various Pr

4.4, 15140.6 3.0, 15129.0 9.2, 15105.0

1.0, 15068.2 1.2, 15043.4

2.4, 15022.4 5.6

9.0, 3.0

2.4

lnm, besides re are two 20cm<sup>-1</sup> below

weak in the and B. Intennarrow lines entration of easing tempert the high ente that C is mmetry of Pr s approximate-case is mainic states with e symmetry.

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Liu, in ence and uangxian, ing, 1985) THE EFFECT OF INFRARED LIGHT ON NO. 3+ LUMINESCENCE IN Zns \*

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IR stimulation and quenching of different Nd<sup>3+</sup> centers in ZnS have been studied. The mechanism of the IR effect has been discussed.

## 1. INTRODUCTION

There exist in ZnS two types of rare earth centers, one is preferentially excited by 4f excitation, the other by band edge excitation <sup>1,2</sup>. The latter is a kind of donor-like center <sup>1</sup>. The decay of the luminescence under band edge excitation, which reflects the process of excitation transfer, is significantly different from that under characteristic excitation <sup>3</sup>.

In ZnS:Nd, two centers effective to band edge excitation were distinguished by time resolved spectra and laser selective excitation<sup>2</sup>. In this paper, their properties are further studied.

## 2. EXPERIMENT AND RESULTS

ZnS:Nd powder in a sample cell was immersed in liquid nitrogen. 337.1nm from a pulsed nitrogen laser was used as the UV source and a tungsten lamp with a 700nm cut off filter was used as the IR light source. Fig. 1 is the emission spectra of  ${}^4{\rm G}_{5/2}$  —  ${}^4{\rm I}_{9/2}$  of Nd $^{3+}$ , which indicate that the luminescence of center B is stimulated after applying IR, while that of center A quenches a little.

Center A can also be characteristically excited, when this is done, no variation was found for the emission intensity with and without applying IR. This excludes intra-ion process, such as absorption of the low lying states, from the origin of IR effect.

IR stimulation spectrum of the luminescence

of center B was measured at room temperature (Fig. 2). There are two bands peaked at about 900nm and 1300nm.

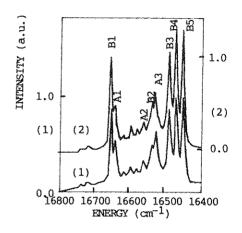


FIGURE 1  $^{4}$ G<sub>5/2</sub>  $^{4}$ I<sub>9/2</sub> emissiom spectra of Nd<sup>3+</sup> in ZnS:Nd at  $^{4}$ 7K. (1) Excited with 337.1nm; (2) excited with 337.1nm and irradiated with IR light. B1-16655; A1-16644; A2--16564; B2-16541; A3-16530; B3-16491; B4-16472; B5-16455(cm<sup>-1</sup>) .

## 3. DISCUSSION

The peaks in the IR stimulation spectrum of center B are close to the IR quenching or stimulation peaks of Cu center 1. It is also noted that the sample with significant IR effect always contains trace Cu. These facts indicate that IR stimulation is related to Cu. To understand the role of Cu, intentionally Cu-codoped sample was prepared. Intensities of both A and

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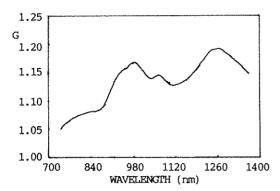


FIGURE 2

Stimulation spectrum of the 607nm luminescence of center B at room temperature. 365nm from a mercury lamp is used as the UV source.

B luminescence decrease, while no evident variation can be observed for the relative intensity. This result shows that Cu is involved in neither center A nor center B, Cu acts as a hole trap for the rare earth luminescence. As the IR light is applied, the holes trapped on Cu are librated and migrate in the valence band. Once they approach to the occupied donors,  $(D^0,h)$  recombination takes place and excitation is then transfered to  $Nd^{3+}$ .

Electrons on the donors related to center A and center B may also be excited by IR to conduction band. Conduction electrons then redistribute between A and B donors. The steady state rate equations can be written as

$$\dot{N}_{C} = 0 = N_{0}R_{0} + R_{A}N_{A} + R_{B}N_{B} - (F_{A} + F_{B})N_{C}$$

$$\dot{N}_{A} = 0 = F_{A}N_{C} - (R_{A} + W_{A})N_{A}$$

$$\dot{N}_{B} = 0 = F_{B}N_{C} - (R_{B} + W_{B})N_{B}$$

where  $N_0$ ,  $N_C$ ,  $N_A$ ,  $N_B$  are the populations of electrons on valence band, conduction band, donor A and donor B;  $R_0$  is the excitation rate of electrons from VB to CB by UV light,  $R_A$ ,  $R_B$  are the excitation rates of electrons from donor A and donor B to CB by IR;  $F_A$ ,  $F_B$  are the relaxation rates from CB to A and B;  $W_A$ ,  $W_B$  are the recombination rates. If no IR light is applied,  $R_A = R_B = 0$ . With these notations we have

$$G_{A} = \frac{N_{A}(R_{A}, R_{B})}{N_{A}(0,0)} = \left[1 + \frac{R_{A}W_{B} - R_{B}W_{A}}{(R_{B} + W_{B})(F_{A} + F_{B})W_{A}^{2}}\right]^{-1}$$

and similar for  $G_B = N_B(R_A, R_B)/N_B(0, 0)$ . From (2) it follows that

$$G_A$$
 1,  $G_B$  1, if  $R_A/A_B$   $W_A/W_B$  (3-1)

 $G_A$  1,  $G_B$  1, if  $R_A/R_B$   $W_A/W_B$ . (3-2) Our result can be explained by (3-2). That is, center A contributes more electrons to the conduction band but gets back less, the net result will be electrons moving from A to B, and luminescence of center A IR quenches, while that of B is IR stimulated.

In summary, we have such a picture about the IR effect: UV light produces e-h pairs. Rare earth centers capture electrons and act as donors. When the electrons recombine with holes, energy is transferred to RE center. Some holes are captured by traps, such as Cu, which quenches RE luminescence in ZnS. If IR light is applied, holes are librated from the traps, RE luminescence is then stimulated. On the other hand, electrons on the donors may also be excited to the conduction band. If there are two or more donor levels, the electrons will be redistributed among them, population will be changed, as described by the condition (Eq. 3).

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