Photo and electroluminescence properties in Zns : (Cu, La) and Zns : (Ag, La) phosphors

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Abstract. A method for preparation of ZnS: (Cu, La) and ZnS: (Ag, La) phosphors is described. Photo and electroluminescence of these phosphors have been studied. The voltage and frequency variation of EL brightness have also been reported. The results agree with the collision-excitation mechanism in the Schottky barrier. The emission of blue, green and yellow bands has been interpreted in terms of different electronic transitions. Simultaneous action of both the field and the 3650 Å radiation has been studied. An attempt has also been made to explain the quenching and enhancement.

Keywords. Electroluminescence; photoluminescence; phosphors; ZnS: (Cu, La); ZnS: (Ag, La).

1. Introduction

ZnS phosphors doped with rare-earth ions find application in many electro-optical devices. This phosphor activated with metal ions and rare-earth ions emits a broad range of colours depending upon the nature of the impurity ions incorporated in the host lattice. Activation of ZnS with acceptor impurities like silver and copper results in emission of colours falling in the blue and green spectral regions (Toporec 1940; Kroger et al 1949; Alentsev and Cherepnev 1954; Leverenz 1968), while Mn gives an orange emission band in the same lattice (Kroger 1940; Levshin and Tunitakaya 1965). Froelich (1953 a & b) reported yellow and red emission bands in copper activated ZnS under special conditions of preparation. Incorporation of donor impurities such as rare-earth ions in ZnS lattice (Trapeznikova and Shchaenko 1956; Trapeznikova 1959; Ibuki and Langer 1963; Anderson et al 1965) produces various emission bands on both ultraviolet and alternating electric field excitations.

It is well known that lanthanum is the basic element of the lanthanide series and shows its specific luminescent behaviour in many compounds (Poluektov and Gava 1971; Poluektov et al 1971). Recently the present authors (Tripathi et al 1980a) reported the photoluminescence (PL) and electroluminescence (EL) properties of ZnS phosphors doped with Tb donor and Cu, Ag acceptor impurities, in which an interesting colour emission was found with change in the activator concentrations.

Kingsley et al (1965) reported the fluorescence due to energy transfer from copper and silver centres to rare-earth centres in the ZnS lattice. These authors reported

that line spectrum due to 4*f* electrons (*f—f* transition) of rare-earth ions is super-imposed over the general brightness.

The 4*f* electrons in the rare-earth ions are shielded from the outer shell electrons and therefore behave as if they were free ions. The crystalline field effect on these ions is small. La^{3+} ion differs from the rare-earth ions in that there is no electron in the 4*f* shell. The $5d\,6s^2$ electrons are ionised in the ZnS lattice. Lanthanum ion in such a situation behaves more like a 3rd group ion (like Al^{3+}) donor in ZnS lattice than a rare-earth ion. ZnS phosphors doped with both La (donor) and Cu or Ag (acceptor) impurities have not been studied. This paper presents the PL and EL properties of ZnS: (Cu, La) and ZnS:(Ag, La) phosphors on sinusoidal electric field and 3650 Å photon excitations.

2. Experimental

ZnS:(Cu, La) phosphors were prepared by firing a mixture of ZnS (luminescent grade), copper acetate ($Cu(CH_3COO)_2$), lanthanum sulphate ($La_2(SO_4)_3$) (analar grade) and excess of sulphur (0·5% by weight in each sample) in appropriate proportions. The charge was placed in a silica crucible. The firing was done in a silica tubular furnace maintained at 1000°C in the inert atmosphere of flowing argon gas. After the firing was complete, the charge was taken out of the furnace and immediately crushed and finely powdered to have a uniform particle size. ZnS: (Ag, La) phosphors were prepared by analogous method using requisite proportions of ZnS, $AgNO_3$, $La_2(SO_4)_3$ and excess of sulphur (0·5% by weight in each sample). The concentration of Cu/Ag and La varied between 0·01% to 0·1% (by weight). In the paper equal concentrations of activators Cu or Ag and coactivator La have been reported because they give intense emissions.

