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# Energy transfer from Mn to Tm ions in ZnS at high pressure

Wu Xu, Xinyi Zhang and Xurong Xu

*Changchun Institute of Physics, Academia Sinica, 1 Yan'an Road, Changchun 130021, Jilin, People's Republic of China*

The interaction of Mn and Tm ions in ZnS at high pressure is systematically studied. We have found that the energy transfer probability between Mn and Tm increases with an increase in the pressure. We have also discussed in detail the experimental results.

## 1. Introduction

We have investigated the interaction between Mn and Tm ions in ZnS materials. In this paper, we have measured the luminescence and luminescence decay of Mn and Tm ions in ZnS under various pressures from 0 to 4 GPa at room temperature. We have found that the interaction of Mn and Tm ions increases with an increase in pressure.

## 2. Experimental procedure

High pressure was obtained in a diamond anvil cell using a mixed fluid of methanol and ethanol as the pressure medium. The pressure calibration was confirmed by measuring the photoluminescence of ruby. The range of pressure varied from 0 to 4 GPa.

## 3. Results and discussion

The emission spectra of ZnS:Mn, ZnS:Tm, and ZnS:Mn,Tm are shown in fig. 1. The broad band peaking at 585 nm is specific to the emission of Mn ions. There are five emission bands of Tm ions in the emission spectra of ZnS:Tm. The typical emission lines of the Tm ions are situated at 383, 477, 650, 705, and 802.6 nm. The emission spectra of ZnS:Mn,Tm consist of the broad band of Mn and the lines due to Tm. The intensity of the Tm emission peaking at 477 and 802.5 nm increases with increased concentration of Mn ions. We only study the intensity change of Tm ions emission peaking at 477 and 802.6 nm, i.e., the blue and red lines.

In figs. 2 and 3, we present the luminescence of Mn and Tm ions in ZnS:Mn and ZnS:Tm at various pressures. A red shift of the peak of the Mn emission band takes place with increased pressure. When the pressure increases from 0 to 4 GPa, the emission peak decreases from 17094 to 15500 $cm^{-1}$. The red shift of the Tm ion emission peak with the pressure is very small.

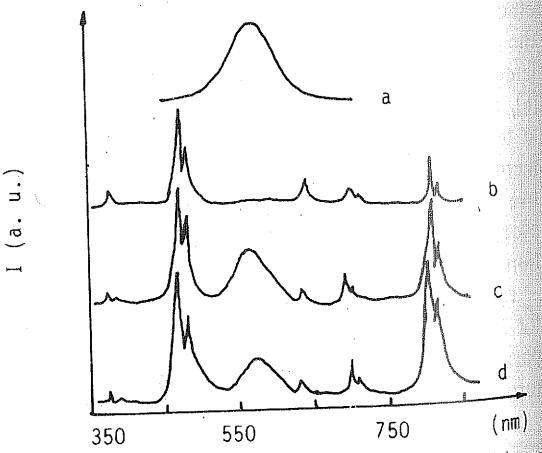


Fig. 1. Emission spectra of ZnS:Mn (a), ZnS:Tm (b) and ZnS:Mn,Tm (c, d) excited by 337 nm at room temperature.

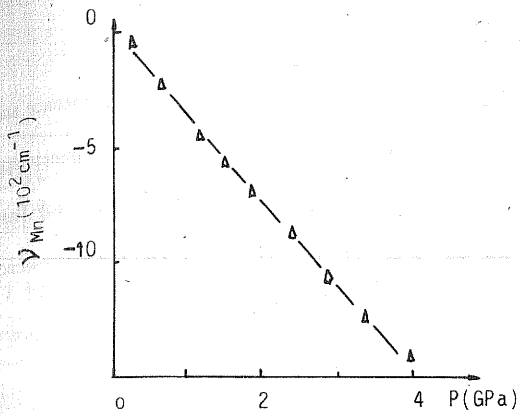


Fig. 2. Pressure dependence of emission peak of Mn in ZnS:Mn.

