Chalcogenide glasses with embedded ZnS nanocrystals: Potential mid-infrared laser host for divalent transition metal ions

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ABSTRACT

Chalcogenide glasses (ChGs) containing II-VI chalcogenide (ChG) nanocrystals such as ZnS/Se have recently been intensively studied as promising mid-infrared nonlinear optics and laser materials, yet preparation of pure-phase II-VI nanocrystals embedded in ChGs via controlled crystallization is still very challenging. In this paper, a new system of ChGs and glass-ceramics (GCs), viz., (100-x)As$_2$S$_3$-xZnSe (x = 0 ~ 30 mol. %) is synthesized, and its physical and optical properties including density, molar volume, micro hardness, glass transition temperature, glass network structure, transmission and refractive index comprehensively characterized. Significantly, it is initially demonstrated that pure ZnS nanocrystals can be precipitated in GCs simply by a thermal treatment process. The composition and thermal treatment temperature dependencies of crystallization are studied using X-ray diffraction spectroscopy, and the morphology of the nanocrystals by high resolution transmission electron microscope. The ChG GCs with embedded ZnS nanocrystals retaining good transparency can be a potential host laser material for divalent transition metals (e.g., Cr$^{2+}$/Fe$^{2+}$, etc.), and thus used for ultrabroadband tunable continuous or ultra-short pulsed mid-infrared fiber lasers.

Keywords: chalcogenide glass; II-VI chalcogenide crystal; chalcogenide glass ceramics; fiber laser material

I INTRODUCTION

Divalent transition metal (TM$^{2+}$: e.g., Cr$^{2+}$/Fe$^{2+}$ etc.) doped II-VI chalcogenide (ChG) crystals (e.g., ZnS/Se etc.) show extremely broad and intense mid-infrared photoluminescence in the range from 2 to 5 μm, and thus are considered as excellent gain media for high-power tunable continuous or ultra-short pulsed mid-infrared lasers [1]. The lasing wavelengths of the TM$^{2+}$: II-VI crystals lie in the “atmospheric window”, “water absorption
band” and “molecular fingerprint region”, and hence are excellent potential candidates for applications in long-haul free space communication, remote chemical sensing, laser surgery and infrared countermeasures [2]. The last two decades has witnessed major progress in the development of solid state mid-infrared lasers based on the TM$^{2+}$: II-VI materials which can now rival even “superstar” Ti$^{3+}$-doped sapphire crystals (e.g. Ti$^{3+}$: Al$_2$O$_3$) lasing in the near-infrared wavelengths [1, 3]. However, the significant thermal lensing effect due to the relatively large thermo-optic coefficient of the TM$^{2+}$: II-VI (six times that of Ti$^{3+}$: Al$_2$O$_3$) poses a serious problem to obtaining a laser beam of sufficiently high quality and output power [2].

Optical fibers, owing to the unique large surface area to volume ratio, possess good heat-dissipating characteristics, are an ideal gain media for high power lasers [2]. However, the crystals, with a few notable exceptions are notoriously poor in terms of their incompatibility with conventional fiber drawing processes such as drawing out of fiber preforms, and unfortunately this is exactly the case for the II-VI ChG [4]. Two methods have been proposed to date to produce the II-VI ChG compounded optical fibers. The first one proposed by J. Badding et al. is based on the high-pressure chemical vapor deposition (HPCVD) technique, in which ZnS/Se layers are chemically deposited onto the inner surface of the silica capillaries in the preform and hence within the resulting optical fibers [4-5]. However, the fibers resulting from this method suffer from limited length (being only a few centimeters long) and relatively large optical losses (1 dB cm$^{-1}$ or 100 dB m$^{-1}$).

