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OPTICAL FIBRES AND THIN-FILM WAVEGUIDES

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Mid-IR luminescence of Cr^{2+} : II – VI crystals in chalcogenide glass fibres

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***Abstract*. Optical fibres have been fabricated for the first time from As_2S_3 glass containing chromium-doped ZnS and ZnSe crystals, and their optical loss and luminescence spectra have been measured in the mid-IR. In the spectral range 2 – 3 μm, the optical loss in the fibres is 2 – 4 dB m^{-1}. The fibres have a broad luminescence band in the range 1.8 – 3 μm, with a maximum near 1.9 μm, which is due to Cr^{2+} $^5E - {}^5T_2$ intracentre transitions in the II-VI host.**

Keywords: *Cr^{2+}: II – VI, infrared lasers, IR gain media, chalcogenide glass fibres.*

Chromium-doped II – VI semiconductor materials (Cr^{2+} : II – VI) were first proposed as mid-IR lasing media more than ten years ago [1]. Since then, this area of research has seen rapid progress and Cr^{2+} : II – VI crystals have been demonstrated to lase in the range 1.9 – 3.6 μm. In Cr^{2+} : ZnSe crystals, lasing efficiencies above 60 % have been achieved in the continuous regime and 80-fs pulses have been obtained in mode-locked operation [2]. Further advances in research aimed at creating mid-IR gain media based on Cr : II – VI materials might be ensured by optical fibre technology. Its main advantages are the high stability of the cavity of fibre lasers, effective cooling, efficient pumping and high beam quality.

There are currently effective approaches for producing II – VI nanocrystals evenly distributed over host glass and controlling their size by varying synthesis conditions [3]. The ability to fabricate active optical fibres containing chromium-doped II – VI nanocrystals makes it possible to create an all-fibre laser source for the spectral range 2 – 3 μm pumped by existing fibre lasers at 1.6 – 1.9 μm. This would enable fibre lasers to take full advantage of achievements made with Cr^{2+} : II – VI crystals. In this paper, we report the first As_2S_3 glass fibres containing crystalline Cr^{2+} : II – VI. To produce low-loss optical fibres containing crystalline inclusions, the particle size of the crystalline phase should be small compared to optical wavelengths.

Attractive hosts for the fabrication of optical fibres containing Cr^{2+} : II – VI crystals are As – S glasses. They have been used to produce fibres with low mid-IR losses [4]. Zinc chalcogenides and arsenic-sulphur glasses differ little in refractive index, which reduces scattering losses in such fibres.

As_2S_3 glass was chosen as the most resistant to crystallisation among chalcogenide glasses [4]. The starting semiconductor materials, ZnS and ZnSe doped with 1 wt % chromium, were prepared by solid-state reactions between ZnS (ZnSe) and CrSe conducted in evacuated (10^{-4} Torr) silica tubes at 1000 °C for 144 h.

As_2S_3 glasses containing Cr^{2+} : ZnS and Cr^{2+} : ZnSe crystals were prepared in three steps: (1) distillation of the As_2S_3 host glass in order to remove insoluble impurity particles, (2) dissolution of the semiconductor phase in molten glass and (3) annealing intended to relieve the internal stress in the glass and ensure effective diffusion of the dissolved semiconductor phase. Cr^{2+} : ZnS(ZnSe) was dissolved at temperatures from 600 to 750 °C over a period of 1 – 5 h in a rocking furnace. The annealing temperature was varied from 200 to 280 °C, and the annealing time, from 12 to 65 h. The semiconductor content of the glass was varied in the range 0.1 wt % to 4 wt %.

The bulk samples thus prepared were drawn, using a single-crucible process, into As_2S_3 fibres 170 – 300 μm in diameter and 2 – 20 m in length, containing the semiconductor phases Cr^{2+} : ZnSe and Cr^{2+} : ZnS. Cr^{2+} luminescence was excited by a 1602-nm single-mode cw Er – Yb fibre laser. The luminescence was excited at one end of the fibre and detected at the other end. Luminescence spectra were measured using a monochromator, InAs photovoltaic detector and lock-in amplifier. The optical loss spectra of the fibres were taken on a Bruker IFS-113V Fourier transform spectrometer.

In the spectral range 1.5 – 2.7 μm, the loss in the fibres containing Cr^{2+} : ZnS was determined to be 2 – 4 dB m^{-1}, which was about three times the loss in the semiconductor-free glass fibre (Fig. 1). Transmission spectra were measured using ~ 1-m-long sections of the fibres, so the absorption band of chromium was masked by the scattering background. The absorption peaks at 1.9 and 2.25 μm are due to impurities in the host glass [4].