The EL condenser was designed by sandwiching a thin layer of phosphor dispersed in castor oil between two electrodes, one of which was a polished plane aluminium sheet and the other a plane conducting glass plate. The EL cells were excited by alternating electric field obtained from an audiofrequency oscillator coupled to a wide band amplifier. Phosphors were excited by 3650 Å radiation from a high pressure mercury lamp maintained to operate at a constant voltage. PEL was obtained by combining the PL and EL excitations. Spectral distribution of emitted radiation was determined by using a constant deviation spectrograph.

For detecting the integrated light output in PL, EL and PEL emissions, an RCA IP 21 photomultiplier tube having S-4 response was used. The multiplier was corrected to the response at various wavelengths. The output terminal of photomultiplier tube was connected to a sensitive multiflex galvanometer whose deflections give brightness in arbitrary units.

3. Result and discussion

3.1 *Fluorescence spectra*

3.1a *Photon excitation.* Samples of phosphors were irradiated by 3650 Å radiation and the spectral energy distribution curves of the PL emission were obtained for

different concentrations of activators and coactivators. In ZnS:(Cu, La) the spectrum consists of intense green emission band around 5300 Å which gradually shifts towards a lower wavelength on increasing the Cu^+ and La^{3+} concentrations (figure 1). This shows that these ions are also situated at interstitial positions (Leverenz 1948). The yellow emission band around 5700 Å also appears as a shoulder over the green band. This band is conspicuous at 0·05% and 0·1% of the Cu^+ and La^{3+} concentrations. In ZnS:(Ag, La) phosphors the peak emission occurs around 5200 Å with two bands with medium intensity around 4600 Å and 5700 Å (figure 2). The green
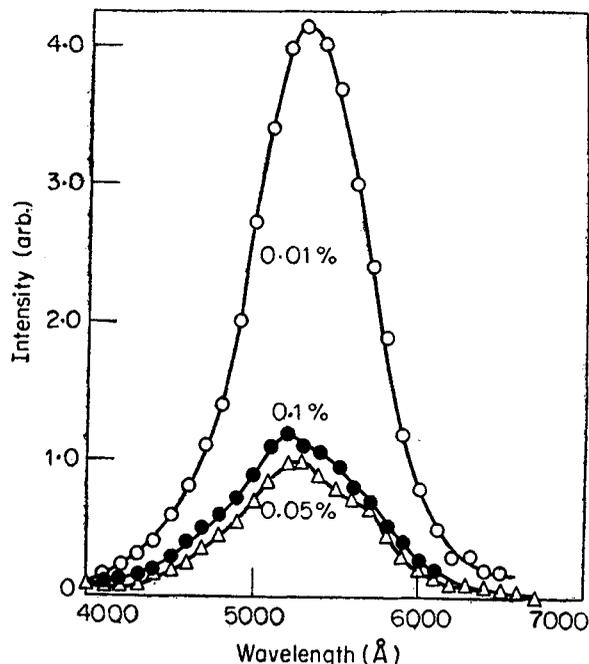

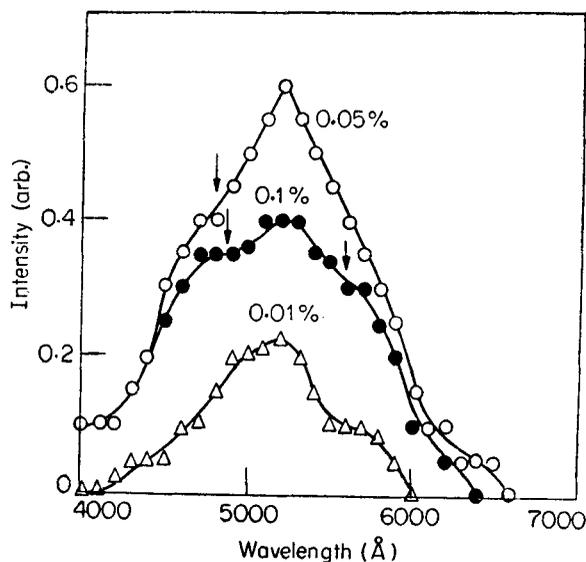**Figure 1.** PL spectra in ZnS (Cu, La) phosphor.