The other method proposed by Mironov et al. consists of the following steps: 1) prepare II-VI ChG powders by mechanical grinding to micrometer scale, 2) prepare chalcogenide glasses (ChGs, e.g., As$_2$S$_3$) using a conventional melt-quenching method, 3) mix the II-VI micro-powders with the ChGs, and 4) synthesize the II-VI micro-crystals embedded ChG glass preforms for fiber drawing using the conventional technique [6-7]. This method is capable of producing fibers typically of a few meters in length, and thanks to the refractive index matching between the II-VI crystals and ChGs, the optical losses can be restricted to relatively low levels (2~4 dB cm$^{-1}$).
dB m\(^{-1}\)) which is an advantage for practical applications [8]. However, the relatively large size of the embedded II-VI micro-crystals (comparable to the pumping and lasing wavelengths) would cause Mie scattering in laser applications. To avoid such losses, it is necessary to further reduce the particle size to the nanometer scale which is unfeasible by mechanical grinding.

Glasses are thermodynamically metastable such that it is possible to produce highly transparent GCs containing nano-crystals by post thermal treatment. ChGs containing functional nanocrystals (e.g., Ga\(_2\)S\(_3\)) are currently subject to intensive investigation for applications in infrared (IR) and nonlinear optics, fiber amplifiers and lasers [9-11]. Although a number of glass systems containing II-VI ChG compounds, such as GeS\(_2\)-Ga\(_2\)S\(_3\)-CdS [12], GeS\(_2\)-Sb\(_2\)S\(_3\)-CdS [13], GeS\(_2\)-Na(K)\(_2\)S-CdS [14], GeS\(_2\)-BaS-Cd(Zn)S [15], GeS\(_2\)-AgS-ZnS [16], and GeSe\(_2\)-Sb\(_2\)Se\(_3\)-ZnSe [17] etc have been explored, it appears that the II-VI nanocrystals embedded ChGs have not been reported to date. Generally, it is difficult to obtain pure II-VI ChG nanocrystals without the formation or incorporation of undesirable phases from Ge-based ChGs. The controllability of the crystallization process can also be problematic because of the strong tendency of Ge-based ChGs towards crystallization. In this respect, As-based ChGs with better thermal stability against crystallization are likely to be superior candidates.

In this paper, a new As-based ChG fiber laser compatible material, i.e. As\(_2\)S\(_3\)-ZnSe is introduced and has been successfully synthesized. The physical and optical properties were systematically characterized using micro-sclerometry, differential scanning calorimetry (DSC), Raman and IR spectroscopy, as well as variable angle spectroscopic ellipsometry. A range of samples with different ratios of As\(_2\)S\(_3\) to ZnSe were thermally treated under different temperatures to investigate the composition and influence of the heating temperature
on the crystallization of the II-VI nanocrystals. The crystallization process and the morphology of the nanocrystals were studied using an X-ray diffractometer and high-resolution transmission electron microscope (HRTEM).

II EXPERIMENTS

Samples of compositions (100-x)As<sub>2</sub>S<sub>3</sub>-xZnSe (for x = 0, 2, 5, 10, 20, 30 mol. %) were prepared from high purity elements (As and S, 5N) and compounds (ZnSe, 5N). The weighed raw materials were melted at 900 ºC for 12 hr in an evacuated (10<sup>-3</sup> Pa) and pretreated silica glass tube, and then cooled to 750 ºC within 1 hr. The melt was rapidly quenched in water and then annealed at different temperatures (180, 200, 240, 280 ºC) for 5hr. The resulting samples were sliced into cylindrical sections of Φ10 mm × 2 mm and polished to good optical quality.

The density of the samples was obtained using the Archimedes method with alcohol as the immersion liquid. Microhardness was measured using an MXT 70 type micro-sclerometer (MATSUZAWA, Japan). DSC were carried out using a TA D2000 (New Castle, DE) under non-isothermal conditions from room temperature to about 500 ºC (773 K) with a linear ramp heating rate of 10 K/min. X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer (D/MAX 2550VB/PC, Rigaku Corporation, Japan) with Cu-Kα irradiation. The microstructure of the resulting samples was studied by means of Transmission Electron Microscopy (TEM) (JEM-2100, JEOL Ltd, Japan). For the measurement, TEM samples were prepared by deposition of a drop of finely ground bulk sample suspended in ethanol onto the surface of a carbon coated copper grid.

