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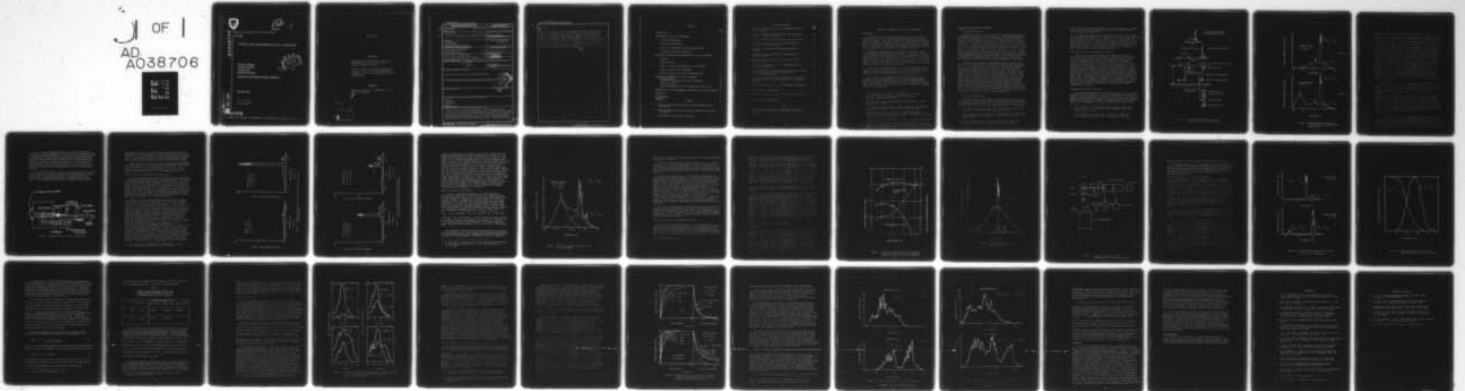
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SYNTHESIS AND LUNINESCENCE OF ZnS:Er, Cu PHOSPHORS

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Joseph O'Connell
Guy DeLhery
Benjamin Frowner

Electronics Technology & Devices Laboratory

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broad-band component in ZnS:Er,Cu phosphor with increasing firing time has been demonstrated. High concentrations of both, RE activator and sensitizer ions support the formation of cubic ZnS which reduces the luminescence efficiency and monochromatic character of the hexagonal ZnS:Er,Cu phosphor. The temperature dependence, as well as the excitation spectrum and the build-up and decay times of the Er^{3+} fluorescence have been investigated. A comparison of the line structure of the fluorescence bands due to the crystal field splitting of the Er^{3+} energy levels involved in the transitions, led to the conclusion that more than one possible lattice site exists for the Er^{3+} ion in these host lattices.

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CONTENTS

	<u>Page</u>
INTRODUCTION	1
LUMINESCENCE SPECTRA OF ZnS PHOSPHORS	2
Broad-band Luminescence	2
Narrow-band Luminescence	2
Model for Transitions in Sensitized RE-Phosphors	3
Luminescence Spectrum of ZnS:Er,Cu	3
PREPARATION CONDITIONS AND LUMINESCENCE OF ZnS:Er,Cu PHOSPHORS	6
Materials	6
Firing Procedure	6
Effect of Er and Cu Concentrations on Luminescence	8
Erbium Activated Cubic ZnS Phosphor	11
Effect of Firing Time on the Broad-Band Emission	13
LUMINESCENCE PROPERTIES OF ZnS:Er,Cu PHOSPHOR	14
Instrumentation	14
Temperature Dependence of the Er ³⁺ Fluorescence	18
Excitation Spectra	23
Build-up and Decay of the Er ³⁺ Fluorescence in ZnS:Er,Cu	25
COMPARISON OF THE Er FLUORESCENCE IN HEXAGONAL & CUBIC ZnS PHOSPHORS	28
CONCLUSIONS	31
ACKNOWLEDGMENTS	32
REFERENCES	33
FIGURES	
1. Model of Recombination Processes in Sensitized RE-Activated ZnS phosphor.	4
2. Photoluminescence Spectrum of Cu and Ag Sensitized Er Activated ZnS Phosphors.	5
3. Arrangement Used to Prepare the Phosphors.	7

CONTENTS (Continued)

	<u>Page</u>
4. Effect of Cu-Sensitization on the Er-Emission Intensity in ZnS Phosphor.	9
5. Effect of Er and Cu Concentrations on the Luminescence Spectrum of ZnS:Er,Cu Phosphor.	10
6. Er ³⁺ and Broad-band Emission in Cubic ZnS:Er,Cu Phosphor.	12
7. Effect of Firing Time on Er and Broad-band Emission Intensity in ZnS:Er,Cu Phosphor.	15
8. Comparison of Narrow-band and Broad-band Emitting Phosphors.	16
9. Diagram of Spectrometer System for Measuring of the Phosphor Properties.	17
10. Er ³⁺ Fluorescence Spectrum in ZnS:Er,Cu at RT and at Low Temperature.	19
11. Temperature Dependence of the Er ³⁺ Fluorescence Bands in ZnS:Er,Cu Phosphor.	20
12. Excitation Spectra of the Er Emission in ZnS:Er,Cu, and the Green-Cu and Blue-Cu Emissions in ZnS:Cu,Cl at Room-and Low Temperatures.	24
13. Build-up and Decay of Emission at Different UV Excitation Intensities of (A) ZnS:Er,Cu Phosphor, (B) ZnS:Cu,Cl Phosphor.	27
14. Details of the ${}^4S_{3/2} - {}^4I_{15/2}$ Er ³⁺ Transition in Hexagonal and Cubic ZnS:Er,Cu Phosphor.	29
15. Details of the ${}^2H_{11/2} - {}^4I_{15/2}$ Er ³⁺ Transition in Hexagonal and Cubic ZnS:Er,Cu Phosphor.	30

