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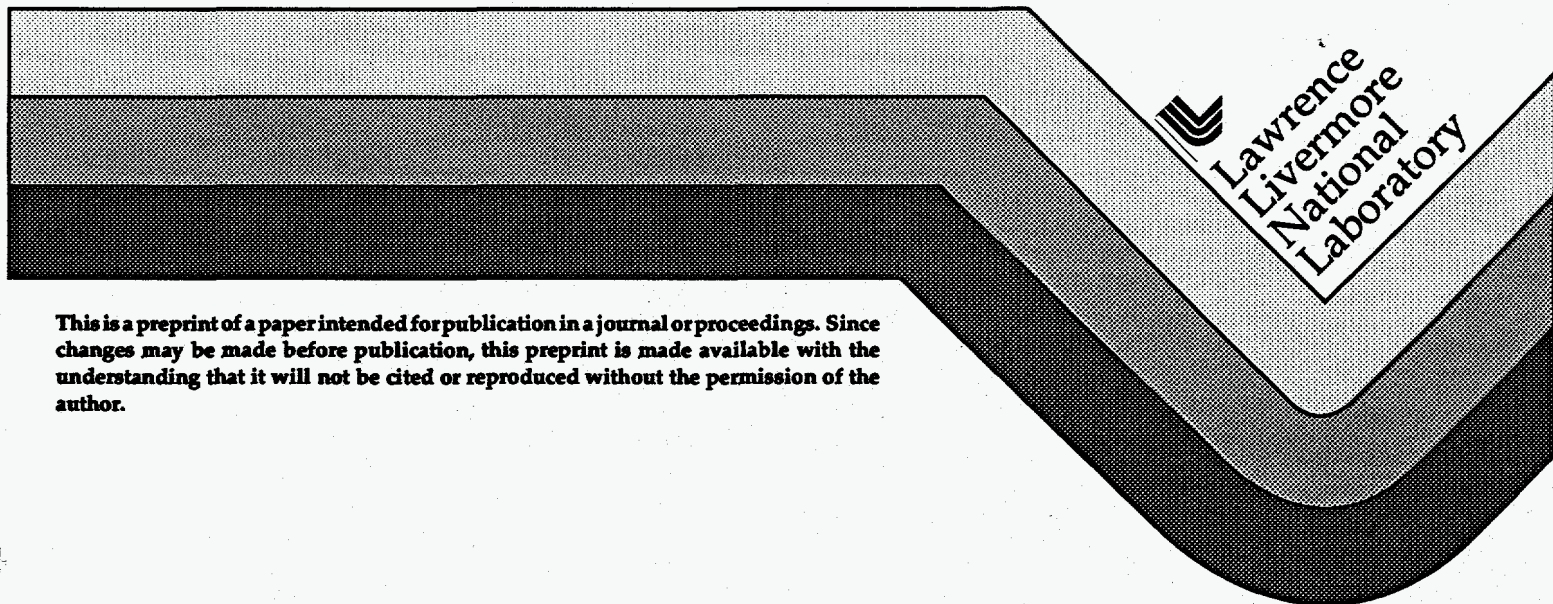
UCRL-JC-118192  
PREPRINT

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Crystals for Tunable IR Laser Radiation**

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**This paper was prepared for submittal to the  
Advanced Solid State Lasers 10th Topical Meeting  
Memphis, Tennessee  
January 30-February 2, 1995**

**March 17, 1995**



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**Properties of Transition Metal-Doped Zinc Chalcogenide  
Crystals for Tunable IR Laser Radiation**

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## Abstract

The spectroscopic properties of  $\text{Cr}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$ -doped single crystals of ZnS, ZnSe, and ZnTe have been investigated to understand their potential application as mid-IR tunable solid-state laser media. The spectroscopy indicated divalent Cr was the most favorable candidate for efficient room temperature lasing, and accordingly, a laser-pumped laser demonstration of Cr:ZnS and Cr:ZnSe has been performed. The lasers' output were peaked at  $\sim 2.35 \mu\text{m}$  and the highest measured slope efficiencies were  $\sim 20\%$  in both cases.