Visible-to-near infrared (NIR) transmission spectra in the range of 500-2500 nm were measured using a Perkin-Elmer Lambda-950 spectrophotometer. IR transmission spectra (3-14 μm) were measured using a Fourier transform infrared (FTIR) spectrophotometer (NICOLET NEXUS firm: Thermo Scientific). Mid-infrared
refractive indices were measured using an infrared variable angle spectroscopic ellipsometer (IR-VASE, J. A.
Woollam Co.) with rotating analyzers [18]. Raman spectra were measured using a RenishawInvia Raman
microscope (Renishaw, Gloucestershire, UK) at an excitation wavelength of 532 nm.

III RESULTS AND DISCUSSION

The XRD patterns are shown in Fig. 1. When heat treated at 180 °C (Fig. 1(a)), the samples remain amorphous
up to 5 mol.% ZnSe, at which point diffraction peaks at 28.56°, 47.52° and 56.29° appear which are well
matched to the (111), (220) and (311) - Miller indices of the sphaleritic ZnS (JCPDS cards NO 05-0566, a=5.406)
for samples containing higher ZnSe content (≥ 10 mol.%) [19]. The intensity of the diffraction peaks gradually
increases with the increasing ZnSe content, pointing to increased crystallinity. However, the transmission
properties of the samples containing higher ZnSe content (≥ 10 mol.%) degrade severely following thermal
treatment (Fig. 3) which restricts their use for optical applications, and hence these sample did not warrant
further study. The crystallinity (volume fraction of the crystalline phase) can be approximately estimated
according to the ratio of the area under the indexed diffraction peaks to that under the whole XRD patterns
[20]. The calculated value of the sample containing 5 mol.% ZnSe is below 1%, which indicates that subsequent
endeavor is needed to raise the extent of crystallization given that the good optical quality of the samples will
not be undermined. Since the formed nanocrystal is ZnS, it seems to be a natural option that ZnS should be
used as the raw material. However, ZnS has an extremely high melting point (1850 °C), and thus is nearly
impossible to be completely melted at the synthesize temperature (e.g., 900 °C) used in this work. Melting at
higher temperature is limited by the softening temperature (1100 °C) of the silica glass tube, and the very
explosive nature of the glass preparation procedure.
Samples containing 2 and 5 mol.% ZnSe were chosen to study the influence of the thermal treatment temperature on the crystallization process (Fig. 1(b) and Fig. 1(c)). For both samples, the higher the annealing temperature, the greater the amount of ZnS crystals precipitating from the samples. It is noted that although ZnSe is used as the raw material, only ZnS crystals grow out of the samples upon thermal treatment, indicating that ZnSe is fully dissolved into and mixed with the As$_2$S$_3$ compound. Since zinc has a higher propensity to bonding with sulfur than selenium because of the larger difference in the electron negativities between Zn and S, it is expected that thermal treatment facilitates formation of ZnS crystals. Also ZnS is not a typical glass forming compound [14]. The crystal size was calculated using the Scherrer Equation, $D = K\lambda/\beta\cos\theta$, where $K$ is taken as 0.89, $\lambda$ (the wavelength of the CuK$\alpha_1$ source) is 0.15405 nm, $\beta$ is the full-width-at-half-maximum of the diffraction peaks, and $\theta$ is the diffraction half-angle. The particle sizes are in a range between 30-80 nm. The sample containing 5 mol.% ZnSe appears to be the optimal component when considering its controlled crystallization and excellent transparency. Given the charge balance and size matching between Zn$^{2+}$ and TM$^{2+}$, it is expected that TM$^{2+}$ ions can readily substitute for Zn$^{2+}$ sites provided by the embedded II-VI nanocrystals, and hence achieving the favorable chemical environments to lase in the mid-infrared wavelengths [21].

The morphology, distribution and size of the embedded nanocrystals were characterized using a TEM (Fig. 2). Fig. 2(a) shows that ZnS nanocrystals within the amorphous glass take on the typical needle-like shape [22] and are 40 ~ 80 nm in length size, in line with the XRD results and the Scherrer equation calculation. Besides, the measured d-spacings in Fig. 2(b) are fully consistent with pure ZnS.