TABLE

1. Thermal Activation Energies Derived From The Temperature Dependence Of The Er ³⁺ Fluorescence Bands In ZnS:Er,Cu Phosphor.	22
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SYNTHESIS AND LUMINESCENCE OF ZnS:Er,Cu PHOSPHORS

INTRODUCTION

Phosphors emitting in a narrow-band luminescence spectrum are of particular interest in visual displays where high ambient illumination levels are present. Under such conditions the contrast and resolution of information displayed on phosphor screens have to be sufficiently high in order to maintain good readability. This applies to displays, as in cathode ray tubes (CRT) for radar, to graphical displays in computer outputs, in flat panel indicators, or displays in aircraft cockpits.

Narrow-band luminescence due to trivalent rare earth (RE) ions in II-VI compounds has been studied for many years. Little work, however, has been reported on RE activated zinc sulfide (ZnS) phosphors with narrow-band luminescence in the visible region of the spectrum.^{1,4} The Er-activated ZnS phosphor is of special interest since its emission spectrum consists of a single intense narrow-band in the green, very close to the wavelength of the maximum of the CIE photopic eye response and of a very low intensity band at a slightly longer wavelength.

It has been observed, however, that for apparently similar prepared phosphors, the Er emission may or may not be the dominant emission, but appears superimposed on a broad luminescence band.⁵ Variations in the appearance of the Er emission bands have also been observed.⁶

The purpose of this investigation was to determine the effect of synthesis and material parameters on the broad-band and narrow-band emission in ZnS:Er,Cu phosphors, to study the temperature dependence of the Er emission bands, the excitation spectrum, the luminescence rise and decay characteristics, and the difference of the Er emission in hexagonal and cubic ZnS host lattices.

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1. G. S. Goldsmith, S. Larach, R. E. Shrader and P. N. Yocom, "AC Field Excitation of Rare Earths in Zinc Sulfide," Sol. Stat. Comm. 1, pp. 25, 1963.
 2. S. Ibuki and D. Langer, "Energy Terms of ZnS:Tm and Ho," J. Chem. Phys., 40, pp. 796, 1964.
 3. W. W. Anderson, S. Razi and D. J. Walsh, "Luminescence of Rare-Earth-Activated Zinc Sulfide," J. Chem. Phys., 43, pp. 1153, 1965.
 4. M. Bancie-Grillot and M. P. Bourtayre, "Spectres d'émission photoluminescente du sulfure de zinc activé par les éléments des terres rares," J. de Phys. 27, C-2, pp. 116, 1966.
 5. E. Schlam, "ZnS:Er,Cu Phosphor Study," ECOM Technical Rpt. 3420, May 1971.
 6. M. Bancie-Grillot, "Étude de la fluorescence de l'erbium trivalent inclus dans le réseau cristallin du sulfure de zinc (wurtzite)," Compt. Rend. 267, pp. 1157, 1963. 1

LUMINESCENCE SPECTRA OF ZnS PHOSPHORS

Broad-band Luminescence

Luminescence spectra in ZnS and other II-VI compounds usually are of a bell-shaped broad-band type with a half-width of about 50-100 nanometers (nm). In ZnS phosphors, two types of intentionally added impurities are essential for the luminescence process, the activator which determines the wavelength of the broad-band peak and the co-activator which is necessary but has only a small effect on the spectrum. Copper (Cu) for example, as the activator substituting zinc (Zn) and chlorine (Cl) substituting sulphur, leads to the well known green emission band centered at $\lambda = 523$ nm. Trivalent ions such as Ga^{3+} or Al^{3+} at Zn sites, also act as co-activators and lead to the same green Cu emission when Cu is the activator ion. In photo-conducting phosphors such as ZnS, the transfer of the excitation energy can be described by the energy band model in terms of electron and hole recombination between localized acceptor and donor levels in the ZnS energy gap produced by the activator and co-activator impurities respectively.

In recent years, the concept of donor-acceptor pair association has been introduced in describing the luminescence process in ZnS type phosphors.^{7,8} It is reasonable to assume that at the preparation temperature of the phosphor (above 1000°C) ion diffusion is rapid and enhances the electrostatic attraction between the effective positive and negative charged activator and donor ions to form such pairs. The degree of association into pairs depends strongly on the intra-impurity distance in the crystal lattice. Depending on the firing conditions, the type and concentration of activator and co-activator ions incorporated, there will be a finite number of donors and acceptors close enough to be considered as pairs. The luminescence process is attributed to electron-hole recombination transitions within such pairs of various intra-pair distances. These distances in some cases can be next-nearest neighbor distances, in other cases, nearest neighbor distances or even distances over many lattice sites. The structureless broad-band luminescence spectrum in ZnS can be interpreted as resulting from the overlap of single emission bands involving transitions within pairs of various intra-pair distances.⁹

Narrow-band Luminescence

Rare-earth (RE) ions, particularly the trivalent RE ions as activator in ZnS and other II-VI compounds exhibit narrow-band luminescence resulting from transitions within the shielded 4f electron shell. The donor level associated with the RE^{3+} ion is due to the valence electrons and is located

7. J. S. Prener and F. E. Williams, "Activator Systems in Zinc Sulfide Phosphors," J. Electrochem. Soc. 103, pp. 342, 1956.
8. E. F. Apple and F. E. Williams, "Associated Donor-Acceptor Luminescent Centers in Zinc Sulfide Phosphors," J. Electrochem. Soc. 106, pp. 204, 1959.
9. K. Era, S. Shionoya and Y. Washizawa, "Mechanism of Broad-band Luminescence-I," J. Phys. Chem. Solids 29, pp. 1827, 1968.

about 0.4eV below the ZnS conduction band. It is estimated that the energy level structure of the inner shell of the RE ion is situated somewhere below the valence band edge of ZnS.