Figure 2. PL spectra in ZnS (Ag, La) phosphor.

band is more prominent than the blue or the yellow one. These phosphors also show the presence of a weak red band around 6300 Å.

3.1b *Field excitation.* The EL brightness of these phosphors was obtained by exciting the samples with sinusoidal electric field using various frequencies and amplitudes. The spectrum consists primarily of blue and green bands in ZnS:(Cu, La) phosphors positioned at 4700 Å and 5300 Å (figure 3); while in ZnS:(Ag, La) the spectra consist of emission bands around 4600 Å (blue) and 5700 Å (yellow) with comparable intensities (figure 4). A shoulder band around 5100 Å (green) also appears. The blue and green emission bands in both phosphors shift towards lower wavelength side on increasing the frequency of exciting field (Ostaszewiez 1965), whereas the yellow emission band (5700 Å) in ZnS:(Ag, La) is seen to shift towards higher wavelength side with frequency. The yellow band in ZnS:(Ag, La) appears more prominently than that in ZnS:(Cu, La). The other important feature of the PL and EL spectra in ZnS:(Cu, La) is that while the green band appears strongly in the PL spectrum at all concentrations shown in figure 1, the same appears strongly at lower frequencies ($<$ 50 Hz) in EL. Amazingly at higher frequencies ($>$ 500 Hz), the blue band appears with much higher intensity than the green one (figure 3). The brightness of the blue band is maximum at the field frequency of 2 kHz.

The emission of light from the above phosphors may be explained on the basis of associated donor-acceptor model (Prener and Williams 1956) of luminescence. The green band appears due to radiative D-A electron transition between La^{3+} (donor) and Cu^+/Ag^+ (acceptor) in the host lattice. The yellow emission band (5700 Å) may be ascribed to radiative transition ($E_g \rightarrow T_{2g}$) between the localised electronic states of the La^{2+} ions. As soon as La atom enters the lattice of ZnS occupying Zn^{++} ion site,
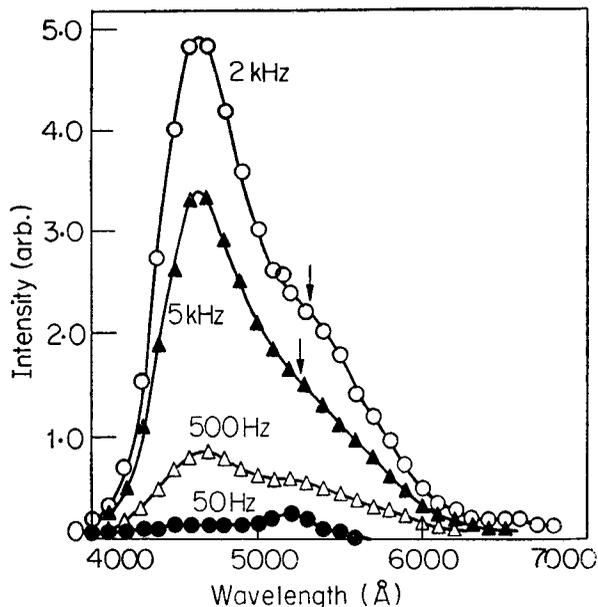