## Introduction

Room temperature solid state lasers capable of generating tunable radiation in the mid-infrared (IR) region are rare among transition metal ion lasers [1]. Consequently, optical parametric oscillators/amplifiers (OPO/OPA) are currently employed which offer wide wavelength tunability, but which impose certain pulse format requirements [2]. The development of tunable solid state lasers, although not as broadly tunable as OPO's, are desired as an alternative technology owing in part to their simplicity and compactness especially when pumped by diode lasers. To this end, we have initiated a search among a new class of potential laser media based on transition metals doped into crystals of II-VI compounds. In particular, our initial investigations have focused on the  $\text{Cr}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$ -doped crystals of ZnS, ZnSe, and ZnTe, otherwise referred to as the "zinc chalcogenides."

Most reported crystalline paramagnetic ion lasers have been based on oxide and fluoride media which incorporate the activator ions onto octahedral substitution sites [1]. Some exceptions include  $\text{Mn}^{5+}$  and  $\text{Cr}^{4+}$ -doped into the tetrahedrally-coordinated environment of a few different oxide hosts [3,4]. Interestingly, the acentricity of a tetrahedral lattice site offers some important advantages for long wavelength emission from transition metal ions, including a strong dipolar field, and the weaker crystal field splittings characteristic of the tetrahedral site over the octahedral site. The derived benefits are expected to include enhanced radiative emission rates which are more likely to compete favorably with nonradiative decay, and lower energy transitions which give rise to longer wavelength luminescence. The zinc chalcogenides are a class of materials based on tetrahedrally-coordinated arrangements of  $\text{S}^{2-}$ ,  $\text{Se}^{2-}$ , or  $\text{Te}^{2-}$  anions about the zinc cation. Accordingly, the transition metal (TM) ions doped into the zinc site of these hosts are more likely to demonstrate higher quantum yield efficiencies and luminesce at longer wavelengths than may be observed for many of their oxide and fluoride counterparts. We have measured the absorption and emission spectroscopic properties of the Cr, Co and Ni-doped crystals of ZnS, ZnSe and ZnTe with the intent of evaluating their potential for room temperature lasing in the 1.5 - 4.0  $\mu\text{m}$  range. Notably, the emission cross section and temperature-dependent lifetimes have been considered and would indicate that the  $\text{Cr}^{2+}$  ion has a potentially high gain cross section and low

nonradiative decay losses implying a favorable system with high emission quantum yields. Employing a Co:MgF<sub>2</sub> laser to optically pump these materials, we have demonstrated the first lasers based on Cr:ZnS and Cr:ZnSe. A survey of the measured TM ion spectroscopic properties in the zinc chalcogenides, and a description of the Cr<sup>2+</sup> lasing demonstrations performed in ZnS and ZnSe are presented in the following.

### Spectroscopic Results

Samples of Cr<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup> individually doped into ZnS, ZnSe, and ZnTe have been grown for us by Eagle-Picher Industries, Inc. The doped crystals were melt grown by the Bridgman technique and produced multicrystalline ingots which were approximately 2 cm in length by 2 cm in diameter. Unoriented spectroscopic samples were cut from single crystal regions and concentration analyses were made by inductively coupled plasma and mass spectrometry on sample volumes in immediate proximity. Room temperature absorption spectra were collected and converted to cross section values using the measured pathlength and the impurity concentration data. Room temperature emissions were collected by pumping samples with 1.907 μm light from a H<sub>2</sub> Raman-shifted Nd:YAG laser and looking for the lowest energy transitions between the crystal field split d levels. The emission cross sections were assessed using the Einstein relation [5]:

$$\sigma_{em} = \frac{\lambda^2 g(\nu)}{8\pi c n^2 \tau_{rad}} \quad (1)$$

where  $\lambda$  is the emission wavelength,  $g(\nu)$  represents the lineshape of the emission spectrum,  $c$  is the speed of light,  $n$  is the refractive index and  $\tau_{rad}$  is the radiative lifetime. Finally, the emission lifetime was measured as a function of temperature between 20 and 375 K. The value of  $\tau_{rad}$  used in Eq. (1) is taken from the extrapolated value of the lifetime at room temperature, irrespective of the onset of nonradiative decay. An important application of these data are in estimating the emission quantum yields,  $\eta_{QY}$ , where an approximation of the quantum yield efficiency at room temperature is given by the ratio of the room temperature lifetime to the low temperature

lifetime (where quenching can be neglected and decay is assumed to be purely radiative).