Figure 2 shows the luminescence spectra of the $As_2S_3 - Cr^{2+}$: ZnSe and $As_2S_3 - Cr^{2+}$: ZnS glass fibres and, for comparison, the spectrum of a chromium-doped ZnSe crystal [5]. The fibres have a broad luminescence band in the range 1.8 – 3 μm, with a maximum around 1.9 μm. This band is due to Cr^{2+} $^5E - {}^5T_2$ intracentre transitions in

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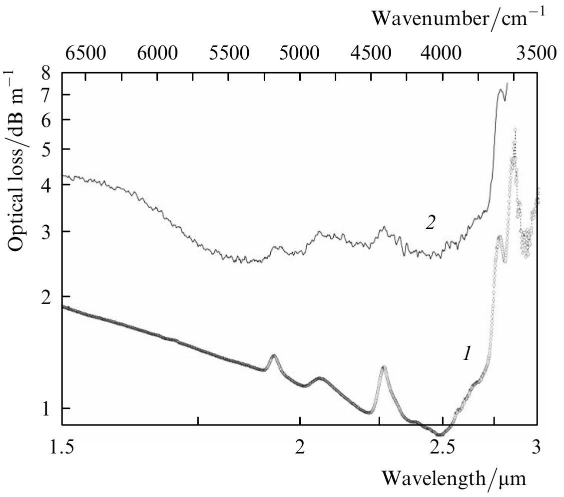

Figure 1. Optical loss spectra of (*1*) As_2S_3 and (*2*) As_2S_3 + 0.1 wt % Cr^{2+} : ZnS glass fibres.

the ZnS host. According to DeLoach et al. [1], the peak-emission wavelength of Cr^{2+} in ZnS is approximately 100 nm shorter than that in ZnSe. At the same time, the luminescence spectra of the $As_2S_3 - Cr^{2+}$:ZnSe and $As_2S_3 - Cr^{2+}$:ZnS glass fibres differ little in shape, and their maxima coincide. This may be the result of sulphur substitution on the selenium site in the ZnSe crystals. The nature of this effect remains to be established.

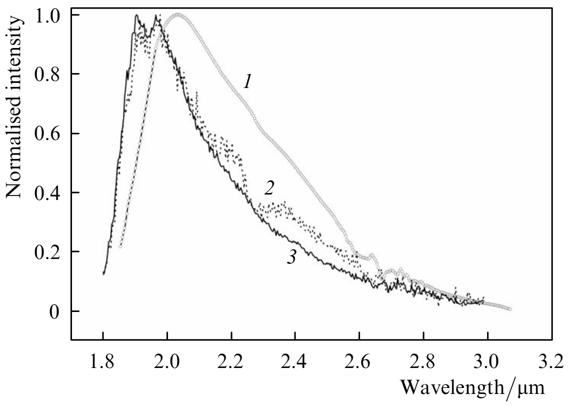

Figure 2. Luminescence spectra of (*2*) $As_2S_3 - Cr^{2+}$:ZnSe and (*3*) $As_2S_3 - Cr^{2+}$:ZnS glass fibres and (*1*) a bulk Cr^{2+} : ZnSe sample.

To detect the absorption band of chromium, we used ~ 20-m-long sections of the fibres. The concentration of tetrahedrally coordinated Cr^{2+} in the unannealed As_2S_3 glass fibre containing 0.1 wt % Cr^{2+} : ZnS was estimated at ~ 10^{15} cm^{-3}. The estimate was made using optical loss spectra and the formula [6] $\alpha_p = 0.144 \times 10^{-17} n_{Cr^{2+}}$, where α_p is the peak absorption coefficient for the Cr^{2+} $^5T_2 - {}^5E$ transition in ZnSe near 1.8 μm. According to DeLoach et al. [1], the absorption peak of Cr^{2+} in ZnS is shifted to shorter wavelengths by 80 nm relative to Cr^{2+} : ZnSe, so we used α_p at 1.7 μm. Assuming that all the Cr^{2+} : ZnS is crystalline and that the absorption on the $^5T_2 - {}^5E$ transition is only contributed by Cr^{2+} surrounded by ZnS, we find that the Cr^{2+} concentration in ZnS is at a level of 10^{18} cm^{-3}, which is close to the value optimal for the luminescence of bulk samples [6].

Thus, we have for the first time demonstrated 1.8- to 3-μm luminescence in As_2S_3 glass fibres containing chromium-doped ZnS and ZnSe crystals. The luminescence spectra of the $As_2S_3 - Cr^{2+}$:ZnSe and $As_2S_3 - Cr^{2+}$:ZnS glass fibres produced under identical conditions differ little in shape. The fibres range in optical losses from 2 to 4 dB m^{-1}. The present results suggest that materials based on chalcogenide glasses containing crystalline Cr^{2+} : II – VI inclusions may be suitable as gain media in fibre optics.

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