A strong tendency exists for the RE activator ion to pair with other defects in ZnS, with either lattice defects or intentionally added impurities which introduce an acceptor level. Kingsley, et. al.¹⁰ have shown that added impurities such as Cu increase the RE emission significantly. From this and similar results by others, the conclusion has been drawn that the RE luminescence in ZnS type host lattices is a sensitized luminescence by which energy transfer to the RE activator takes place via the Cu or other IB group elements acting as the sensitizer.

Model For Transitions in Sensitized RE-Phosphors

Unlike the broad-band emitting phosphors where the luminescence is associated with the radiative recombination transition of electrons and holes within donor-acceptor pairs, the recombination transition in RE activated ZnS phosphors is radiationless whereby the recombination energy is transferred directly to the 4f electrons of the RE³⁺ ions by a resonance transfer process. While the broad-band luminescence, as discussed above, is associated with transitions involving donor-acceptor pairs with intra-distances reaching over several atomic distances, it can be reasonably assumed that the non-radiative transitions and its subsequent energy transfer by resonance is favored when RE-sensitizer (donor-acceptor pairs) ions are paired at neighboring lattice sites to form the luminescence center. Depending on the concentration of the RE and sensitizer ions present, and on the preparation conditions of the phosphor, both types of processes may exist yielding a luminescence spectrum composed of a superposition of the broad-band and the narrow-band RE emission as frequently found in such RE activated ZnS phosphors. This situation is shown schematically in Figure 1.

Luminescence Spectrum of ZnS:Er,Cu

A typical room-temperature (RT) photoluminescence spectrum of ZnS:Er,Cu phosphor is shown in Figure 2A. This spectrum illustrates the simple Er³⁺ emission spectrum associated with transitions within the 4f shell, and the frequently observed broad-band emission spectrum associated with transitions within the ZnS band-gap. According to the energy level for trivalent RE ions,¹¹ the term assignment of the most intense Er³⁺ fluorescence band

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10. J. D. Kingsley, J. S. Prener and M. Aven, "Energy Transfer from Copper and Silver to Rare Earths in II-VI Compounds," Phys. Rev. Ltrs. 14, pp. 136, 1965.
 11. G. H. Dieke and H. H. Crosswhite, "The Spectra of Doubly and Triply Ionized Rare Earths," Appl. Optics, 2, pp. 675, 1963.

