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Crystal-field engineering of ultrabroadband mid-infrared emission in Co^{2+} -doped nano-chalcogenide glass composites

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ABSTRACT

Tunable and ultrabroadband mid-infrared (MIR) emissions in the range of 2.5–4.5 μm are firstly reported from Co^{2+} -doped nano-chalcogenide (ChG) glass composites. The composites embedded with a variety of binary (ZnS, CdS, ZnSe) and ternary (ZnCdS, ZnSSe) ChG nanocrystals (NCs) can be readily obtained by a simple one-step thermal annealing method. They are highly transparent in the near- and mid-infrared wavelength region. Low-cost and commercially available Er^{3+} -doped fiber lasers can be used as the excitation source. By crystal-field engineering of the embedded NCs through cation- or anion-substitution, the emission properties of Co^{2+} including its emission peak wavelength and bandwidth can be tailored in a broad spectral range. The phenomena can be accounted for by crystal-field theory. Such nano-ChG composites, perfectly filling the 3–4 μm spectral gap between the oscillations of Cr^{2+} and Fe^{2+} doped II–VI ChG crystals, may find important MIR photonic applications (e.g., gas sensing), or can be used directly as an efficient pump source for Fe^{2+} : II–VI crystals which are suffering from lack of pump sources.

1. Introduction

Much attention has been paid to broadband mid-infrared (MIR) light sources in the wavelength range of 2–5 μm , covering the important “atmospheric window of transparency”, “water absorption band” and “molecular fingerprints” [1]. Since firstly demonstrated by Laura et al in 1996 [2], MIR light sources based on divalent transition metal ions (TM^{2+} : Cr^{2+} , Fe^{2+} etc.) doped group II–VI chalcogenide (ChG) crystals (e.g., ZnS, ZnSe etc.) have achieved remarkable progress and become commercially available [3]. The most favorable attributes of TM^{2+} -doped II–VI crystals include but are certainly not limited to that: they have an extremely broad laser-wavelength tuning range ($\sim 0.5\lambda_0$, λ_0 is the emission peak wavelength). Such a merit stems from the unique photoluminescence (PL) properties of TM^{2+} which are extremely sensitive to local crystal-field environment. It has been demonstrated that the PL band positions and correspondingly, the lasing wavelengths

of Cr^{2+} and Fe^{2+} can be tailored by a solid solution and crystal-field engineering (CFE) approach [4], viz., forming ternary or quaternary ChG crystals by cation and/or anion substitution (scheme figure, Fig. 1) [5–7]. For example, through Mg^{2+} substitution for Zn^{2+} in $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ crystals, the lasing wavelengths of Cr^{2+} and Fe^{2+} dopants can be tuned from 2.2 to 2.6 μm [5], and from 4.5 to 5.1 μm [6], respectively. Despite that Cr^{2+} and Fe^{2+} doped ChG crystals have enjoyed a great success in covering wide MIR spectral ranges, the 3–4 μm wavelength range still remains as a spectral gap waiting for its competitive candidates.

Divalent cobalt ions, when tetrahedrally coordinated in II–VI ChG crystals, show strong PL in the 3–4 μm wavelength range, perfectly filling the spectral gap mentioned above [2]. Because of the spectral overlap between Co^{2+} emission and Fe^{2+} absorption bands, Co^{2+} has been proposed as an effective sensitizer for Fe^{2+} MIR lasing via the $\text{Co}^{2+} \rightarrow \text{Fe}^{2+}$ energy transfer (ET) [8]. Moreover, Co^{2+} has two strong absorption bands at ~ 730 and 1600 nm, which can be potentially

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Fig. 1. Scheme of crystal field engineering of TM^{2+} (e.g., Co^{2+}) emission via cation or anion substitution. CB: conduction band; VB: valence band. The indicated energy (in eV) correlates with the emission peak wavelength of Co^{2+} in the corresponding crystals derived from Fig. 7 shown below.

excited by readily available bulk, fiber or diode lasers. Recently, Co^{2+} activated II–VI ChG crystals have attracted increasing interest. For example, Chen et al reported broadband MIR emissions upon 808 nm excitation in Co^{2+} : ZnSe nanocrystals (NCs) prepared by hydrothermal method [9]. Ali et al observed a MIR emission in a Co^{2+} doped metal-organic framework glass [10]. For bulk photonic applications, NCs should be incorporated and well protected in an inert host free of undesirable hydroxyl and organic species [10]. However, we have not been aware of any studies pertaining to Co^{2+} MIR emissions in inorganic glasses, let alone the CFE of the Co^{2+} emissions [11,12]. The inorganic glasses, when compared to their crystal counterparts, have the following advantages of: 1) feasibility of waveguiding (e.g., by drawing into optical fibers) and thus being potentially free of the detrimental thermal lensing effect [13]; and 2) capability of chip-scale production for integrated optics [1,11].

