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X-ray studies and luminescence of ZnS-phosphor doped with silver and cobalt

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Measurements were carried out on a series of (ZnS : Ag : Co) with different concentrations of cobalt. The emission spectra were studied at liquid nitrogen and room temperatures. Introducing cobalt dopant into the lattice decreased the efficiency of emission for the first band but produced no shift in the maximum intensity. This phenomenon has been noted by other workers. The approximate average internuclear spacing between activator atoms in hexagonal (ZnS : Ag : Co) was calculated. It is apparent that the average distance between the cobalt atoms for lower concentrations is too large compared with the average distance between the silver atoms. A Siemens D-500 X-ray diffractometer was used to clarify the characteristic features of the phases and the crystallite size estimation.

1. Introduction

Some phosphors are widely used in industry, especially in the television, radar and oscilloscope screens, and personal dosimetry. The phosphors of ZnS-type show two bands of emission under excitation by ultraviolet light or high-energy particles. One band was found to be activator dependent and independent of coactivators. This band is attributed to the transition from the conduction band to the activator level which is just situated above the valance band (classical Riehl-Schon-Klasen model [1–3]. On the other hand, the second band depends on both activator and coactivator. It is thought that such a band is produced by acceptor–donor association (Prener and Williams model [4, 5]).

Van Gool [6–8] showed that the green emission band in (ZnS : Cu) phosphor is independent of the coactivator used. Similar studies were carried out on (ZnS : Ag). The blue emission band was the dominant one. Evidence for the occurrence of the blue and green emission bands has been given by Henderson *et al.* [9]. The height of the green band would never exceed 10 to 25% of the main (blue) band. A comprehensive study on ZnS : (Cu or Ag) : (Ga, In) was made by Apple and coworkers [10–14]. Two emission bands were observed in each series. It was proposed that the long wavelength emission involved transition between a highly associated donor–acceptor pair.

The association between the acceptor ion and the donor ion was discussed by Prener and Williams [4, 5]. This kind of association requires approximately equal concentrations of the activator and coactivator to be gradually introduced into the lattice of the ZnS-type phosphor. For such experimental conditions, the intensity of the green band is much higher than the intensity of the blue band [15]; this supports the assumption that the green band is due to the associated donor–acceptor system. On the other hand, an excess of acceptor ions increased the intensity of the first band. This fact leads to the assumption that the blue band is not due to an association between the activator and the coactivator ions [16].

The presence of transition metal impurities such as nickel and cobalt centres in the sulphide lattice reduces the luminescent intensity [17]. They form a series of closely spaced energy levels in the forbidden band so that the recombination may occur in steps with the emission of phonons or infrared radiation. Cobalt levels are located above the Fermi level and are usually empty. Thus radiationless transitions of excited electrons from either impurity levels or the conduction band to the killer levels can take place immediately after excitation.

2. Experimental techniques

The phosphor powder used during this work was obtained from Thorn Electrical Industries, UK. The measurements were carried out on four samples of (ZnS : 5×10^{-6} Ag) with additional cobalt impurity of 5×10^{-8}, 5×10^{-7} and 5×10^{-6}. For photo luminescence studies, a small cryostat with large optical aperture similar to that used by El-Manharawy [18] was employed. A Siemens D-500 X-ray diffractometer was used to clarify the characteristic features of the phases and crystallite size estimation.

3. Results and discussion

ZnS crystallizes mainly in the hexagonal and cubic structure. Differences in luminescent properties of both types are expected. The sites of the activators and coactivators in the matrix lattice determine the characteristics of the electron traps and the luminescent centres.

The corresponding X-ray powder diffraction pattern of (ZnS : Ag : Co) with different concentrations of cobalt is shown in Fig. 1 and the data are listed in

