Towards Mid-IR Waveguide Lasers: Transition Metal Doped ZnS Thin Films

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Abstract: Thin films of Cr and Fe-doped ZnS suitable for waveguide mid-IR applications, with well-isolated TM^{2+} peaks, and Cr^{2+} absorption and fluorescence comparable to bulk crystals were investigated. Raman data indicate that the TM is substitutional.
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1. Introduction

Mid-infrared spectroscopy has a wide range of applications including medical and environmental diagnostics. One of the present limitations to the wide scale deployment of systems in this wavelength range is the size and cost of the sources, which are based on bulk gain materials [1,2]. Fabrication of waveguide lasers is desirable, but to date the best results have been obtained by defining a waveguide within a bulk material [3]. Polycrystalline and ceramic [4–6] materials have been used successfully for lasing, which suggests that thin film materials of sufficient quality for the production of channel waveguide devices are possible, and some progress has been made with pulsed laser deposition and molecular beam evaporation of TM doped films [7,8].

The most studied mid-IR gain and saturable absorber materials are ZnSe and ZnS, doped with Cr and Fe. We studied Fe and Cr doped ZnS, and also looked at co-doped material, since possible energy transfer from the Cr to the Fe [9] would allow pumping with shorter wavelengths.

2. Film growth and characterization

Films were deposited using an electron-beam for the metal, and a Knudsen cell for the ZnS, onto sapphire, CaF_2 and silicon substrates, at a base pressure < 10^{-5} Pa. Linear optical properties were measured in a spectrophotometer, and the optical constants (n,k, α) were derived using the Swanepoel [10] method. Fluorescence was measured using 1.6 μm excitation [11], and $\chi^{(3)}$ from the optical Kerr effect was measured at 0.8μm.

3. Optical and structural properties

Well-isolated absorption peaks (Fig. 1a) for Fe^{2+} were observed for concentrations up to ~4%, while for Cr, additional valence states and broadband absorption was observed for concentrations above ~0.3%, and co-doped films had a superposition of elemental absorption. The fluorescence in the vicinity of 2 μm for Cr:ZnS was compared to a bulk sample by calculating $e^{-\alpha t}$ for each sample to estimate the absorbed light and using this to normalize the fluorescence output(Fig. 1b). Yields comparable to the bulk were observed for concentrations <0.1%

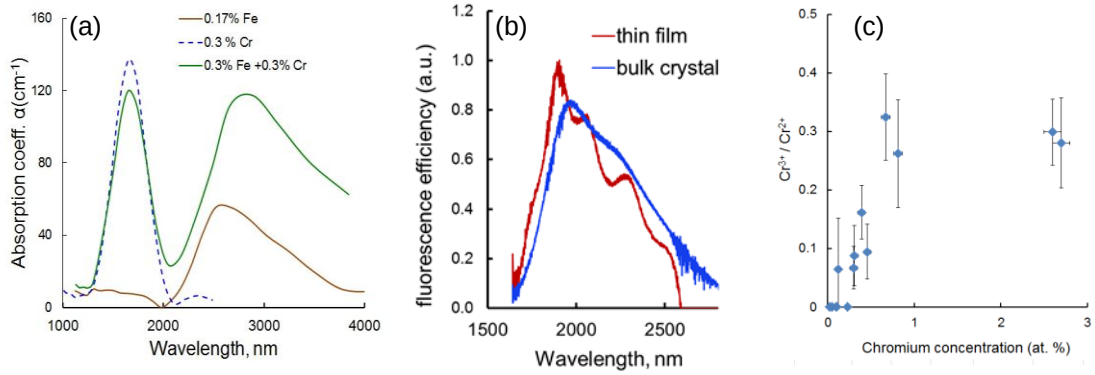

Fig. 1 Optical properties of TM-doped ZnS films (a) absorption coefficient of 4 μm thick films with 0.17% Fe, 0.3% Cr, and 0.3% of both Fe and Cr, showing isolation of the peaks (b) fluorescence of Cr:ZnS film, compared to bulk sample, normalized by the sample absorption. Oscillations in film data are interference effects.(c)Ratio of $Cr^{3+}$to Cr^{2+} as a function of Cr concentration.