By the aid of diffusion limited crystallization, we have previously synthesized nanoscale Cr^{2+} : ZnS crystals embedded in inorganic Ge-As-S ChG glass [13,14]. The nano-ChG glass composites thus obtained retain good IR transparency and more importantly show intense ultrabroadband MIR emission of Cr^{2+} [14]. In this work, an ultrabroadband MIR emission was obtained in a similar type of transparent nano-ChG glass composites embedded with Co^{2+} : ZnS NCs. It is, however, important to note that by proper adjustment of glass compositions, various Co^{2+} doped ternary ChG NCs can be thermally grown in the designed ChG glasses for the first time. Those ternary crystals formed due to cation or anion substitution (Fig. 1) impart a variety of crystal-field environments for Co^{2+} . As such, the emission properties including the peak wavelength and bandwidth can be engineered in a broad spectral

range.

2. Experiments

Samples with the compositions of (in mol.%) $90\text{Ge}_{2.5}\text{As}_{1.5}\text{S}_6 - 10\text{ZnSe}$ (ZnS), $90\text{Ge}_{2.5}\text{As}_{1.5}\text{S}_6 - 5\text{ZnSe} - 5\text{CdSe}$ (ZnCdS), $90\text{Ge}_{2.5}\text{As}_{1.5}\text{S}_6 - 10\text{CdSe}$ (CdS), $90\text{Ge}_{2.5}\text{As}_{1.5}\text{S}_3\text{Se}_3 - 10\text{ZnSe}$ (ZnSSe), and $90\text{Ge}_{2.5}\text{As}_{1.5}\text{S}_6 - 10\text{ZnSe}$ (ZnSe), all doped with 0.2 mol.% CoCl_2 were prepared by melt-quenching method. Raw materials (Ge, As, S, Se, ZnSe with 5N-purity, and CoCl_2 , CdSe with 4N-purity) were weighed in a glove box purged with nitrogen gas, and melted at 950 °C for 12 h in an evacuated (10^{-3} Pa) silica glass tube. The melts were then quenched in cold water and for 5 h.

X-ray diffraction (XRD) patterns were measured by an X-ray diffractometer (D/MAX 2550VB/PC, Rigaku Corporation, Japan) with the Cu-K α irradiation. High-angle-annular-dark-field scanning TEM (HAADF-STEM) was measured using FEI Talos F200x, USA, operating at 200 kV and equipped with an energy-dispersive spectrometer (EDS) system. The elemental mapping was measured in the STEM-EDS mode [15]. Optical transmission spectra were measured by a Perkin-Elmer Lambda 950 UV-VIS spectrophotometer from 500 to 2500 nm, and by a Bruker Tensor 27 Fourier transform infrared spectrophotometer (FTIR, Ettlingen, Germany) from 2.5 to 15 μm . PL spectra were measured by an Edinburgh FLS980 fluorescence spectrometer (Edinburgh Instruments), with the PL intensity corrected by the instrumental response. The excitation source was a 1570 nm erbium-doped fiber laser.

3. Results and discussion

Limited by the softening temperature of the silica glass tube (1100 °C), the ZnSe and CdSe compounds were used as the Zn and Cd metal sources. However, because the standard enthalpy of formation for ZnS (-205 kJ/mol) is greater than that of ZnSe (-170.3 kJ/mol), the former crystal is expected to grow with a larger formation probability in sulfur-containing ChG glasses upon thermal annealing [13,14]. It is indeed the case as shown in XRD spectra (Fig. 2). Several sharp diffraction peaks are superimposed on a broad amorphous background typical of nano-glass composites. Referring to the standard crystals from the Joint Committee on Powder Diffraction Standards (JCPDS), wurtzite ZnS (PDF No. 36-1450), cubic CdS (80-0019), hexagonal ZnSe (37-1463) and $(\text{Zn}_{0.5}\text{Cd}_{0.5})\text{S}$ (01-089-2943 in Highscore software) crystals can be identified unambiguously from the ZnS, CdS, ZnSe and ZnCdS samples, respectively. The success in the formation of the ternary $(\text{Zn}_{0.5}\text{Cd}_{0.5})\text{S}$ crystal benefits from the complete solid solution of ZnS and CdS (Fig. 2(a)) [16].