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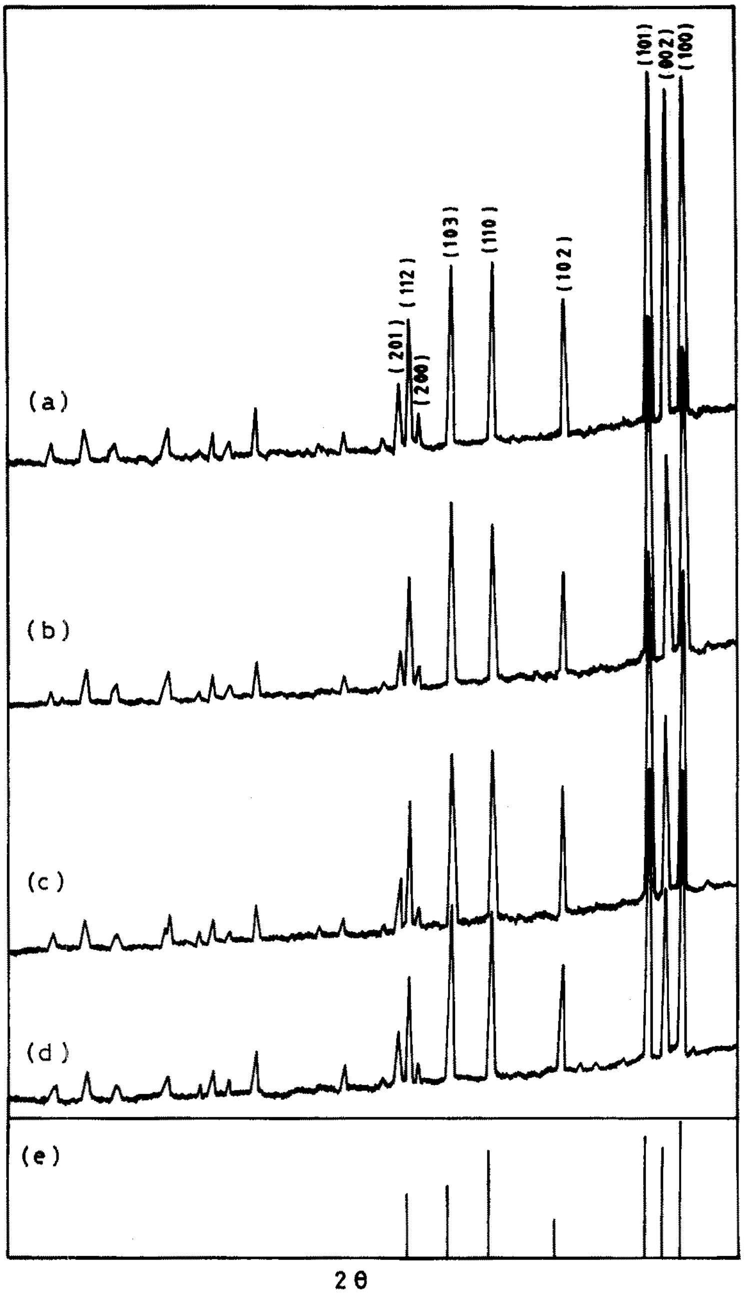

Figure 1 X-ray diffractogram of (ZnS : Ag : Co) powder. (a) ZnS : 5 × 10^{-6} Ag. (b) ZnS : 5 × 10^{-6} Ag : 5 × 10^{-8} Co. (c) ZnS : 5 × 10^{-6} Ag : 5 × 10^{-7} Co. (d) ZnS : 5 × 10^{-6} Ag : 5 × 10^{-6} Co. (e) ZnS hexagonal.

Table I compared with the pure hexagonal ZnS phosphors of the JCDPS card file data. It is concluded that the four samples were of hexagonal structure with traces of cubic phase. Introducing silver and cobalt into the lattice of ZnS produced a minute shift in the interplanar distances and an ordered variation in the intensity of a large group of planes, especially when the concentration of cobalt was increased. This means that cobalt and silver atoms replaced some of the zinc atoms in the host lattice and did not lodge themselves as interstitials. This idea is confirmed by the noticeable increase in the crystallite size with increasing cobalt concentration as shown in Table II.

TABLE I X-ray powder diffraction data

d (nm) (JCDP5)	ZnS (hexagonal)			
	Sample a, *d* (nm)	Sample b, *d* (nm)	Sample c, *d* (nm)	Sample d, *d* (nm)
0.3306	0.3312	0.3318	0.3322	0.3331
0.2899	0.2923	0.2928	0.2934	0.2938
0.1771	0.1785	0.1791	0.1804	0.1812
0.1563	0.1571	0.1582	0.1591	0.1596
0.1149	0.1152	0.1158	0.1160	0.1165

