Journal of Luminescence 48 & 49 (1991) 224–226
North-Holland

Energy transfer from the higher excited state of Mn to Tm in ZnS:Mn,Tm

Xu Wu, Zhang Xinyi and Xu Xurong

Changchun Institute of Physics, Academia Sinica, Changchun, Jilin, PR China

This paper describes a systematic investigation of the interaction between the higher excited state of Mn and Tm ions in a ZnS material and proves that there is energy transfer from the higher excited state of Mn to Tm ions.

1. Introduction

We have systematically studied the interaction between the Mn and rare-earth ions in a ZnS material [1–4]. However, this research was limited to energy transfer between the rare-earth ions and the $^4T_1(G)$ excited state of the Mn ion. The present paper deals with the characteristics of the interaction between the higher excited state of Mn and Tm ions.

Our investigation indicated that there is also energy transfer between the higher excited state of Mn and Tm ions. This provided further insight into the nature of the interaction between transition metal and rare-earth ions and is helpful for enhancement of rare-earth ion luminescence efficiency in ZnS materials.

2. Experimental conditions

A double-beam excitation experiment was performed with Ar^+ ion- and He–Ne lasers as sources for collinear excitation of a single point in the material. The luminescence from the material passed through a Spex-1403 double-grating spectrometer and was amplified by a photon counter before being recorded. The power of the Ar^+ ion laser was 20 mW and that of the He–Ne laser ranged from 15 to 40 mW.

The Mn ion concentration in the experimental material varied from 10^{-4} to 5×10^{-3} mol and the Tm ion concentration from 5×10^{-5} to 10^{-3} mol.

3. Experimental results and discussion

Figure 1 shows the Mn and Tm ion excitation spectra in ZnS:Mn, ZnS:Tm, and ZnS:Mn,Tm material. The Mn ion excitation spectra consisted of six spectral bands. Among these, the excitation band with its peak at 337 nm was produced by interband excitation of the ZnS. The other five bands corresponded to Mn ion excitations from $^6A_1$ to $^4T_2(D)$, $^4T_1(D)$, $^4E(G)$, $^4T_2(G)$, and $^4T_1(G)$.

The Tm ion excitation spectra consisted of two spectral bands. The excitation band with its peak at 337 nm was associated with interband ZnS excitation. The excitation band with its peak at 370 nm is probably related to the Tm ion charge transfer state. As for the Tm ion excitation spectra in

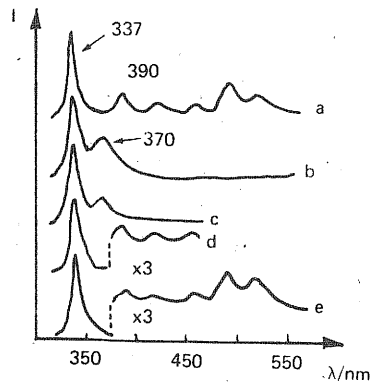

Fig. 1. Excitation spectra at RT. (a) ZnS:Mn, $\lambda_{em}=585$ nm; (b) ZnS:Tm, $\lambda_{em}=477$ nm; (c) ZnS:Tm, $\lambda_{em}=802.6$ nm; (d) ZnS:Mn,Tm, $\lambda_{em}=477$ nm; (e) ZnS:Mn,Tm, $\lambda_{em}=802.6$ nm.

ZnS:Mn,Tm, we found Mn ion doping to result in the appearance of five new excitation bands in the long wavelength region, the positions of whose peaks corresponded to those of the characteristic Mn ion excitation bands. This implied that Mn excitation resulted in Tm ion emission, i.e. there was energy transfer from Mn to Tm. Also of great interest was the fact that the relative intensities of the five new excitation bands were different from the pattern of the Mn ion excitation spectra: the higher the band energy, the more apparent was the decrease in intensity. We assume this to have been caused by a larger energy mismatch between the higher excited state of Mn ion and Tm ion absorption level. Double-beam excitation experiments were conducted to verify our hypothesis.