The transmission spectra are shown in Fig. 3. The Vis-to-IR transmission decreases with the increasing ZnSe content (Figs. 3(a) and (c)), which is caused by two factors: the increased crystallinity and the refractive index (inset in Fig. 3(c)). The former leads to an increased Rayleigh scattering because the particle size of the
embedded ZnS crystals approaches one tenth to one fiftieth of Vis and NIR wavelengths. The latter results in the increased reflectivity because it is proportional to the refractive index according to the Fresnel formula [18]. The transmission drops below 50 % when the ZnSe content is greater than 10 mol.%, thus samples containing higher ZnSe concentrations are not suitable for drawing fibers. On the other hand, the 5 mol.% ZnSe sample retains reasonably good transparency (~ 60 %) in a spectral range from 1 to 10 μm after crystallization, which covers both the pump (1.55 ~ 2.1 μm) and the lasing (2.0 ~ 5.0 μm) wavelengths of Tm³⁺, therefore, the absorption losses of the pump and the laser emission power can be reduced. However, the transmission decreases to an unacceptable level for optical applications when samples are heat treated at higher temperatures (≥ 240 °C) (Figs. 3 (b) and (d)). The arrows shown in the IR transmission spectra (Fig. 3(c)) indicate the existence of absorption bands due to impurities: -OH in 2.8 and 6.3 μm, Se-H in 4.12 and 4.5 μm, SeO₂ in 8.7 μm, -Se-O in 10.7 μm. Therefore, the samples have to be further purified to minimize the impurity-induced losses.

The structure of the samples was studied using Raman microscopy (Fig. 4). For samples containing a limited amount of ZnSe (≤ 5 mol.%), three major vibrational bands can be observed, namely, the 180 cm⁻¹ band is ascribed to the intra-cage bond-stretching mode of As₂S₄ monomers [22], the 230 cm⁻¹ is the As-As stretching with some admixture of As-S bending modes, and the 340 cm⁻¹ is the asymmetric As-S stretching mode [23-24]. For the higher ZnSe concentration samples (≥ 10 mol.%), a new vibrational band appears at 252 cm⁻¹ which is due to the presence of the Zn-Se mode [25-26]. When As₂S₃ is replaced by ZnSe, both the 230 and 252 cm⁻¹ bands become stronger (Fig. 5(b)), and the former also shifts to a lower frequency of 228 cm⁻¹ indicative of the formation of the antisymmetric As-Se-As stretching mode [27]. In summary, the addition of ZnSe facilitates the formation of Zn-Se and As-Se at the expense of As-S bond.

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The variations of density, molar volume ($V_m$), micro hardness ($H_v$) and glass transition temperature ($T_g$) as a function of the ZnSe content are shown in Fig. 5. The more $As_2S_3$ being replaced by ZnSe, the higher the density and the smaller the molar volume of the samples. The micro hardness initially decreases until the concentration value 5 mol.% ZnSe is reached, and then increases with further increase in the ZnSe content (Fig. 5(a)). Density is determined by the average molecular mass and atomic packing efficiency (APE). The average molecular mass of ZnSe is larger than that of $As_2S_3$, thus it is obvious that as lighter $As_2S_3$ being replaced by heavier ZnSe the density should increase. Moreover, both $As_2S_3$ and $As_2Se_3$ ChGs are characterized by the layered-continuous-random-network [23]. The addition of ZnSe introduces Zn$^{2+}$, which possibly plays the role of inter-layer-linking and results in a compact glass network. The validity of such an assumption can be reflected by the decreased molar volume as the ZnSe content increases. Generally, the micro hardness of glasses is smaller if the glass network consists of weaker chemical bonds. Therefore, as ZnSe is substituting for $As_2S_3$, a decreased micro hardness should be expected because of the formation of weaker chemical bonds attributed to Zn-Se and As-Se as indicated by the Raman spectra shown in Fig 4. The micro hardness decreases when ZnSe increases up to 5 mol.%. However, for the crystallized glasses (also referred to as glass-ceramics, GCs), the micro hardness usually increases with increasing crystallinity [28]. As illustrated in Fig. 1(a), the crystallinity which is indicated by the marked increase in intensity of XRD diffraction peaks for ZnSe concentration values above 5 mol.%. As a result, the micro hardness increases. On the other hand, the glass transition temperature which bears a close relationship with the average bond strength of glasses decreases as the stronger As-S bonds are being replaced by weaker chemical bonds (Fig. 5(b)).