The Scherrer formula is used to estimate the crystallite size, *S*, of very small crystals from the measured width of their diffraction curves [19]

$$S = \frac{K\lambda}{B\cos\theta} \tag{1}$$

where λ is the wavelength of the X-rays (λ = 0.154 04 nm), and θ is the Bragg angle. The width, β, is measured in radians at an intensity equal to half the maximum intensity. As a rough measure of β, we can take half the difference between the two extreme angles at which the intensity is zero, which amounts to

TABLE II Crystallite size of the samples

Sample	Crystallite size (nm)
ZnS : Ag	14.97
ZnS : Ag : 5 × 10^{-8} Co	15.59
ZnS : Ag : 5 × 10^{-7} Co	17.2
ZnS : Ag : 5 × 10^{-6} Co	19.05

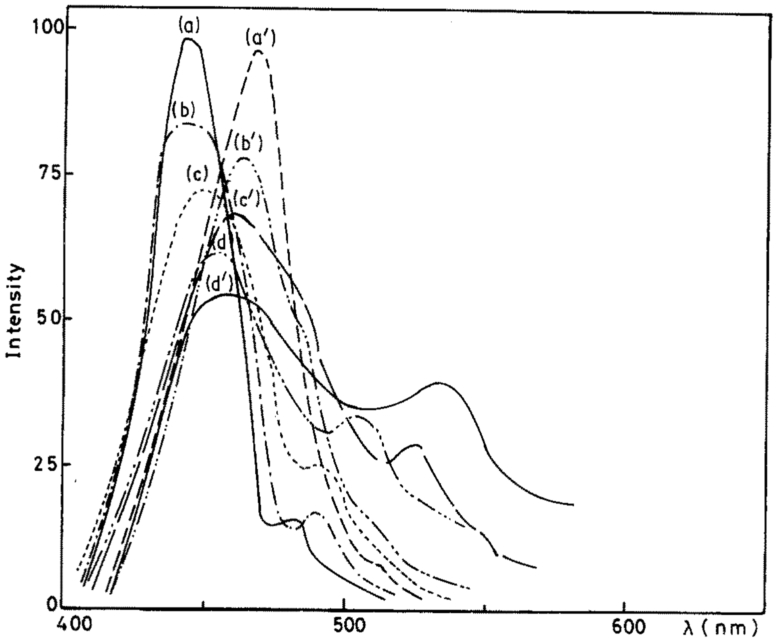

Figure 2 The intensity of the emission spectra plotted against wavelength. T = 78 K: (a) ZnS:5 × 10^{-6} Ag; (b) ZnS:5 × 10^{-6} Ag:5 × 10^{-8} Co; (c) ZnS:5 × 10^{-6} Ag:5 × 10^{-7} Co; (d) ZnS:5 × 10^{-6} Ag:5 × 10^{-6} Co. T = 300 K: (a′) ZnS:5 × 10^{-6} Ag; (b′) ZnS:5 × 10^{-6} Ag:5 × 10^{-8} Co; (c′) ZnS:5 × 10^{-6} Ag:5 × 10^{-7} Co; (d′) ZnS:5 × 10^{-6} Ag:5 × 10^{-6} Co.

assuming that the diffraction line is triangular in shape.

Fig. 2 shows the emission spectra of (ZnS:Ag) containing different amounts of cobalt dopant studied at liquid nitrogen and at room temperatures. The positions of the bands for the series employed in the present work are summarized in Table III. At low temperature, two emission bands can be distinguished, but at room temperature, one major band is observed with a shoulder for free and low cobalt concentration, while two bands are observed for the phosphors of relatively high cobalt concentration. In addition, the same sample at 78 and 300 K, the intensity decreases as the temperature increases. This is due to the temperature quenching of emission by the positive hole migration [20].

The main reason for the shift in the wavelength of the emission band recorded at 78 K towards longer wavelength recorded for the same band at 300 K may be mainly explained in terms of the estimated decrease in the energy gaps with temperature, according to the formula [21]

$$E_{\text{gap}}(T) = E_{\text{gap}}(0) - \alpha T \qquad (2)$$

with $\alpha = 5.5 \times 10^{-4}\,\text{eV}\,^\circ\text{C}^{-1}$.