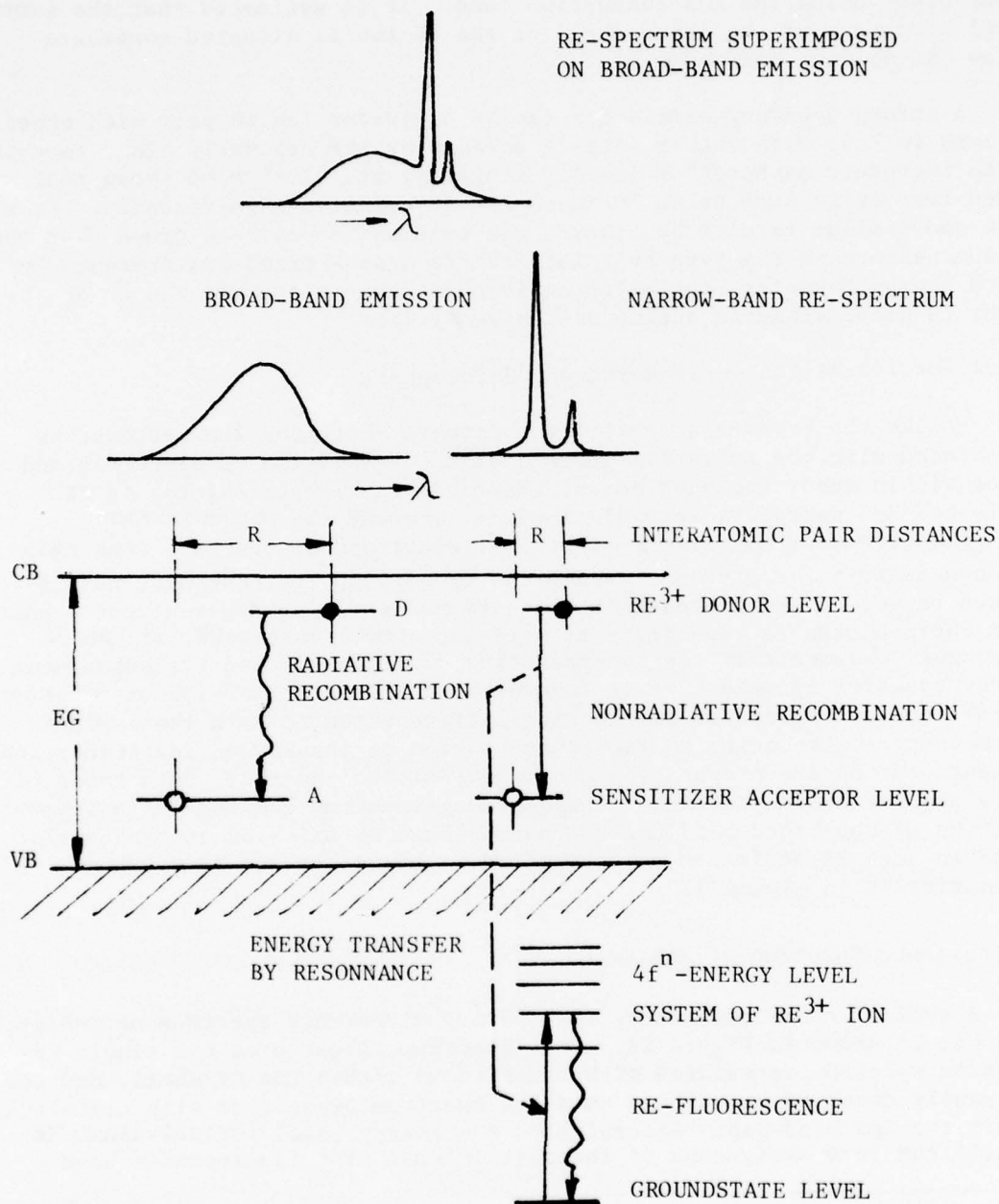


Figure 1. Model of Recombination Processes in Sensitized RE-Activated ZnS Phosphor.

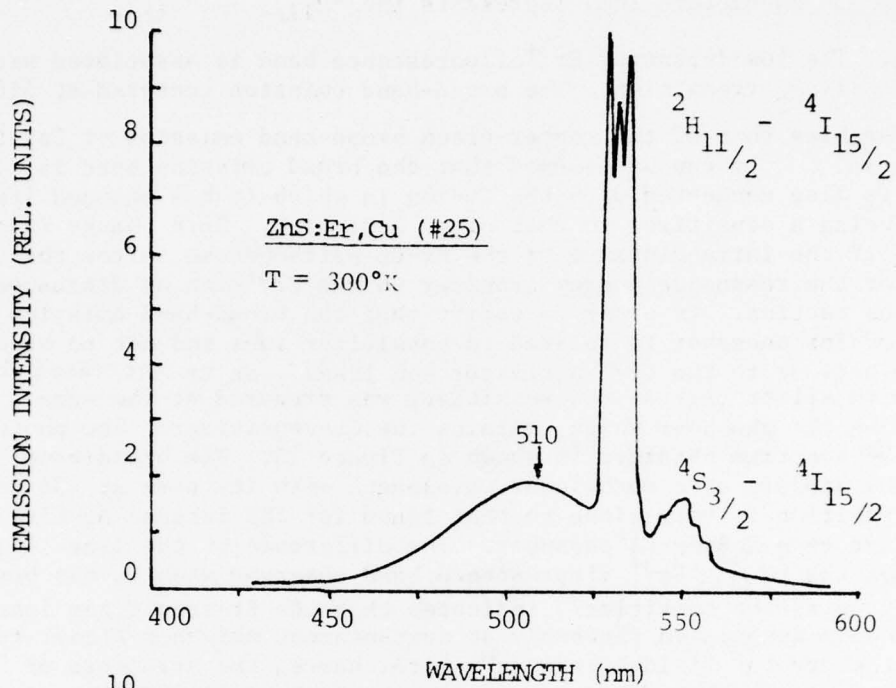


Figure 2A

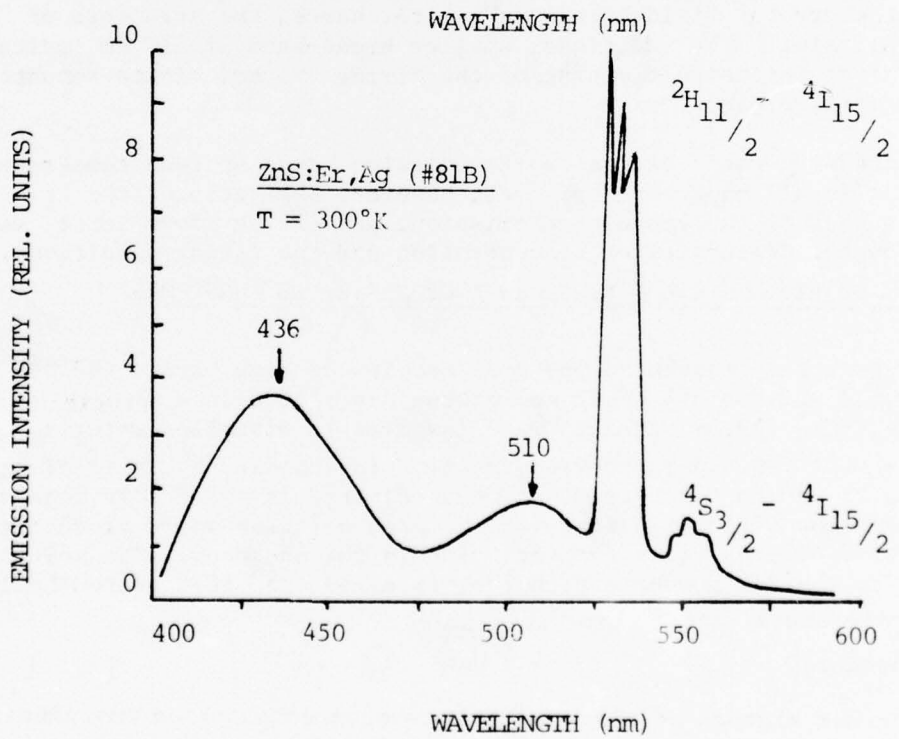


Figure 2B

Figure 2. Photoluminescence Spectrum of Cu and Ag Sensitized Er Activated ZnS Phosphors.