Strong absorption bands are in the range of 1.4-2.0 μm for Cr<sup>2+</sup> in the zinc chalcogenides and usefully match the output of the strained-layer InGaAs diode lasers [6]. The emission spectra are shown plotted in Fig. 1 and exhibit broad bands at ~2-3 μm with cross sections of ~75-188 × 10<sup>-20</sup> cm<sup>2</sup>. Both absorption and emission spectra have been obtained for the Co<sup>2+</sup> ion in the three hosts, and absorption spectra have been collected for the Ni<sup>2+</sup> ion in ZnS and ZnSe. The room temperature luminescence for Co is weaker than observed for Cr and is at 2.8-4.0 μm, while Ni emission at 2.5 μm is not observed above ~150 K.

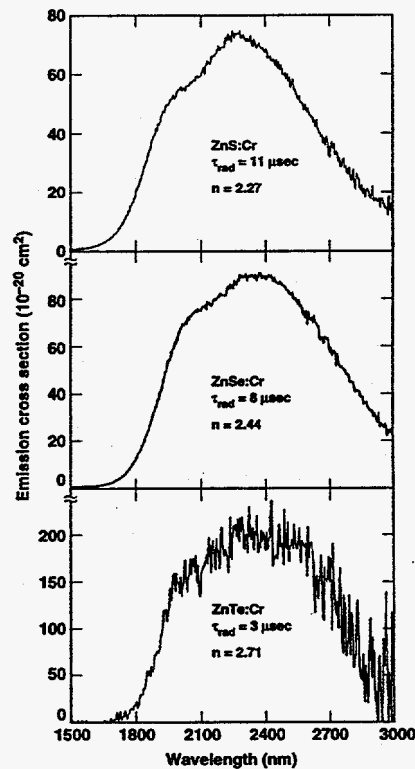


Figure 1. Emission spectra of Cr-doped zinc chalcogenides plotted in cross section units.

A comparison of the lifetime data measured as a function of temperature are presented in Figs. 2a-2c and more clearly demonstrate the differences among the three impurity ions. In particular, the Cr emission lifetime is very short,  $\tau_{em} \sim 7-10$  μsec, and apparently mostly radiative even near  $T = 300$  K, whereas the longer lifetime of Co,  $\tau_{em} \sim 0.6-1.1$  msec, appears to be impacted by nonradiative decay at