Figure 3. EL spectra in ZnS (Cu, La) phosphor having 0·05% Cu and La concentration at 750 V (rms) at different frequencies.
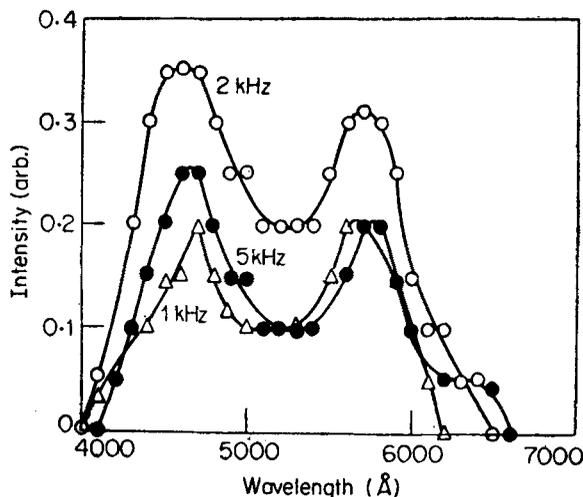
Figure 4. EL spectra in ZnS (Ag, La) phosphor having 0·01% Ag and La concentration at 750 V (rms) at different frequencies.

it gives off its two outermost valence electrons ($6s^2$) to the neighbouring sulphur atoms to form a stable bond. It then becomes La^{2+}. There is still one $5d^1$ electron on its outer shell which it can donate to the lattice. This outer d electron is subjected to the intense octahedral electric field of the neighbouring ions. The degeneracy of the d orbital is removed and splitting of the energy level (original D state) into triply degenerate T_{2g} and doubly degenerate E_g states takes place. The transition $E_g \to T_{2g}$ is allowed.

To confirm the above phenomenon, the PL and EL spectra of the ZnS phosphor doped with La only were studied using its different concentrations. It shows that the yellow band appears in EL and PL spectra. This band is sharp and intense (Tripathi *et al* 1980b). The EL spectrum of ZnS:La is also reproduced in figure 5.

The blue band may be ascribed to the electronic transition from the bottom of the conduction band to the Cu^+/Ag^+ recombination centre which have captured a hole from the valence band. The yellow band occurs very weakly in the PL and EL of ZnS:(Cu, La). This anomaly could be explained if we suppose that La^{3+} and Cu^+ form a tightly bound pair and the probability of occurrence of D-A transitions is more than the direct excitation of the La^{2+} ion. The weak red band may be attributed to electronic transition between donor-like S^{--} ion vacancies and Ag^+ or Cu^+ ion acceptor levels (Aven and Potter 1958).

3.2 *Variation of EL brightness with voltage and frequency of exciting field*

The EL brightness of the integrated light output as a function of applied a.c. voltage is shown in figure 6a. It is observed that the relation between the mean brightness (B) of the EL condenser and the voltage (V) is expressed by the equation (Zalm *et al* 1955; Zalm 1956)

$$B = B_0 \exp\left(- b/\sqrt{V}\right)$$

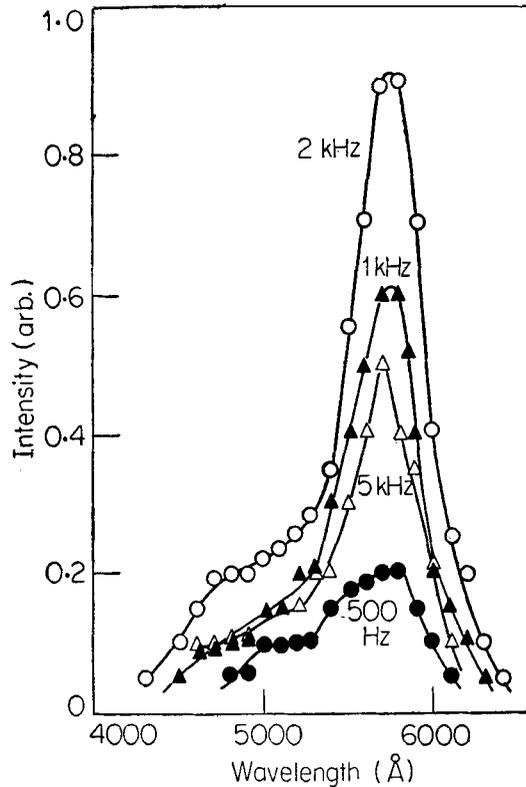where B_0 and b are constants independent of the voltage.

Figure 5. EL spectra in ZnS:La phosphor having 0.1% La concentration at 750 V (rms).

