in diameter, the examined area ($\sim 800 \times 800 \text{ nm}^2$) was divided by 2048×2048 pixels and the dwell time was 20 μs per pixel. It took approximately 20 s per one frame and 120 s for acquiring a complete mapping image. There were no obvious damages to the samples after the mapping measurements. The TEM samples were prepared by manual grinding to 200 μm and then processed by ion beam milling technique (PIPS II system from GATAN) to about 40 nm thick. Optical transmission spectra were measured using a Perkin-Elmer Lambda 950 UV-VIS spectrophotometer. Photoluminescence (PL) spectra were measured by the SDL-1 double grating spectrometer, with the PL intensity corrected by the instrumental response. The excitation light source was 808 nm continuous wave output from a semiconductor laser.

3. Results and discussion

As shown in Fig. 1(a), XRD pattern of the BG sample is typical of amorphous materials, and that of the GC sample exhibits sharp diffraction peaks which can be well identified to be the $\gamma\text{-Ga}_2\text{S}_3$ crystalline phase (zincblende-type, space group $F\bar{4}3m$). The average size of the NCs is about 40 nm calculated by the Scherrer formula. The crystalline volume fraction is $15 \pm 5\%$ estimated by the proportion of the integrated area under the crystalline peaks [24]. HAADF-STEM image (Fig. 1(b)) and STEM-EDS mappings show clearly that the precipitated NCs are Ga_2S_3 , in the size of about 50 nm, and distributed evenly in the

GCs. The distributions of Ge^{4+} (Fig. 1(c)) and Ga^{3+} (Fig. 1(d)) are complementary to each other, i.e., Ga_2S_3 NCs are surrounded by a germanium-enriched shell. This suggests such a self-limited crystallization process that the crystal growth can be inhibited by a diffusion barrier of the highly viscous germanium-rich shell, akin to the diffusion-limited Ostwald ripening process [25]. According to Lin [26], crystallization of the Ga_2S_3 NCs in glasses may be initialized by the molecular scale phase separation of the topological structural units $[\text{S}_3\text{Ga-X-GaS}_3]_n$ ($X = \text{S}$ or none, $n > 1$), which is intermediate in between short and medium range order. Benefiting from the self-limited crystallization, the GCs embedded with the Ga_2S_3 NCs retain excellent IR transparency, which is important for IR optical applications [10].

Although the distribution of RE ions such as Dy^{3+} and Tm^{3+} has been studied by TEM in GCs embedded with the Ga_2S_3 NCs, the low doping concentration of RE ions ($\sim 0.5 \text{ mol.}\%$) adopted in the previous studies prohibited a conclusive elemental mapping by STEM-EDS [16,17]. In the current work, using a heavily Tm^{3+} -doped (2.0 mol% Tm^{3+}) GC sample without sacrificing its controlled crystallization, we are able to provide, for the first time, distinct evidence of how Tm^{3+} ions are distributed in the Ga_2S_3 GCs. Comparing STEM-EDS elemental mappings of Ga^{3+} and Tm^{3+} (Fig. 2(b)), it is interesting to note that the distribution of Tm^{3+} ions appears to be complementary to that of Ga^{3+} ions, viz., Tm^{3+} ions are homogeneously dispersed in the residual Ge^{4+} -rich glassy matrix, rather than accumulated into the body of or particularly on the surface of the Ga_2S_3 NCs as suggested by Wang [16]. Further evidence is also obtained from STEM-EDS linescan measurement (Fig. 2(e)), where it is clearly shown of the exclusion of Tm^{3+} ions from the Ga_2S_3 NCs and their uniform distribution in the residual glass matrix. In contrast, the preferential incorporation of Ni^{2+} ions in the Ga_2S_3 NCs can be noticed from Fig. 2(d), which is possibly due to the substitution of the Ni^{2+} ions for tetrahedrally coordinated Ga^{3+} sites given the similarity of the ionic radii between Ga^{3+} (0.47 Å) and Ni^{2+} (0.55 Å) [27].