Similar results have been observed before by Henderson [9] for (ZnS:Cu) and (ZnS:Ag) free of cobalt. One may assume that in both bands the silver activator which produces a localized acceptor level at 0.85 eV above the valance band is the centre of recombination involved in both transitions. The first band is produced by the recombination of an excited electron either from the conduction band or some shallow traps just below the bottom of the conduction band with a positive hole captured at the acceptor level of silver. The Riehl-Schon-Klasen model [1–3] can be applied to this band in the light of the information given about the width of the forbidden gap (3.7 eV for würtzite ZnS form) and the position of the acceptor level introduced by silver in the energy gap (0.85 eV above the valence band). The second band of longer wavelength is produced by a radiative transition of an excited electron captured at a donor level associated with an impurity coactivator (probably bromine, iodine, oxygen or lattice defects situated at 0.28 eV below the lower edge of the conduction band) to recombine with a positive hole captured at the acceptor level of silver (i.e. the Prener and Williams model [4, 5] may be applied).

TABLE III Wavelengths corresponding to the maximum emitted intensity

Sample	Band I λ_m (nm)	Band II λ_m (nm)	T (K)
a	445	482	78
b	445	490	
c	450	495	
d	452.5	505	
a′	465	512.5	300
b′	463.5	512.5	
c′	461.5	525	
d′	460	535	

Introducing cobalt dopants into the lattice decreased the efficiency of emission for the first band and produced no shift in the maximum intensity. This effect is due to the killing effect of cobalt [12]. On the other hand, the shift in the maximum and the increase in intensity of the second band with cobalt concentration is clear. This seems to be logical, because the spectral distribution of the long wavelength emission depends on the identities of both acceptor and donor. This leads to the proposal that the long wavelength band involved transition between highly associated donor–acceptor pairs. This phenomenon has been noted by other workers [10–14].

It is of interest to calculate the approximate average internuclear spacing between activator atoms in

TABLE IV

Sample	Average distance (nm)
$\bar{X}_{\text{Ag-Ag}}$(ZnS:Ag:5 × 10^{-6})	27.35
$\bar{X}_{\text{Co-Co}}$(ZnS:Ag:5 × 10^{-8} Co)	155.29
$\bar{X}_{\text{Co-Co}}$(ZnS:Ag:5 × 10^{-7} Co)	72.08
$\bar{X}_{\text{Co-Co}}$(ZnS:Ag:5 × 10^{-6} Co)	33.46

hexagonal (ZnS : Ag). In this case, it is possible to correlate the average spacing between activator impurity atoms with the spacing between certain host-crystal atoms, because the number of suitable interstitial sites in hexagonal ZnS is roughly equal to the number of zinc atoms. If one assumes, as a first approximation, a uniform distribution of the zinc host-crystal atoms in ZnS, the average centre to centre spacings between zinc atoms is given by [22]

$$\bar{X}_{\text{Zn-Zn}} \approx (\sigma N_v N_A / M_w)^{-1/3} \text{ cm} \quad (3)$$

where σ is the density of the host crystal (g cm^{-3}), N_v is the number of zinc atoms per simple molecules, N_A is Avogadro's number and M_w is the gramme molecular weight per simple molecule. The average distance between activator atoms, assuming a uniform distribution, is

$$\bar{X}_{\text{Zn-Zn}}(R_{\text{Zn}}/\text{act.})^{1/3} \quad (4)$$

where R_{Zn}/act. is the ratio of zinc to activator atoms in the particular phosphor.

The values of $\bar{X}$ calculated from Equation 4 are given in Table IV. It is clear from this table that the average distance between the cobalt atoms for the lower concentration is too large compared with the average distance between the silver atoms. This means that at low cobalt concentrations, resonance transfer between cobalt and silver is not recommended. On the other hand, at high concentrations of cobalt, resonance transfer is recommended and the effect of the cobalt centre is clear in the luminescence mechanism.

The results of thermoluminescence [23, 24] show that cobalt creates deep traps in the ZnS phosphor (0.55 eV). The killing action is due to the recapture and subsequent radiationless de-excitation between the already existing impurity levels and the localized level of cobalt. Accordingly, one may conclude that:

1. the blue band of energy ~2.8 eV in both (ZnS : Ag) and (ZnS : Ag : Co) is due to a transition either from the conduction band or from a shallow level just below the lower edge of the conduction band to the acceptor level of silver. The transition from the lower edge of the conduction band is recommended because (ZnS : Ag) and (ZnS : Ag : Co) are both photoconductors;

2. in (ZnS : Ag) the green band of energy 2.55 eV is due to a transition either from an impurity donor level or lattice defects at 0.28 eV below the lower edge of the conduction band to silver acceptor level;