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IV CONCLUSION

A new system of ChGs and GCs, (100-x)As$_2$S$_3$-xZnSe ($x = 0 \sim 30$ mol. %), has been successfully synthesized which is compatible with a low loss fiber drawing method and is a viable candidate for Mid-IR fiber lasing applications. When As$_2$S$_3$ was replaced by ZnSe, the density was found to increase while the molar volume decreases, owing to the increased atomic packing efficiency induced by the presence of Zn$^{2+}$. The glass transition temperature decreases because of the decreased average bond strength. The variation of the microhardness was determined by two factors, namely, the bond strength and the crystallinity which vary with opposing trends as the ZnSe concentration increases. Transparent GCs containing pure needle-like ZnS nanocrystals in the size range 30-80 nm were obtained using refined thermal treatment. The tendency for devitrification was found to increase with increasing ZnSe content such that the transmission properties severely degrade when the ZnSe was increased above 5 mol.%. When heat treated at higher temperatures ($\geq 240$ °C), the GCs were also found to suffer from decreased transmission (increased loss) which restricts their optical applications. In view of crystallinity and transparency, the 5 mol.% ZnSe glass heat treated at 200 °C could be the optimum target for TM$^{2+}$ doping. The next stage of this investigation will be to dope Cr$^{2+}$ ions in such GCs and study their mid-infrared photoluminescence properties.

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REFERENCES


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[26] Lin CM, Chuu DS, Yang TJ, et al., Raman spectroscopy study of ZnSe and Zn$_{0.84}$Fe$_{0.16}$Se at high pressures. Phys Re B. 1997;55:13641-13646.


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Figure caption list

Fig 1. (a) XRD patterns of powdered samples (100-x)As_{2}S_{3-x}ZnSe (x = 0, 2, 5, 10, 20, 30 mol. %) heat treated at 180 °C for 5hr.; (b) and (c) XRD patterns of the samples containing 2 and 5 mol.% ZnSe respectively, heat treated at different temperatures for 5hr. (with unified Y axis).

Fig. 2 (a) TEM bright field image of the crystallized 5 mol.% ZnSe glass; (b) HRTEM image of the selected area indicated by the red rectangle. Here only one spot showing the d-spacing is selected for demonstration.

Fig. 3 (a) Vis-NIR and (c) IR transmission spectra of samples (100-x)As_{2}S_{3-x}ZnSe (x = 0, 2, 5, 10, 20, 30 mol. %) heat treated at 180 °C for 5hr. Insets in (a) and (c) are digital photos of the samples and dispersion of refractive indices (from 1.5 to 20 μm) for samples x = 0, 2, 5; (b) Vis-NIR and (d) IR transmission spectra of the 5 mol.% ZnSe sample heat treated at different temperatures (180, 200 and 240 °C).

Fig. 4 (a) Raman spectra of samples (100-x)As_{2}S_{3-x}ZnSe (x = 0, 2, 5, 10, 20, 30 mol. %). The spectra are normalized with respect to the 340 cm\(^{-1}\) band; (b) Intensity ratios of the 228 and 252 cm\(^{-1}\) to the 340cm\(^{-1}\) band.

Fig. 5 (a) Variations of density (g/cm\(^{3}\)), molar volume (Vm, cm\(^{3}\)/mol), micro hardness (Hv, Kg/mm\(^{2}\)) and (b) glass transition temperature (Tg, °C) as a function of the ZnSe content. Inset in (b) shows a typical DSC curve and the way to obtain the Tg value.

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