Among all crystallographic forms of Ga_2S_3 – hexagonal $\alpha\text{-Ga}_2\text{S}_3$, monoclinic $\alpha'\text{-Ga}_2\text{S}_3$, wurtzite-type $\beta\text{-Ga}_2\text{S}_3$, and zincblende-type $\gamma\text{-Ga}_2\text{S}_3$, gallium atoms are fourfold-coordinated in the tetrahedral configuration [28]. For $\gamma\text{-Ga}_2\text{S}_3$, known for its face-centered-cubic structure, two thirds of its general tetrahedral sites are zincblende structure constructed by Ga^{3+} , and the rest are empty cationic tetrahedral sites formed by structural vacancies [29]. In fact, $\gamma\text{-Ga}_2\text{S}_3$ may be regarded as a sort of cubic $\beta\text{-ZnS}$ crystal (defect sphalerite) in terms of the similarities of the crystalline structure and ligand field between these two crystals. However $\gamma\text{-Ga}_2\text{S}_3$ has a lower phonon energy ($\sim 235 \text{ cm}^{-1}$) [15] than the typical ZnS laser crystals ($\sim 350 \text{ cm}^{-1}$) [30]. Considering the similarity of the ionic radii between tetrahedrally coordinated Mn^{2+} (0.66 Å), Cr^{4+} (0.41 Å) and Ga^{3+} , the enhanced Mn^{2+} and Cr^{4+} emissions as previously observed in the Ga_2S_3 GCs [15,23] may be understood to be due to the preferential incorporation of the TM ions in the low-phonon-energy Ga_2S_3 NCs. In this work, the chemical environment around the Ni^{2+} ions when incorporated into the Ga_2S_3 NCs, suffers from distinct variations, exerting prominent influence on the optical properties of Ni^{2+} ions. For example, pronounced changes can be found comparing the absorption spectra of the Ni^{2+} doped BG and GC samples as shown in Fig. 3. In the BG sample, the 760 and 1400 nm absorption bands are due to the spin-forbidden $^3\text{A}_2 \rightarrow ^1\text{E(D)}$ and the spin-allowed $^3\text{A}_2(\text{F}) \rightarrow ^3\text{T}_2$ transitions of 6-fold octahedrally coordinated Ni^{2+} ions ($^{[6]}\text{Ni}^{2+}$), respectively [22]. In the crystallized GC sample, the absorption bands are converted into the 860, 1023, 2057 nm bands which are attributed to the transitions from the $^3\text{T}_1(\text{F})$ ground state to the excited $^3\text{T}_1(\text{P})$, $^3\text{A}_2(\text{F})$, $^3\text{T}_2(\text{F})$ states of 4-fold tetrahedrally coordinated Ni^{2+} ions ($^{[4]}\text{Ni}^{2+}$) [20]. The absorption of $^{[4]}\text{Ni}^{2+}$ is much stronger than $^{[6]}\text{Ni}^{2+}$ because of the lack of inversion symmetry and the removal of degeneracy in the lower symmetry tetrahedral sites. It is well known that the octahedrally coordinated Ni^{2+} ions can give rise to an ultra-broad NIR emission, which is indeed observed albeit only weakly in the Ni^{2+} -doped BG sample as shown in

Fig. 1. (a) XRD patterns of base glass (BG) and glass-ceramic (GC) samples. The stars indicate the characteristic diffraction peaks corresponding to γ -Ga₂S₃ crystal (JCPDS card No. 43-0916). (b) Typical HAADF-STEM image of the GC and corresponding STEM-EDS elemental mappings of (c) Ge, (d) Ga, and (e) S, whose concentrations are reflected by the brightness in colors.

Fig. 3(b). Notably, the Ni²⁺ NIR emission almost totally quenches in the crystallized GC sample, which is in agreement with the fact that most Ni²⁺ ions are entering into the tetrahedral sites during the crystallization process and thus become NIR-emission inactive. In fact, Ni²⁺ ions doped II–VI chalcogenide crystals (e.g., ZnS, ZnSe etc.) are known for their ultrabroadband MIR emission only at low temperatures (< 150 K). There have been no measurable room temperature MIR emissions reported to date [20].

Unlike Ni²⁺ ions, Tm³⁺ ions are expelled from the γ -Ga₂S₃ NCs (**Fig. 2(b)**). This is also contrary to the case of RE ions doped oxide GCs containing γ -Ga₂O₃ NCs, where it has been revealed of the preferential accumulation of the RE ions in the Ga₂O₃ NCs. The discrepancy arises due to differences in the crystal structures between γ -Ga₂S₃ and γ -Ga₂O₃. In the γ -Ga₂O₃ NCs, it has been suggested that RE ions may substitute for the octahedral Ga³⁺ sites or vacancies [22]. However, as mentioned above, there are only 4-fold tetrahedrally coordinated Ga³⁺ sites in the Ga₂S₃ NCs. Previous EXAFS study has proved that RE ions tend to be 6- or 7-fold coordinated in Ge-Ga-S ChGs [31], therefore the lack of suitable substituting sites imposes considerable energy barrier

for the RE ions to be accumulated into the γ -Ga₂S₃ NCs.

To clearly reveal the differences between the absorption spectra of the Tm³⁺-doped base and crystallized GC samples, the absorption spectrum of the Tm³⁺-doped GC sample was shifted upwards by 0.7 unit. Otherwise, the absorbance of the GC samples studied in this work is of the similar values to those reported by Wang [16]. We did not observe any splitting of the Tm³⁺ absorption bands in the crystallized GC sample (**Fig. 4(a)**), again corroborating the opinion that most RE ions are residing in the residual amorphous matrix. Generally, emissions of RE ions in glasses are subject to the following factors [2,10]: a) concentration of the doped RE ions which is reflected by the ion-to-ion distance, b) local asymmetry around the RE ions which is reflected by the degree of breaking the Laporte selection rule, c) multi-phonon relaxation which is related to the phonon energy of the matrix, and d) refractive index which is reflected by the local electric field correction factor, viz., $(n^2 + 2)/3$ or $3n^2/(2n^2 + 1)$ in the Lorentz virtual or real cavity model, respectively [2]. The phonon energy of the glassy matrix (~ 340 cm⁻¹) is higher than that of γ -Ga₂S₃, which is in favor of increasing of multi-phonon deactivation and thus quenching of the RE