centered at 530 nanometers (nm) represents the ${}^2H_{11/2} - {}^4I_{15/2}$

transition. The low intensity Er^{3+} fluorescence band is associated with the ${}^4S_{3/2} - {}^4I_{15/2}$ transition. The broad-band emission centered at 510 nm closely resembles that of the copper-green broad-band emission of ZnS:Cu,Cl P-2 phosphors. It can be assumed that the broad emission band in ZnS:Er,Cu is also connected with the Cu-ion in which it has changed its role from being a sensitizer to that of an activator. Such change in role can result if the intra-distance of the Er-Cu pairs become larger than that required for the resonance energy transfer to the Er^{3+} -ion as discussed in the previous section. In order to verify that the broad-band emission of RE activator ZnS phosphor is related to sensitizer ions and not to other lattice defects or to the Er^{3+} activator ion itself, an Er activated ZnS phosphor with silver (Ag) as the sensitizer was prepared at the same conditions as the phosphor which contains the Cu-sensitizer. The photoluminescence spectrum obtained is shown in Figure 2B. The broad-band emission now appears at a much lower wavelength with its peak at 436 nm. This peak position is very close to that found for the intense Ag-blue emission band of a ZnS:Ag,Cl phosphor. The difference in the line splitting of the ${}^2H_{11/2}$ Er^{3+} fluorescence band observed when Cu has been replaced by Ag as the sensitizer, indicates that the Er-sensitizer ions must be closely associated (probably at next-nearest neighbor sites) to influence the crystal field at the Er^{3+} -site, hence, the structure of the line splitting. The additional smaller broad-band at 510 nm indicates that even after intensive cleaning of the firing system, minute amounts of Cu were still present.

The intensity ratio of the two Er emission bands at room temperature was constant in all phosphors prepared; however, the ratio of the Er emission to that of the broad-band emission, as will be shown later, varied depending on the Er/sensitizer concentration and the firing conditions.

PREPARATION CONDITIONS AND LUMINESCENCE OF ZnS:Er,Cu PHOSPHORS

Materials

To prepare the phosphors, one gram samples of high purity (99.999 percent from A. D. MacKay) cubic ZnS powder was placed in a crucible. High purity $ErCl_3$ (99.99 percent) was dissolved in distilled water and high purity CuCl (99.9 percent) was dissolved in ammonium hydroxide (ultra-pure). The Er and Cu concentrations were adjusted in these solutions such that the addition of 1 milliliter (ml) of each solution would produce the desired activator/sensitizer concentration in the phosphor. The solutions were added to the ZnS powder and thoroughly mixed, and then heated at $100^\circ C$ at least three hours, until completely dried.

Firing Procedure

The powder mixture of the selected phosphor composition was placed in a low copper content (Spectrosil) quartz boat and inserted into a Spectrosil tube with one sealed and one stoppered end. High purity H_2S gas was introduced through the stopper and vented to a Malco-sorb absorber. The reaction tube was first flushed for ten minutes at a H_2S gas flow rate of $1\text{ cm}^3/\text{sec}$, and then stabilized to a rate of $0.1\text{ cm}^3/\text{sec}$ before inserting into the furnace.

Prior to firing, a Lindberg heavy-duty SiC furnace (#54233) was brought up to firing temperatures. The furnace had a regulated power supply for constant temperature operation. The reaction tube was then inserted into the furnace. Firing time was measured from the time the material reached the firing temperature as determined from a thermocouple in the vicinity of the boat. At the end of the firing, the reaction tube was removed quickly from the furnace and placed on a slab of Transite for further cooling. During the cooling cycles, the pre-set H_2S gas flow was maintained. Figure 3 shows the arrangement used to fire the phosphor materials.

The fired phosphor sample was first visually inspected with an ultraviolet lamp and then mounted for spectroscopic investigation on a copper or glass plate using settling techniques with water or amylacetate. The transition temperature for the cubic to hexagonal phase in ZnS is $1020^\circ C$. Since the luminescent properties of hexagonal ZnS in general