Cr [11]. For higher concentrations, absorption due to Cr^{3+} states was seen, as indicated in Fig. 1c and fluorescence was reduced. Raman features between 280 and 340 (Fig 2a) indicate substitutional incorporation of the ions into the lattice. For iron, little degradation of the Raman spectrum was observed even at 4% concentration, in accord with the absorption results, and a large $\chi^{(3)}$ at 7% suggests these films may function as saturable absorbers. By 9%, Raman and $\chi^{(3)}$ results both indicate the onset of considerable lattice disruption (Fig 2a,b). X-Ray data (Fig 2c) show increasing order upon small additions of TM ions, with a significant reduction in the full-width half maximum of the primary diffraction peak (wurtzite (002)/sphaelerite (111)) for concentrations up to 2% for Cr and up to 7% for Fe,

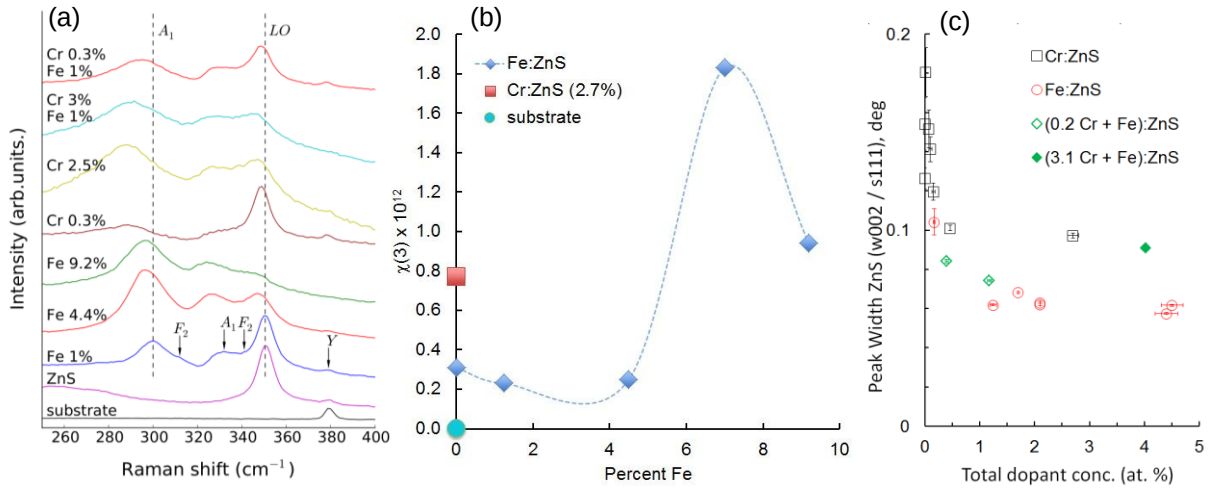

Fig. 2 (a) Raman spectrum of the films studied, showing modes in both spectra associated with substitutional transition metal ions. For Fe, good order is maintained for >4% concentration. (b) $\chi^{(3)}$ derived from optical Kerr effect measurements. Dashed line is a guide to the eye. (c) X-ray diffraction full width half maximum vs concentration for Cr and Fe substitutions in the lattice.

in agreement with Raman data. Fe doping reduces the FWHM more than Cr in both elemental and co-doped films.

5. Conclusion

Thin vapor-deposited films of ZnS with low concentrations of transition metal dopants show promising optical and structural properties for use as waveguide laser materials in the mid-infrared spectral region. Strong absorption with low background is seen for both Cr and Fe ions in these polycrystalline films, and the Cr fluorescence signal is comparable to that from bulk single crystals. So far, there is no indication that Fe and Cr interact in co-doped films.

6. References

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