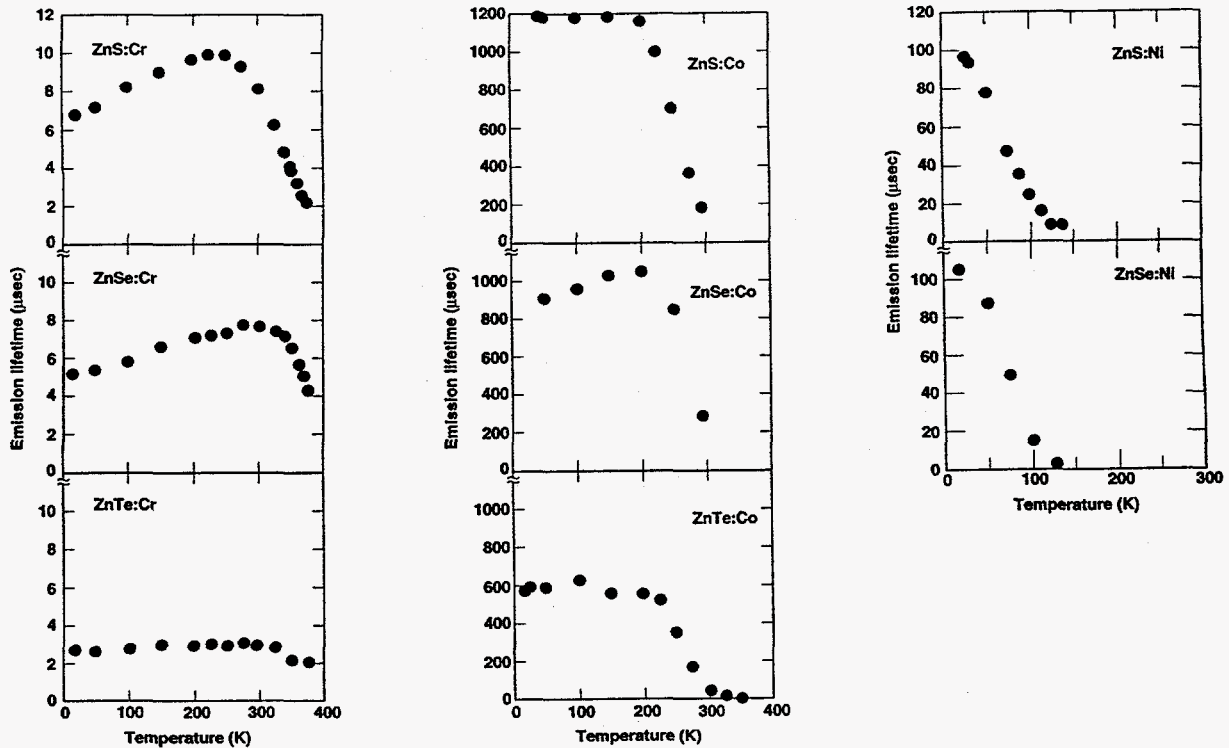


Figure 2. The measured emission lifetimes as a function of temperature for a.)  $\text{Cr}^{2+}$ , b.)  $\text{Co}^{2+}$ , and c.)  $\text{Ni}^{2+}$  in the zinc chalcogenides.

temperatures above 200 K. Finally, the Ni ion is seen to luminesce only at very low temperatures,  $T \leq 150$  K. A summary of the spectroscopic properties is presented in Table 1 where the samples we have characterized are enumerated with the measured impurity concentrations, the absorption cross section,  $\sigma_{\text{abs}}$ , the emission cross section,  $\sigma_{\text{em}}$ ,  $\tau_{\text{rad}}$ , and the room temperature lifetime,  $\tau_{\text{em}}$ , which are used to estimate the emission quantum yield with  $\eta_{\text{QY}} = \tau_{\text{em}}/\tau_{\text{rad}}$ .

The spectroscopic properties of Cr in the zinc chalcogenides are the most amenable to efficient lasing, i.e.  $\eta_{\text{QY}} \sim 100\%$  and  $\sigma_{\text{em}} \sim 10^{-18} \text{ cm}^2$ . In contrast, Co is estimated to have  $\eta_{\text{QY}} \sim 20\%$  and  $\sigma_{\text{em}} \sim 10^{-20} \text{ cm}^2$ , and Ni has no measurable room temperature luminescence. It is also noteworthy that the  $\text{Cr}^{2+}$  energy level schemes in these hosts suggest that excited state absorption losses will be low. Figs. 1 and 2 reveal a single spectral band corresponding to the Cr absorption and emission between the ground  $^5\text{T}_2$  and the excited  $^5\text{E}$  state. It turns out that this feature is the only allowed transition, since spin differences are otherwise involved in all other transitions. Since the spectroscopic properties of

Cr appear to be the most favorable for room temperature lasing, a laser - pumped laser experiment has been set-up for demonstrations.

#### Laser Demonstration

A laser-pumped laser experiment was arranged with Cr:ZnS or Cr:ZnSe situated in a nearly confocal resonator. A Schwartz Electro-Optics Co:MgF<sub>2</sub> laser tuned to  $\sim 1.86 \mu\text{m}$  was employed as a pump source with 10 mJ pulses and  $\sim 80 \mu\text{sec}$  pulsewidths. The laser cavity consists of a high reflecting mirror and an output coupler. Each Cr laser crystal has been prepared with polished, parallel faces and  $\sim 2$  mm of pathlength. The pump light power is controlled and attenuated with a variable neutral density filter, and light power levels of the isolated pump light or Cr laser output are detected using color filters and a pyrometer.

The Cr:ZnS and Cr:ZnSe crystals have both been successfully lased. The pump energy absorbed versus the Cr laser energy out for a 7.5% output coupling element have been plotted for Cr:ZnSe in Fig. 3. The data represent the highest measured slope efficiency currently observed, which is  $\sim 22\%$ . Similarly, Cr:ZnS has demonstrated a slope efficiency of  $\sim 20\%$  for

Table 1. Spectroscopic properties of transition metals in the zinc chalcogenides.