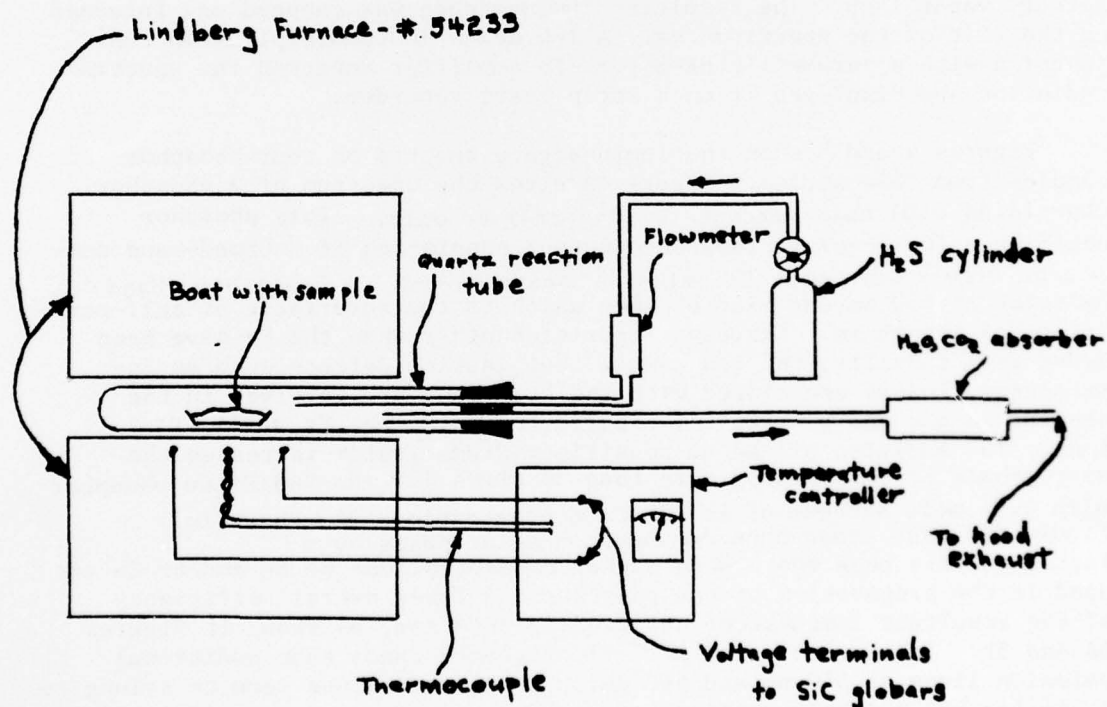


Figure 3. Arrangement Used to Prepare the Phosphors.

are superior to cubic ZnS,¹² initial phosphors were fired above this temperature at 1175°C. Removing the reaction tube from the furnace and letting it cool in air was used as a means of quenching in the hexagonal phase. X-ray diffraction analysis of the resulting phosphors showed that the starting cubic material was converted to the hexagonal phase.

During the course of the investigation, approximately 170 phosphors were fired. The Cu, Er concentrations were in the range 0.001 mole percent (6×10^{16} cm³) to 0.1 mole percent (6×10^{18} cm³). The majority of samples had equal concentrations of Cu and Er, although samples were prepared where the Cu/Er ratio ranged from 0.1 to 10.

Effect of Er and Cu Concentrations on Luminescence

A series of phosphors doped with different Er and Cu concentrations were prepared from ZnS powder mixtures containing Er ranging from 0.01 to 0.1 mole percent and Cu ranging from 0 to 0.1 mole percent. The powder mixtures were fired in an H₂S atmosphere at 1175°C for two hours and rapidly cooled to room temperature. Photoluminescence measurements on these prepared phosphors were made in an experimental set-up using a 1/2 meter Jarrell Ash spectrometer. The excitation was from a ultra-violet mercury vapor lamp. The resulting luminescence was chopped and focussed on the slit of the spectrometer. A low noise photomultiplier in conjunction with a parametric HR-8 lock-in amplifier detected the spectral radiation and displayed it on a strip chart recorder.

Figures 4 and 5 show the luminescence spectra of four phosphor samples from this series. Figure 4A gives the spectrum of a phosphor containing 0.01 mole percent (6×10^{17} /cm³) Er only. This phosphor exhibits a low level luminescence output consisting of a broad-band component with a very weak Er emission superimposed. A small blue band emission at 450 nm can also be seen which is characteristic of self-activated ZnS phosphors. Since no impurities other than the Er have been added intentionally, one can assume that lattice defects such as Zn-vacancies, closely associated with the Er³⁺ ions, are involved in the absorption and energy transfer process to excite the Er activator ions. The addition of the Cu sensitizer dramatically increases the narrow-band Er emission by more than 30 times for the ZnS:Er,Cu phosphor with 0.01 mole percent of Er and Cu concentrations as shown in Figure 4B. The broad-band component has increased by a factor of less than two. When higher concentrations of Er and/or Cu are used in the preparation of the phosphors, a lower overall efficiency of the resultant luminescent spectrum is obtained, as shown in Figures 5A and 5B. Furthermore, the Er³⁺ fluorescence bands show additional emission lines at 540 nm and 560 nm. These extra lines seem to belong to a similar but slightly shifted set of fluorescence bands superimposed on the Er spectrum, obtained with lower Er and Cu concentrations. These phosphors when subjected to X-ray diffraction analysis, revealed the presence of the cubic ZnS phase. Sample Number 87 (Figure 5A) with an