The electrons from donor centres (La^{3+}) or from the intrinsic electron traps are freed by the electric field and they enter the conduction band, where they are accelerated by the positive half cycle of the field until they gain sufficient kinetic energy to ionise or excite activator centres by inelastic impact.   In the reverse half cycle of the field these electrons recombine with the luminescence centres with emission of characteristic radiations. This mechanism corresponds to the impact ionization of the activator centres (Taylor and Alfrey 1955; Destriau and Ivey 1955; Zalm 1956; Piper and Williams 1958).

Variation of mean brightness (*B*) with frequency for different constant voltage is shown in figure 6b. In general the brightness increases with frequency rather linearly between the limits 400 Hz and 3 kHz. There is deviation from this behaviour between the frequency interval 3 and 4 kHz, where the brightness decreases abruptly almost in all the phosphors.   At lower frequencies between 50 and 400 Hz, the El brightness decreases slowly with frequency.   However the linear increase in EL brightness is in accord with the work on the other phosphors (Piper and Williams 1955; Zalm 1956; Matossi 1956).

The abrupt fall in EL brightness of the phosphor may be due to retrapping of some of the electrons in the empty donor levels and/or traps in the frequency range (4-5 kHz) of the applied voltage.   The trapped carriers are subsequently released by the field at still higher frequencies.   This explains the brightness rise beyond 5 kHz.
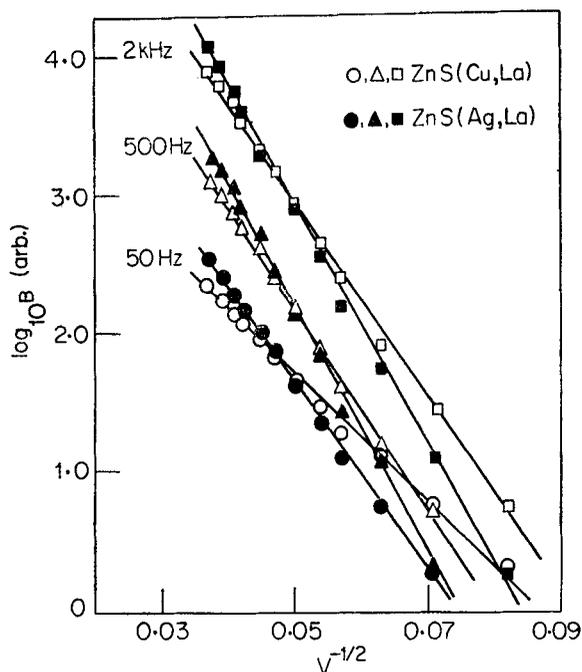
Figure 6a. Voltage dependence of EL brightness in ZnS (**Cu, La**) and ZnS (Ag, La) phosphors for 0·01% concentrations of Cu, Ag and La.
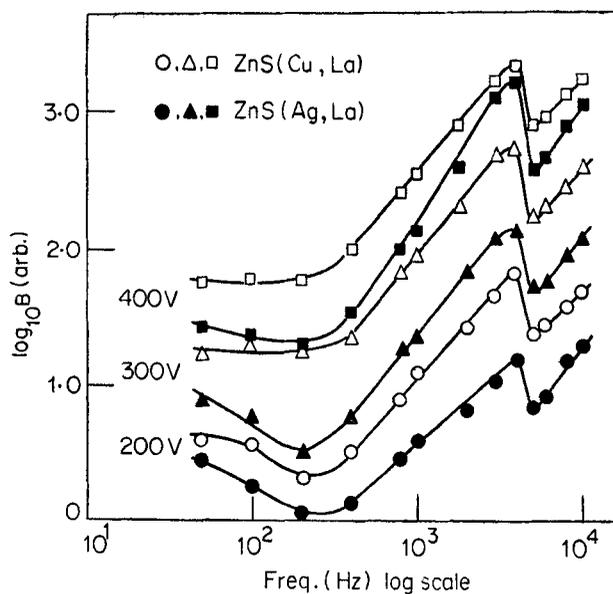
Figure 6b. Frequency dependence of EL brightness in ZnS (Cu, La) and ZnS (Ag, La) phosphors for 0.01% concentration of Cu, Ag and La.