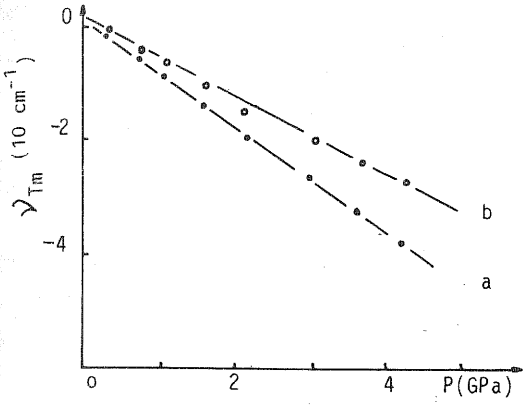


Fig. 3. Pressure dependence of emission peak of Tm in ZnS:Tm: (a) 802.6 nm; (b) 477 nm.

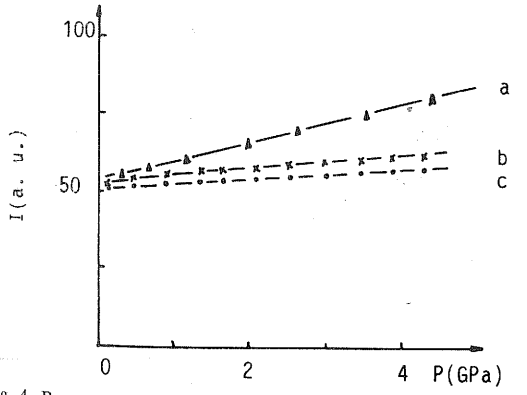


Fig. 4. Pressure dependence of emission intensity of Mn (a) and Tm (b, c) in ZnS:Mn and ZnS:Tm: (b) 477 nm; (c) 802.6 nm.

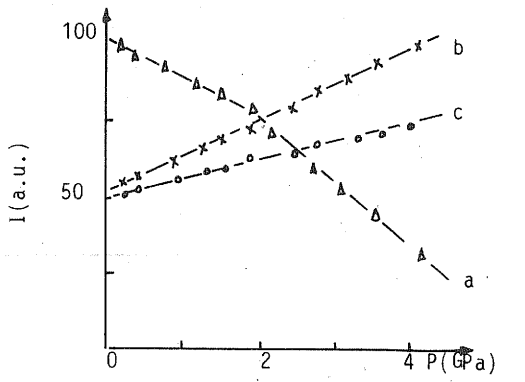


Fig. 5. Pressure dependence of emission intersity of Mn (a) and (b, c) in ZnS:Mn,Tm: (b) 477 nm; (c) 802.6 nm.

Fig. 4 shows the variety of the integral luminescence intensity for Mn and Tm ions in ZnS:Mn and ZnS:Tm. The integral luminescence intensity of Mn ions ($I_{Mn}$) increases with pressure over the range from 0 to 4 GPa. The integral luminescence intensity of Tm ions ($I_{blue}$, $I_{red}$) is unchanged with pressure.

We have measured the decay curves of Mn and Tm ion emission bands of ZnS:Mn and ZnS:Tm. The decay of the Mn emission band consists of two parts: fast and slow decay. The decay time constants are 300 $\mu$s and 1.5 ms. The decay of Tm emission is exponential, having a decay time constant of 40 $\mu$s for the red line.

When the pressure increases, the fast decay component of the Mn ions remains almost unchanged, the slow decay component is decreased slightly, and the decay time constant of Tm is unchanged. We consider that the red shift of Mn ions in ZnS:Mn is caused by intersity variation of the crystal field at high pressure.

Fig. 5 shows the pressure dependence of $I_{Mn}$, $I_{blue}$, and $I_{red}$ in ZnS:Mn,Tm. In contrast to Mn doping or Tm doping alone, one finds that $I_{Mn}$ decreases with an increase in pressure. There is a gradual increase in $I_{blue}$ and $I_{red}$ with pressure over the range of 0 to 4 GPa.

In the case of the ZnS:Mn,Tm material, $I_{Mn}$ decreases with rising pressure. There are evident independent increases in $I_{blue}$ and $I_{red}$ with pressure. It can be assumed that the decrease in $I_{Mn}$ and increase in $I_{blue}$ and $I_{red}$ are caused by energy transfer from Mn to Tm. The probability

of energy transfer between them is closely related to pressure. The experimental results show that the emission of the blue line of Tm is related to two-photon absorption, and energy transfer between Mn and Tm ions is phonon assisted. The emission peak of the Mn ions shows a red shift with pressure. The energy mismatch between Mn and Tm decreases, and their energy transfer probability increases. On the other hand, the interaction distance of Mn and Tm ions decreases with an increase in pressure and the energy transfer between the two also increases.

## References

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