12. H. W. Leverenz, An Introduction to Luminescence of Solids, John Wiley & Sons, New York, N.Y. pp. 331, 1950.

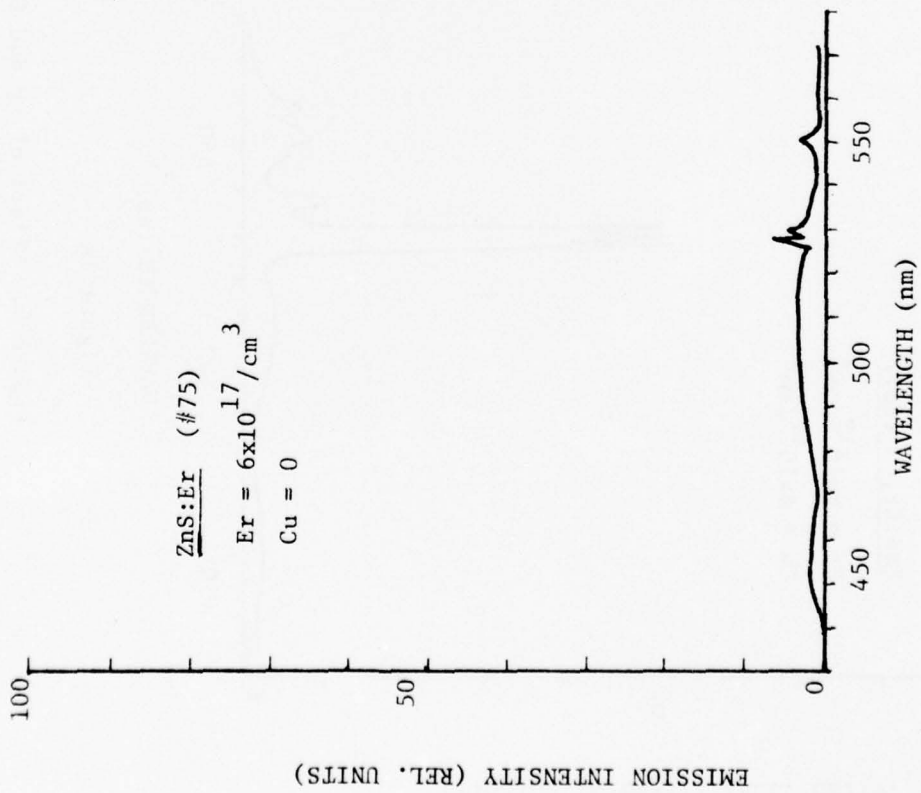


Figure 4A

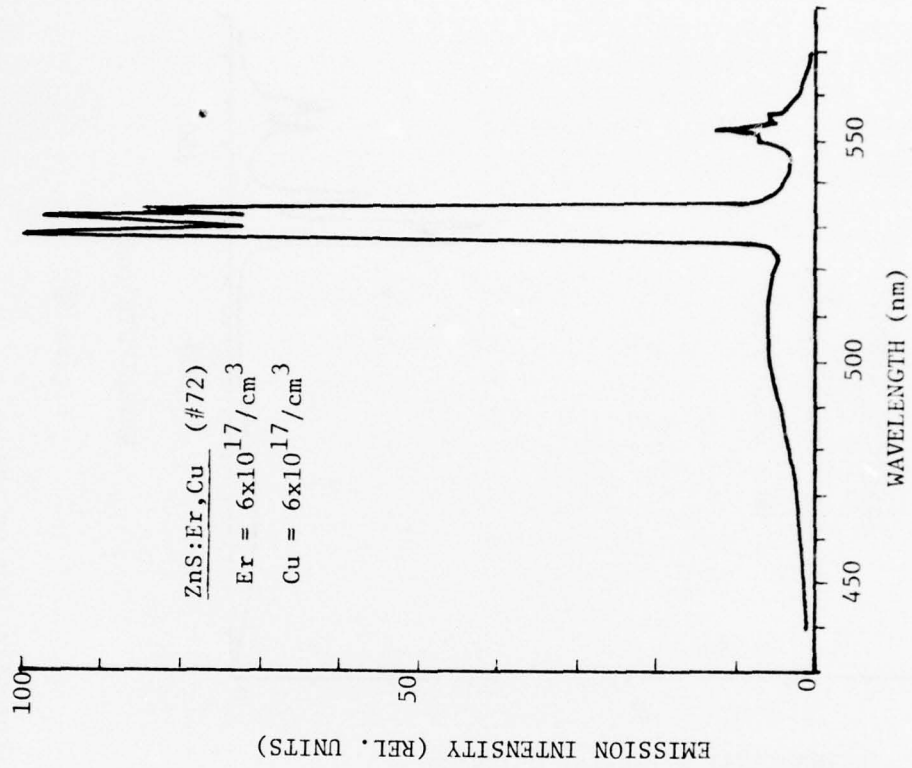


Figure 4B

Figure 4. Effect of Cu-Sensitization on the Er-Emission Intensity in ZnS Phosphor.