The slow decrease of brightness with frequency (< 400 Hz) may be accounted for if it is supposed that the EL light initially acts as an exciting source which fills the traps. The number of conduction electrons therefore is reduced from the original

value.   These traps are later on emptied by the a.c. field and thus increasing the number of carriers for acceleration and subsequent collision with the luminescent centres.

The interpretation given above is only qualitative and no satisfactory theory exists for such a wide range of frequencies.   The heterogeneous structure of the EL cell which consists of the phosphors and the embedding medium together acting as a mixed dielectric also adds to the complexity.   The resistance of the electrodes, the dielectric properties of the phosphor and the medium, and the impedance of the condenser are also some of the important factors to be reckoned with.   It is also seen that the emission colour changes with frequency.   At lower frequencies the ZnS:(Cu, La) phosphor emits a green band while at higher frequencies a blue band also appears with intensity more than that of the green band (figure 3).   In ZnS:(Ag, La) the blue and yellow emission bands appear and their intensities change with frequency.   This is because at lower frequencies mainly the green centres are excited and the contri- bution of the blue centres is negligible or minimum to the light sum.   On gradually increasing the frequency, more and more blue centres are excited to emission over and above the green centres and thus the integrated light sum increases with frequency.

3.3.   *Effect of simultaneous action of field and photons on the luminescence emission*

Photoelectroluminescence (PEL) has been observed by the simultaneous excitation of alternating electric field (frequency 2 kHz and voltage 750 V) and UV radiations (3650 Å).   Figures 7 and 8 represent the variation of brightness of PL, EL and PEL emission with exciting time.   The measurements were carried out at the wavelength positions 4600, 4700, 5200 and 5700 Å.   For higher concentrations of activators and coactivators (0·1 % and 0·05 %) all these emission bands are quenched, while the blue emission band in both phosphors is enhanced for the lower concentrations of activators (0·01 %).
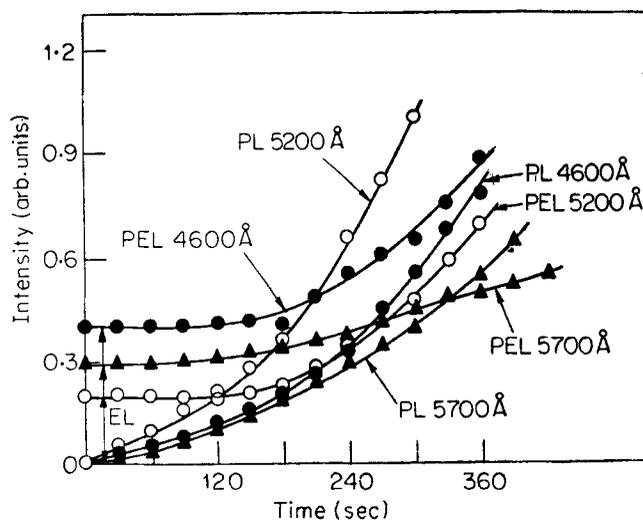