Fig. 2. (a), (c) HAADF-STEM images of selected Ga₂S₃-rich regions in GCs, and corresponding STEM-EDS elemental mappings of (b) Ga/Tm in 2.0 mol.% Tm³⁺-doped, and (d) Ga/Ni in 0.5 mol.% Ni²⁺-doped GCs. The concentrations of elements are reflected by the brightness in colors. (e) linescan analyses for S, Ge, Ga and Tm.

Fig. 3. (a) Absorption and (b) emission spectra of non-doped (80-20 BG), 0.15 mol.% Ni^{2+} -doped base glass (80-20-Ni BG) and glass ceramic (80-20-Ni GC) samples. The excitation wavelength is 808 nm.

ions emissions. However, a significantly enhanced Tm^{3+} MIR emission at $3.7 \mu\text{m}$ is observed in the GC sample, as shown in Fig. 4(b). The residual glass matrix of the GC sample, being rich in GeS_2 and poor in Ga_2S_3 (Fig. 2), is expected to have a lower refractive index than the base glass sample, according to the fact that the refractive index increases with the Ga_2S_3 content in the $(100-x)\text{GeS}_2$ - $x\text{Ga}_2\text{S}_3$ glass system [10]. Therefore, weaker emission would be expected after the crystallization if the refractive index played a dominating role, which is obviously contradict to the observation (Fig. 4(b)). The above results indicate that there must exist some more influential factors to counterbalance the negative effects arising from the larger phonon-energy and smaller refractive index of the residual glass matrix.

In Ga^{3+} -containing ChGs, both experimental and stimulation studies have pointed out preferential spatial correlations between RE ions and $[\text{GaS}_4]^-$ tetrahedra even at low Ga-doping levels ($< 1 \text{ mol.}\%$) [32]. Although the residual glassy matrix is lack of Ga_2S_3 , however, due to the limited crystallinity ($\sim 15\%$, Fig. 1), there may well be enough $[\text{GaS}_4]^-$ tetrahedra being spatially correlated with the 0.4 mol. % Tm^{3+} . It has been proved that the $[\text{GaS}_4]^-$ tetrahedra to RE ions ratio of 10 is already good enough to effectively avoid RE ions clustering [33]. Therefore, it is likely that the local asymmetry around RE ions does not undergo fundamentally different changes after the crystallization. So far, there is only one factor left undiscussed, that is the ion-to-ion distance between RE ions. Because most Tm^{3+} ions are stuffed in the residual glassy matrix, the ion-to-ion distance decreases correspondingly. As a result, stronger mutual interactions may occur between the RE ions. This is indeed the case as confirmed by comparing NIR emission spectra of the Tm^{3+} doped BG and GC samples as shown in Fig. 4(b). The intensity ratio of the Tm^{3+} 1850 to 1450 nm emission band is larger in the GC than in the BG sample — a clear evidence of stronger mutual interactions between Tm^{3+} ions because it is closely

dependent on the Tm^{3+} concentration and the ion-to-ion distance [34]. As a final remark, the unique feature of GCs has to be taken account of multiple scattering due to the presence of the Ga_2S_3 NCs with a larger refractive index (2.563) than the residual glassy matrix [10]. The multiple scattering increases light-matter interaction by ensuring the efficient utilization of the pump light source, and thus leads to the enhanced emissions [18].

4. Conclusions

According to the nanoscale TEM analyses, Tm^{3+} and Ni^{2+} ions are accumulating in the residual glassy matrix and thermally grown Ga_2S_3 NCs, respectively. The 6-fold octahedrally coordinated Ni^{2+} ions convert to the 4-fold tetrahedrally coordinated ones after the controlled crystallization. As a result, the broadband NIR emission from the $^{16}\text{Ni}^{2+}$ ions dramatically quenches in the GC sample. Because most Tm^{3+} ions remain in the residual glassy matrix of the GC sample, the ion-to-ion distance between Tm^{3+} ions decreases after the crystallization. The shortened ion-to-ion distance leads to the stronger mutual interactions as evidenced by the larger intensity ratio of the Tm^{3+} 1850 to 1450 nm emission band. This, together with the increased light-matter interactions due to the multiple scattering, accounts for the enhanced MIR emissions observed in such kind of chalcogenide GCs.

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Fig. 4. (a) Absorption and (b) Emission spectra of 0.4 mol.% Tm^{3+} -doped base glass (0.4 Tm BG) and glass ceramic (0.4 Tm GC) samples. The excitation wavelength is 808 nm.

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