In the ZnSSe sample, though its crystallographic peaks do not match any of those reference ternary $\text{Zn}(\text{S}_x\text{Se}_{1-x})$ crystals included in JCPDS, the crystal composition (the x value) can be estimated according to

Fig. 2. XRD spectra of (a) the ZnS, CdS and ZnCdS samples, and (b) the ZnSe, ZnSSe samples. Reference ZnS, CdS, ZnSe and ZnCdS crystals are also shown at the figure bottom for comparison.

Vegard's law [17]. In the calculation, the *c*-axis lattice parameter is linearly dependent on the composition *x*, $c_{(x)} = x c_{\text{ZnS}} + (1-x) c_{\text{ZnSe}}$, where c_x , c_{ZnS} , and c_{ZnSe} are the lattice parameters of $\text{Zn}(\text{S}_{x}\text{Se}_{1-x})$, ZnS and ZnSe, respectively. For the calculation, we used the diffraction peaks for the (002), (110) and (112) planes of ZnS, which lie at 20–28.5°, 20–47.6°, and 20–56.4°, respectively; and the diffraction peaks for the (111), (220) and (311) planes of ZnSe, which lie at 20–27.3°, 20–45.4°, and 20–53.6°, respectively. The calculated *x* value is 0.52 with an uncertainty of 0.02 related to the composition fluctuation within the XRD probe size (~1 mm).

The crystallinity (volume fraction of the crystalline phase), estimated by the ratio of the crystallographic peak area to the whole XRD pattern, is a critical parameter. The larger the crystallinity, the more tetrahedral crystal sites available for the dopants (Co^{2+}), and thus the stronger the MIR emission. Taken as an example, the crystallinity in the ZnSSe sample is approximately 4%, being four times of that found in the As_2S_3 -ZnSe nano-glass composite (~1%) [13]. We have tried to further increase the crystallinity by tuning the annealing temperature and time. It is found that the annealing temperature plays a more important role in increasing the crystallinity, but the samples with a higher crystallinity also suffer from deteriorated transparency. In this work, the annealing conditions were optimized with respect to the crystallinity and optical transparency.

The microscopic morphology of nano-composites was examined by TEM as shown in Fig. 3. In the ZnCdS sample (cation-substitution), the rod-shaped particles of ~60 nm in width and ~200 nm in length are distributed in the glass matrix (Fig. 3(a)). The lattice fringe as shown in Fig. 3(c) presents the interplanar spacings of 0.34 and 0.30 nm, corresponding well to the (100) and (101) planes of wurtzite ($\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$) crystal, respectively. We have previously shown that pure phase hexagonal wurtzite ZnS nanorods can be formed in a similar ChG glass [14]. Here, we provide important evidence that the crystal morphology is preserved in the cation-substituted ternary ($\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$) NCs [16]. This is in sharp contrast to the ZnSSe sample (anion-substitution). As shown in Fig. 3(d), the ZnSSe NCs have the shape of nanorods with a number of small-sized branches that tend to form clusters. The interplanar spacings are 0.64 and 0.34 nm as marked in Fig. 3(f), corresponding well to the (0001) and (1010) planes of the wurtzite Zn ($\text{S}_{0.51}\text{Se}_{0.49}$) crystal reported previously, and confirming the validity of Vegard's law [17]. In both cases of the ternary ZnCdS and ZnSSe samples, dislocation and stacking faults of the NCs can be found as illustrated in Fig. 3(b) and (e), which are caused by the lattice mismatch [9,18].

The nanoscale distribution of the Co^{2+} dopant as well as the other elements was checked by STEM-EDS elemental mapping. The enrichment of the Zn, Cd and Co elements in the nanorods embedded in the ZnCdS sample can be clearly seen as shown in Fig. 4. While the Ge and

As elements show complementary distributions to the above elements. The results indicate that Co^{2+} is successfully doped into the NCs, and the growth of the NCs is likely to be hindered by a diffusion barrier formed by the highly viscous, germanium and arsenic-enriched shell [14]. Similar results were found in the ZnSSe sample with the embedded tetrapod NCs being enriched in the Zn, S, Se and Co elements (Fig. 5).