Since the 488 nm excitation line for the Ar^+ ion does not correspond to the excitation band of the Tm ion, it cannot excite Tm ions to emission. The experimental results bore this out. When the ZnS:Tm material was simultaneously excited with the 488 nm Ar^+ ion laser and 632.8 nm He-Ne laser lines, we did not observe Tm ion emission also, i.e. the 632.8 nm laser line did not contribute to Tm ion emission. When ZnS:Mn,Tm materials were excited with light at this wavelength, we observed stronger Tm ion emission caused by energy transfer from Mn to Tm. We observed a relationship between R and E, where R is the luminescence intensity ratio for the Tm ion blue (or red lines) excited by the double beam and by the Ar^+ ion laser, respectively (we will only consider the variation of the Tm ion spectral lines with their peaks at 477 and 802.6 nm, referring to them as the blue and red Tm ion lines, respectively). E is the He-Ne laser power (see fig. 2). The value of R increased with the power, which meant an increase in I_{Tm} as well. The rate of increase for I_{blue} was specifically greater than for I_{red}. Figures 3 and 4 show the relationships of the ratio to the Mn [Mn] and Tm [Tm] ion concentrations. When [Mn] was low, R increased with this parameter, reaching a maximum at $[Mn] = 4 \times 10^{-4}$ mol. The value of R also increased with [Tm]: it remained basically unchanged when [Tm] was above 5×10^{-4}.

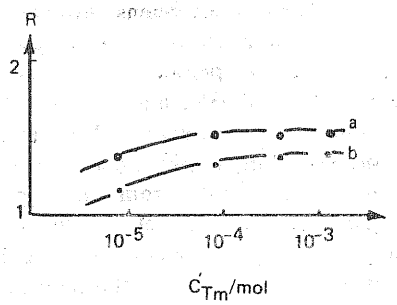

Fig. 3. R as function of [Tm]. (a) = 488 nm + 632.8 nm, (b) = 465 nm + 632.8 nm.

We found that the 632.8 nm He-Ne laser line by itself could not excite Mn or Tm ion emission. Moreover, use of the 632.8 nm laser line and the Ar^+ ion laser line for simultaneous excitation of ZnS:Mn and ZnS:Tm caused no change in luminescence intensity for either Mn ion or Tm ion emission. In addition, no new emission peaks appeared. This suggested that two-photon absorption did not occur at Tm ions in the case of double-

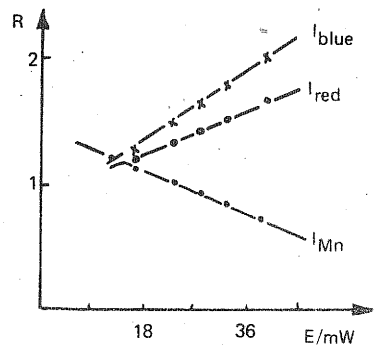

Fig. 2. R as function of He-Ne laser power.

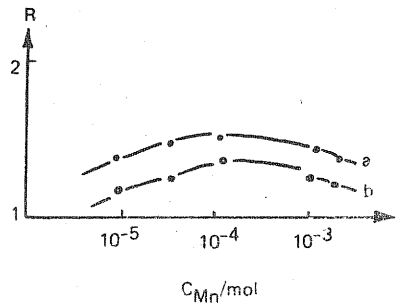

Fig. 4. R as function of [Mn]. (a) = 488 nm + 632.8 nm, (b) = 465 nm + 632.8 nm.

beam excitation. When ZnS:Mn,Tm was simultaneously excited by two beams, however, Tm ion luminescence intensity underwent an obvious increase, which was proportional to the increase in the power at the 632.8 nm line and which was accompanied by a decrease in Mn ion luminescence intensity. This implies that there is another channel of energy transfer from Mn to Tm ion with double-beam excitation, related to the higher excited state of Mn ion. When the power E of the 632.8 nm line was increased, the intensity of Tm ion luminescence increased also. We believe that this was probably due to the occurrence of a new channel of energy transfer involving the Tm ion $^1G_4$ level at double-beam excitation. On excitation by the Ar^+-ion laser 488 nm line, the Tm ion $^1G_4$ level accepted energy transferred from the Mn ion $^4T_1$ level by means of a two-photon absorption process [3], leading to emission of a high-energy photon by the Tm ion on low-energy excitation. The Mn ion can be excited to a higher state by double-beam excitation, which reduces the energy mismatch between the Mn and Tm ions and permits a transition from two-photon to single photon absorption during energy transfer. This view was borne out by the linear relation between I_{blue} and power E at the 632.8 nm line.

References

[1] Xu Wu, Zhang Xinyi and Xu Xurong, Luminescence and Display 4 (1982) 14.
[2] Xu Wu, Zhang Xinyi and Xu Xurong, J. Lumin. 31 & 32 (1984) 808.
[3] Xu Wu, Zhang Xinyi and Xu Xurong, Chin. J. of Rare Earth 4 (1986) 21.
[4] Xu Wu, Zhang Xinyi and Xu Xurong, J. Lumin. 40 & 41 (1988) 167.