3. in (ZnS : Ag : Co) at lower concentrations of cobalt, the green band is still produced due to a transition between the donor level of impurities or lattice defects and the acceptor level of silver. The shifts to longer wavelength in the second band of photoluminescence may be attributed to the perturbation in the depths of these traps due to cobalt, i.e. the impurity donor–acceptor transition is still dominant at low concentrations of cobalt;

4. as cobalt concentration increases to 5×10^{-6} the donor (cobalt)–acceptor (silver) association takes place and becomes dominant. This radiative transition is accompanied by a non-radiative transition between the lower edge of the conduction band and/or donor-impurity levels and donor levels of cobalt. This mechanism leads to the decrease in the intensity of the first band without any displacement in its wavelength, and the increase in the intensity of the second band with the observed displacement towards longer wavelength. Because cobalt introduces its own trap depth at 0.55 eV below the conduction band in the presence of silver, the expected shift to longer wavelength should be larger than that observed experimentally. To explain the observed shift, the interaction between donor (cobalt)–acceptor (silver) has to be considered. This interaction decreases the transition energy, E_r, according to the equation [25, 26]

$$E_r = E_g - \left[(E_A + E_D) + \frac{e^2}{Kr_{AD}}\right] \quad (5)$$

where e^2/Kr_{AD} is the acceptor–donor interaction energy, E_g is the band gap energy, and E_A and E_D are the energies of acceptor and donor, respectively.

Due to this term, the acceptor–donor levels, the separation energy, E_r, is decreased with different values to fit the observed final shift towards the longer wavelength produced due to cobalt inclusion at high dopant levels.

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References

1. N. RIEHL and M. SCHON, *Z. Fur. Phys.* **114** (1940) 682.
2. M. SCHON, *ibid.* **119** (1942) 463.
3. H. A. KLASEN, *J. Electrochem. Soc.* **100** (1953) 72.
4. J. S. PRENER and F. E. WILLIAMS, *J. Phys. Rad.* **17** (1956) 667.
5. *Idem, Phys. Rev.* **101** (1956) 1427.
6. W. VAN GOOL, *Phil. Res. Rep.* **13** (1958) 157.
7. *Idem, Phil. Res. Suppl.* **3** (1961).
8. W. VAN GOOL and A. P. CLEIREN, *J. Electrochem. Soc.* **106** (1959) 672.
9. S. T. HENDERSON, P. W. RANDBY and M. B. HOLSTEAD, *ibid.* **106** (1959) 27.
10. E. F. APPLE, *ibid.* **105** (1958) 251.
11. E. F. APPLE and F. E. WILLIAMS, *ibid.* **106** (1959) 224.
12. E. F. APPLE and J. S. PRENER, *J. Phys. Chem. Solids* **13** (1960) 81.
13. G. CURIE and D. CURIE, *J. Phys. Rad.* **21** (1960) 127.
14. I. SOUDEK, *Brit. J. Appl. Phys.* **11** (1960) 289.
15. W. VAN GOOL and A. P. CLEIREN, *Phil. Res. Rep.* **15** (1960) 238.
16. F. A. KRÖGER and J. HELLINGMAN, *J. Electrochem. Soc.* **93** (1948) 156.
17. N. ARPIARIAN, *J. Chem. Phys.* **55** (1958) 667.
18. M. S. EL-MANHARAWY, *Czec. J. Phys. B* **20** (1970) 746.
19. M. KAKUDO and N. KASAI, "X-ray Diffraction by Polymer" (Kodansha Ltd, Elsevier, 1972).
20. S. E. ROBERTS and F. E. WILLIAMS, *J. Opt. Soc. Amer.* **40** (1950) 516.
21. D. CURIE, "Luminescence in Crystals" (Wiley, New York, 1963).
22. HUMBOLDT W. LEVERENZ, "An Introduction to Luminescence of Solids" (Dover, New York, 1968).

23. M. S. EL-MANHARAWY and A. H. EID, *Acta Phys. Hung.* **44** (1978) 117.

24. A. H. EID, M. S. EL-MANHARAWY and S. T. BADR, *Bull. NRC Egypt* **2** (1977) 339.

25. J. I. BIRMAN, *Proc. Intr. Conf. Lumin.* (1966) 919.

26. H. A. KLASEN, W. RAMSDEN and G. GUANTIE, *J. Opt. Soc. Amer.* **38** (1948) 60.

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