Optical transparency is crucial for such nano-glass composites to be potentially applied to optical fibers, planar waveguides and laser gain media. Transmission spectra of samples are shown in Fig. 6. For all the samples, the transparency in the wavelength range of 0.8–5 μm is over 50%. The overall transparency and particularly that in the NIR range (0.8–2 μm) is higher than that of Cr^{2+} -doped nano-composites studied recently [14]. The good transparency owes its origin to the favorable refractive index matching between the ChG glass matrix and the embedded ChG crystals (~2.40) [19]. Three absorption bands can be observed peaking at ~2800 (ν_1), 1550 (ν_2) and 700 nm (ν_3), which can be assigned to the spin allowed transitions from the $^4\text{A}_2$ (F) ground state to the $^4\text{T}_2$ (F), $^4\text{T}_1$ (F) and $^4\text{T}_1$ (P) excited states of Co^{2+} in tetrahedral site [9]. The crystal field splits the lowest ^4F state of a free Co^{2+} into the $^4\text{T}_1$ (F) and $^4\text{T}_2$ (F) excited states and the $^4\text{A}_2$ (F) ground state. The energy splitting between these ground and excited states is subjected to the crystal field strength 10Dq which can be estimated by [4]:

$$Dq = \frac{Q^2 r^4}{24\pi\epsilon_0 R^5} \quad (1)$$

Where, *Q* is the charge of the ligand, *r* is the mean radius of 3d-electrons, ϵ_0 is the dielectric susceptibility and *R* is the metal ion-to-ligand distance. According to the Tanabe-Sugano (TS) diagram of tetrahedrally coordinated d^7 ion (e.g., Co^{2+}) (Fig. 7(b)), the energy splitting decreases with the decreasing value of *Dq*. The *Dq* and Racah *B* parameter, an interelectronic repulsion parameter, can be obtained by $\nu_1/10$ and $(\nu_2 + \nu_3 - 30Dq)/15$ [20], respectively, which are 329.7 cm^{-1} (633.6 cm^{-1}), 342.7 cm^{-1} (647.2 cm^{-1}), 343.3 cm^{-1} (643.3 cm^{-1}) and 346.8 cm^{-1} (666.2 cm^{-1}), for the ZnSe, ZnSSe, ZnCdS and ZnS samples. The substitutions of Zn and S by Cd and Se of larger ionic sizes result in smaller *Dq* values, and thus “red shift” in the emission band to longer wavelength is expected as indeed observed experimentally (Fig. 7(a)).

Ultra-broadband MIR emissions covering the wavelength region of 2.5–4.5 μm are observed, for the first time to our knowledge, in the Co^{2+} -doped nano-ChG glass composites (Fig. 7(a)). The MIR emission originates from the $^4\text{T}_2$ (F) → $^4\text{T}_1$ (F) transition of Co^{2+} . Its peak wavelength can be tuned from 3.0 (ZnS) to 3.28 (ZnSSe) and 3.34 (ZnSe), and up to 3.5 μm (ZnCdS) via the anion or cation substitution. The emission bandwidth defined by the full-width-at-half-maximum (FWHM) increases following the same order of the red shift in the emission band (λ_0 , E_0). The FWHM broadens from 664 nm in ZnS to 786 nm in ZnSSe and 846 nm in ZnSe, and up to 933 nm in ZnCdS. Generally speaking, crystals with larger lattice constants represent “soft” surroundings for the luminescent ion, and exhibiting a larger Stokes shift ($\Delta\lambda$). This will then produce a broader absorption or emission band (larger ΔE) according to the expression $[(\Delta\lambda/\lambda_0) \propto (\Delta E/E_0)^{1/2}]$ [21]. Furthermore, the multiple crystal sites experienced by Co^{2+} due to CFE of the NCs can also lead to broadened emission band. Such tunable and ultra-broad MIR emissions effectively embrace a number of characteristic emissions of rare-earth (RE) ions, including 2.7 μm of Er^{3+} , 2.9 μm of Ho^{3+} and Dy^{3+} , 3.8 μm of Tm^{3+} , 4.3 μm of Dy^{3+} [22,23]. The emission dip centered at 4.23 μm is due to the absorption of CO_2 in air. The nano-ChG glass composites present herein are potential waveguide materials for gas detection (of H_2O at 2.9 μm, NH_3 at 3.0 μm, CH_4 at 3.2 μm, H_2S at 4.0 μm, N_2O at 4.4 μm, and CO_2 at 4.2 μm etc.) [22].

