Electrical conductivity of doped ZnS

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MS received 8 December 1990; revised 26 February 1991

Abstract. The electrical conductivity of doped ZnS with different impurities (Mn, Fe, Co, Ni and Cu) of various concentrations has been measured to verify the existence of ladder-like levels of 'killers' of luminescence. Attempts have been made to ascertain the separation between the valence band of the host ZnS and the ground state of the acceptor impurities and also to investigate the effect of various concentrations of impurities on the electrical conductivity of doped ZnS.

Keywords. Electrical conductivity of doped ZnS; killers; luminescence; ladder-like level.

1. Introduction

Doped zinc sulphide (ZnS) has been the subject of a large number of investigations because of its practical application as a luminophor (Czajka and Gordon 1983; Renz and Schulz 1983; Warren *et al* 1983; Choudhary *et al* 1984; Maheshwari and Pathak 1984; Chaubey and Tripathi 1985; Brada 1989). Attempts were therefore made to increase its efficiency and improve the breakdown voltage margin (Okamoto *et al* 1979; Ogura *et al* 1986; Okamoto and Hamakawa 1986; Mita *et al* 1987; Milind *et al* 1990). It has been reported that even a small amount of impurities such as Fe, Co and Ni present in the phosphor can greatly hamper the luminescence efficiency or can completely destroy it. These impurities are often called 'killers' of luminescence. Deterioration of luminescence efficiency may be due to the presence of closely-spaced ladder-like levels of impurities spread in the energy gap of ZnS.

The presence of ladder-like levels due to 'killers' in the band gap of ZnS has not adequately been examined. In the present paper, attempts have been made to provide some clues about the existence of such levels through electrical conductivity measurements of doped ZnS with different impurities (Mn, Fe, Co, Ni and Cu) of various concentrations.

2. Experimental

The samples were synthesized by high temperature solid-state reaction of stoichiometric mixtures of ZnS and impurities of Mn, Fe, Co, Ni and Cu preferably in their sulphide form. The concentrations of impurities were varied from 0.01 to 5 mol%. These mixtures were pressed into disc form under a pressure of 8 ton/cm² and fired at a temperature of 1200 K for 24 h in an alumina crucible. Finally, pellets

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were sintered at 1225 K for 24 h. The electrical conductivity of the samples was measured from room temperature (300 K) to 1000 K. The electrodes used were made of platinum.

3. Results and discussion

Results of the electrical conductivity measurements of all doped and undoped ZnS samples are shown in figures 1 to 4. Figure 1 shows the $\log \sigma$ vs $1/T$ curve for undoped ZnS in heating and cooling runs. It is seen that the curve in the heating run has a gradient which corresponds to the band gap $E \approx 3.2$ eV for ZnS semiconductor. In the cooling run, it takes quite a different path and conductivity decreases slowly on cooling. In the heating run the conductivity rises sharply which may be due to traps present in the host ZnS. As the substance is heated, these traps probably emit electrons copiously to the conduction band and hence the conductivity increases sharply. On the other hand, in the cooling run, the conductivity fall is not steep with temperature. This is evident from the rather small gradient shown in $\log \sigma$ vs $1/T$ curve corresponding to the cooling cycle (figure 1). This is to be accounted for by considering the metastable state with longer lifetime of the conduction band of ZnS. This is clear from the fact that in pure ZnS, when the electron is pumped to the conduction band by an external agency, it does

Figure 1. Temperature dependence of conductivity of undoped ZnS.

Figure 2. Temperature dependence of conductivity of ZnS doped with impurities Mn, Fe, Co, Ni and Cu each with a molar concentration of 0.1%.

not make a radiative transition to the valence band and the luminescence in ZnS can be observed only by the addition of certain impurities.

Figure 2 shows the $\log \sigma$ vs $1/T$ curves of ZnS doped with different impurities of Mn, Fe, Co, Ni and Cu each with a fixed molar concentration of 1%. The band gap obtained from different curves shows that it increases from Mn to Cu in order of their positions in the periodic table. In the high temperature region, all the curves asymptotically approach the intrinsic conductivity of pure ZnS.

Figure 3 shows the $\log \sigma$ vs $1/T$ curves of ZnS doped with Cu of molar concentrations 2%, 0.2, 0.1 and 0.01%. It is found that as the impurity concentration is increased, conductivity increases, but after a certain concentration level (0.1 mole%), the trend reverses. The same behaviour has been observed in the case of ZnS doped with Fe (figure 4).

The observed increase of conductivity (figures 3 and 4), with increasing concentration of impurities is explained by the expression (Kittel 1974)

$$n = (N_0 N_a)^{1/2} \exp(-E_a)/2K_B T,$$

where $N_0 = 2(m_n K_B T / 2\pi \hbar^2)^{3/2}$, N_a the concentration of impurity and E_a the activation energy. At higher concentration, the mobility of the impurity carriers becomes low and hence conductivity decreases. It has been found that the separation between acceptor level and the valence band also depends upon the impurity concentration. This may be attributed to the broadening of impurity levels at higher concentration of impurities.

Figure 3. Temperature dependence of conductivity of ZnS doped with Cu of molar concentrations 0.01%, 0.1%, 0.2% and 2%.

If the ladder-like level of 'killer' really existed in the band gap of ZnS, one may expect that in the extrinsic region, the conductivity points should not lie in a smooth straight line but in broken small segments of various straight lines corresponding to the energy difference between the various closely-spaced levels and the valence band. Such broken nature of the straight line was not observed in the present case (figures 2, 3 and 4). In one case (as shown in figure 4), when the concentration of Fe was increased up to 5 mol% only the extrinsic region was observed and not the impurity exhaustion or the intrinsic conductivity region up to the highest temperature at which the conductivity measurements were performed. To confirm the existence of these ladder-like levels by other techniques, absorption spectroscopy work is in progress.

4. Conclusion

The separation between the valence band of the acceptor impurities is found to be impurity concentration-dependent. The variation of electrical conductivity is found such that beyond 0.1% impurity level, the conductivity decreases with increasing concentration and below 0.1%, it depends on the concentration of impurities. It is in accordance with the general theory, which suggests that with increasing concentration, the mobility of current carriers decreases. At this stage, the present

Figure 4. Temperature dependence of conductivity of ZnS doped with Fe of molar concentrations 0.01%, 0.1%, 2% and 5%.

studies do not either refute or support the existence of ladder-like levels of impurities.

Acknowledgements

The authors thank Dr D Bahadur and Dr M Roy of IIT, Kanpur, and Dr M Umar of Aligarh Muslim University for their encouragement and valuable discussions.

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