Property	Cr <sup>2+</sup>			Co <sup>2+</sup>			Ni <sup>2+</sup>	
	ZnS	ZnSe	ZnTe	ZnS	ZnSe	ZnTe	ZnS	ZnSe
concentration (x 10 <sup>20</sup> cm <sup>-3</sup> )	0.18	0.01	0.05	0.17	0.06	0.25	0.18	0.32
$\sigma_{abs}$ (10 <sup>-20</sup> cm <sup>2</sup> )	52	87	123	5.4	7.8	4.4	14.1	8.0
$\sigma_{em}$ (10 <sup>-20</sup> cm <sup>2</sup> )	75	92	188	3.5	3.7	7.1	-	-
$\tau_{em}$ @T=300K ( $\mu$ sec)	8	8	3	184	290	50	-	-
$\tau_{rad}$ ( $\mu$ sec)	11	8	3	1170	1173	610	-	-
$\eta_{QY}$	0.73	1.0	1.0	0.16	0.25	0.08	-	-

an output coupler of 7.5%. Slope efficiencies have been observed to decrease with decreased output coupling which is indicative of passive losses, and which have been estimated to be approximately 18% in the Cr:ZnSe system. In both cases, the laser light was observed to peak at  $\sim 2.35 \mu\text{m}$ , the peak of the measured emission spectra.

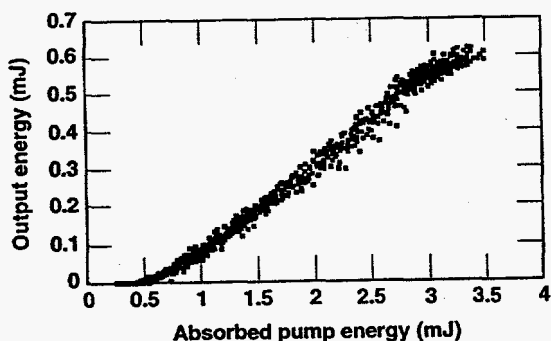


Figure 3. A slope efficiency plot of the  $2.35 \mu\text{m}$  output energy generated from Cr:ZnSe laser as a function of the  $1.86 \mu\text{m}$  pump energy.

### Conclusions

A survey of the absorption and emission properties of Cr<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup> -doped into single crystal ZnS, ZnSe, and ZnTe has been presented. The spectroscopy has been considered from the perspective of developing and employing a new class of tunable, mid-IR laser media based on transition metal-doped II-VI hosts. Cr-doped crystals of the zinc chalcogenides were recognized to have spectroscopic properties that are consistent with efficient lasing. For example, only Cr appears to be free from the deleterious effects of nonradiative decay. The quantum yield

efficiencies were generally approaching 100% for Cr, in contrast to  $\eta_{QY} \sim 20\%$  for Co, while Ni had no detectable room temperature luminescence. Cr also had the highest emission cross sections,  $\sim 10^{-18} \text{ cm}^2$  compared to  $\sim 10^{-20} \text{ cm}^2$  for Co. Although losses arising from excited state absorption were not specifically quantified, Cr is expected to behave favorably based on the lower transition probabilities anticipated between the upper laser level to the higher lying Cr energy levels.

To verify that the spectroscopic properties are consistent with favorable conditions for lasing, a demonstration of a Cr:ZnS and a Cr:ZnSe laser were performed. Employing a Co:MgF<sub>2</sub> laser tuned to  $1.86 \mu\text{m}$  as a pump source, the Cr:ZnS and Cr:ZnSe crystals were each tested in a nearly confocal laser cavity. Both crystals were successfully made to lase at a peak wavelength of  $\sim 2.35 \mu\text{m}$ , and when an output coupling element of  $\sim 7.5\%$  was employed, a slope efficiency of  $\sim 20\%$  was measured. Further investigations will be needed to explore the potential of Co laser media and other transition metal activated II-VI crystals.

### Acknowledgements

We gratefully acknowledge Gene Cantwell of Eagle-Picher, Industries for growing the crystals of transition metal-doped zinc chalcogenides which we have investigated. At Lawrence Livermore National Laboratory, we would like to express our appreciation to Howard Powell for his interest in this work, Theresa Duewar for the inductively coupled plasma and mass spectrometry analyses of the impurity ions, and Peter Thelin and Ron Vallene for the crystal fabrication and polishing of the spectroscopic samples and the laser samples. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract No.



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