It is interesting to note that no MIR emission is observed in the Co^{2+} doped CdS sample, which can be accounted for by the different doping behaviors of Co^{2+} in ZnS and CdS NCs. Previous studies have

Fig. 3. TEM images of (a, b) the ZnCdS and (d, e) ZnSSe samples. HRTEM images of (c) the ZnCdS and (f) ZnSSe samples. The d-spacing are marked by lines in (c) and (f).

Fig. 4. (a) HAADF-STEM image of the ZnCdS sample, and its corresponding STEM-EDS elemental mappings of (b) Zn, (c) Cd, (d) Co, (e) As, (f) Ge, (g) S, with their concentrations reflected by the brightness in colors.

Fig. 5. (a) HAADF-STEM image of the ZnSSe sample, and its corresponding STEM-EDS elemental mappings of (b) Zn, (c) S, (d) Co, (e) As, (f) Ge, (g) Se, with their concentrations reflected by the brightness in colors.

Fig. 6. Transmission spectra of (a) the ZnS, ZnCdS, and CdS samples, and (b) the ZnS, ZnSSe, ZnSe samples with a fixed thicknesses of 2.0 mm. Insets are the expanded and normalized absorption band of Co^{2+} .

demonstrated that the large mismatch between the ionic radii of Co^{2+} ($0.74 \text{ \AA}$) and Cd^{2+} ($0.97 \text{ \AA}$) precludes the internal doping of Co^{2+} in CdS, while the similarity of Zn^{2+} ($0.74 \text{ \AA}$) and Co^{2+} ionic radii allows isotropic incorporation of Co^{2+} in ZnS during nanocrystal growth [24]. Because Co^{2+} ions bond primarily to the surfaces of the CdS NCs, the spectroscopic properties of Co^{2+} doped CdS NCs are much more susceptible to surrounding chemical environments. For example, the

absorption intensity of Co^{2+} in CdS quantum dots solution decays gradually with time because of exposure of surface-bound Co^{2+} ions to solvent. Similarly, because Co^{2+} ions tend to bond to the surface of the CdS NCs embedded in the glasses, Co^{2+} ions are more readily influenced by hydroxyl groups which exist as impurities known for their strong luminescence quenching effect in glasses [25].

Fig. 7. (a) MIR emission spectra of the ZnS, ZnSSe, ZnSe, ZnCdS, and CdS samples excited by a 1570 nm Er^{3+} -doped fiber laser (0.6 W). The characteristic emission spectra of some selected rare-earth ions are also included. The shaded area corresponds to the absorption band of carbon dioxide. (b) Tanabe-Sugano (TS) diagram for the tetrahedrally coordinated Co^{2+} in the investigated samples.

4. Conclusion

A variety of Co^{2+} -doped binary and ternary ChG NCs is thermally grown in the ChG glasses. The nano-ChG glass composites thus obtained possess good optical transparency, and show MIR emissions perfectly filling the 3–4 μm spectral gap. By adjustment of the glass compositions, the NCs embedded in the glasses can be engineered through the cation- and anion-substitutions such that new ternary $(\text{Zn}_{0.5}\text{Cd}_{0.5})\text{S}$ and $\text{Zn}(\text{S}_{0.52}\text{Se}_{0.48})$ ChG NCs are obtained for the first time. The composition of the $\text{Zn}(\text{S}_{0.52}\text{Se}_{0.48})$ NCs is determined with respect to Vegard's law and finds a good agreement with the TEM data. The TEM examination also provides direct evidence that Co^{2+} is enriched/doped in the precipitated ChG NCs. Because of the variations in the crystal field environments surrounding Co^{2+} , the MIR emission peak wavelength can be tuned from 3.0 up to 3.5 μm , and the bandwidth (FWHM) from 664 up to 933 nm. The phenomena can be understood by referring to the changes in the crystal field strength according to the TS diagram of tetrahedrally coordinated Co^{2+} . The CFE strategy demonstrated in this work can be extended to other ChG crystals and composites doped with TM^{2+} ions. It will be our next step to draw nano-ChG glass composite fibers based on the developed materials.

Declaration of Competing Interest

There are no conflicts to declare.

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