Figure 7.   Variation of PL and PEL intensity in ZnS (Ag, La) for 0·01 % Ag and La concentration.
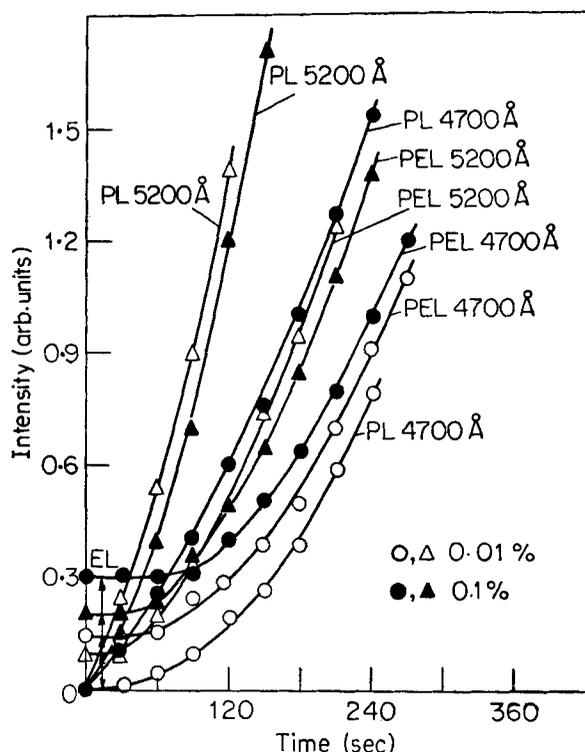
Figure 8. Variation of PL and PEL intensity in ZnS (Cu, La) for 0·01% and 0·1% Cu and La concentrations.

The quenching of these emission bands could be qualitatively understood if we suppose that some kind of trapping of excited carriers takes place at some deeper traps. Fewer electrons and holes are thus available and therefore lesser number of centres are excited to light emission whereas at lower concentrations of impurities, the lesser number of traps are available for trapping the electrons and therefore the probability of host lattice emission becomes maximum. This explains the enhancement of blue band.

Acknowledgement

References

Alentsev M N and Cherepnev A A 1954 *Zh. Eksp. Teor. Fiz.* **26** 473
Anderson W W, Razi S and Walsh D J 1965 *J. Chem. Phys.* **43** 1153
Aven M H and Potter R M 1958 *J. Electrochem. Soc.* **105** 134

Destriau G and Ivey H F 1955 *Proc. IRE* **43** 1911
Froelich H C 1953a *J. Electrochem. Soc.* **100** 280
Froelich H C 1953b US Patent 2 566, 660
Ibuki S and Langer D W 1963 *Appl. Phys. Lett.* **2** 93
Kingsley J D, Prener J S and Aven M 1965 *Phys. Rev. Lett.* **14** 136
Kroger F A 1940 *Luminescence in solids containing manganese*, Dissertation (Amsterdam: J. Van
    Campen)
Kroger F A, Hellingman J E and Smit N W 1949 *Physica* **15** 990
Leverenz H W 1948 *Preparation and characteristics of solid luminescent materials*, Cornell
    Symposium (New York: John Wiley) p. 146
Leverenz H W 1968 *An introduction to luminescence of solids* (New York: Dover) p. 74
Lvshin V L and Tunitakaya V F 1965 *Opt. Spectrsc.* **18** 182
Matossi F 1956 *J. Electrochem. Soc.* **103** 662
Ostaszewiz E 1965 *Acta Phys. Pol.* **27** 67
Piper W W and Williams F E 1955 *Br. J. Appl. Phys. Suppl.* **4** S39
Piper W W and Williams F E 1958 *Solid State Phys.* **6** 95
Poluektov N S, Efryushina N P and Smirdova N I 1971 *Opt. Spectrosc.* **31** 323
Poluektov N S and Gava S N A 1971 *Opt. Spectrosc.* **31** 45
Prener J S and Williams F E 1956 *Phys. Rev.* **101** 1427
Taylor J B and Alfrey G F 1955 *Br. J. Appl. Phys. Suppl.* **4** 44
Tripathi L N, Chaubey B R and Mishra C P 1980a *Phys. Status Solidi* A**60** 185
Tripathi L N, Chaubey B R and Mishra C P 1980b *Z. Natuurforschung* (Communicated)
Toporec A 1940 *Mem. Phys. (Keiv)* **8** 161
Trapeznikova Z A 1959 *Izv. Akad. Nauk SSR Ser. Fiz.* **23** 1319
Trapeznikova Z A and Shchaenko V V 1956 *Sov. Phys. Doklady* **1** 28
Zalm P 1956 *Phillips Res. Rep.* **11** 353, 417
Zalm P, Diemer D and Klasens H A 1955 *Phillips Res. Rep.* **10** 205