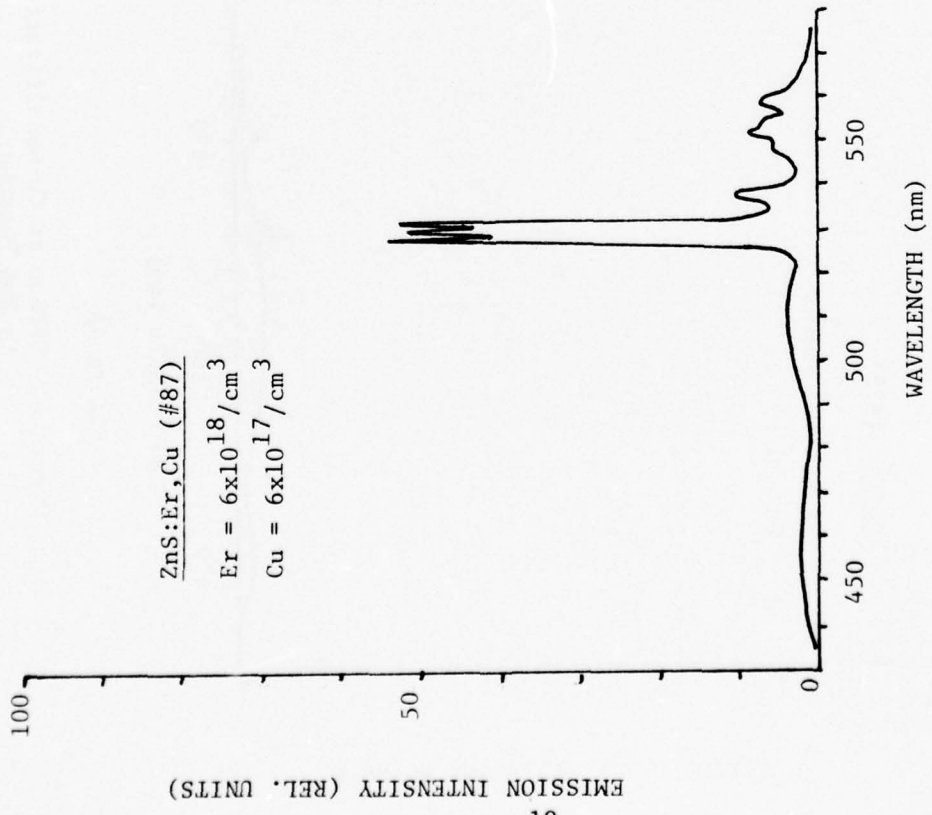


Figure 5A

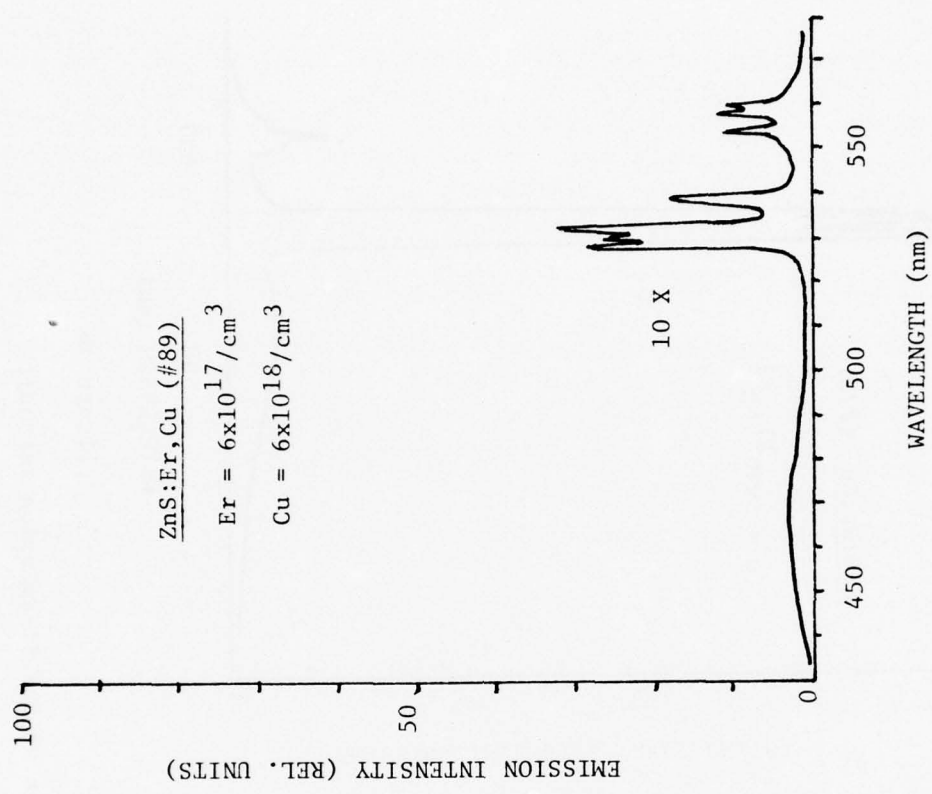


Figure 5B

Figure 5. Effect of Er and Cu Concentrations on the Luminescence Spectrum of ZnS:Er,Cu Phosphor.

Er and Cu concentration of 0.1 and 0.01 mole percent, respectively was composed of approximately 75 percent hexagonal and 25 percent cubic ZnS. Sample Number 89 (Figure 5B) with 0.01 mole percent of Er and 0.1 mole percent of Cu, however, showed approximately 25 percent hexagonal and 75 percent cubic ZnS. These results show that in these phosphors, even if prepared at temperatures as high as 1250°C, well above the cubic hexagonal transition temperature (1020°C), the high impurity concentrations stabilized the cubic ZnS phase above the normal transition temperature, and also reduced the phosphor efficiency. While in both phosphor samples the total amount of Er and Cu impurities is the same, it appears, however, that high Cu concentration more readily stabilizes the cubic ZnS phase than does the high Er concentration. Aven and Parodi¹³ have shown that copper concentrations in excess of 10⁻⁴ atomic fraction in ZnS can trigger a rapid transformation of hexagonal to cubic ZnS. They believe that this trigger effect results from the precipitation of copper sulfide as a separate phase which supplies the energy necessary to nucleate the cubic ZnS. These findings suggest that a similar catalytic effect may be responsible for the presence of the cubic ZnS phase in our phosphors containing high concentrations of Cu and/or Er.

Erbium Activated Cubic ZnS Phosphor

In order to determine the component of the Er³⁺ fluorescence spectrum that belongs to the cubic ZnS phase in the emission spectrum of the phosphors with high Er and Cu concentrations as described in the previous paragraph, a phosphor with 0.1 mole percent of Er and Cu was prepared at 990°C. X-ray diffraction analysis showed that the phosphor represented a pure cubic ZnS. The photoluminescence spectrum of this cubic ZnS:Er,Cu phosphor is given in Figure 6. The Er emission bands appear superimposed on a broad-band emission peaking at 464 nm. Similar to the hexagonal ZnS phosphor, the two Er³⁺ fluorescence bands in the cubic ZnS phosphor are associated with the $^2H_{11/2} - ^4I_{15/2}$ and $^4S_{3/2} - ^4I_{15/2}$ transitions. Also, the intensity ratio of both bands

are similar. The line structure of the Er³⁺ fluorescence bands, however, is different from that in the hexagonal ZnS phosphors. In addition, the two Er emission bands are slightly (about 2.5 nm) shifted toward the longer wavelength side with respect to their positions in the hexagonal ZnS.

The difference in line structure and the spectral shift of the Er³⁺ fluorescence bands in cubic ZnS account for the additional lines observed in the Er emission bands if both the hexagonal and cubic ZnS phase types are present in the ZnS phosphor. Generally this occurs if either the

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13. A. Aven and J. A. Parodi, "Study of the Crystalline Transformations in ZnS:Cu, ZnS:Ag and ZnS:Cu,Al," J. Phys. Chem. Solids, 13, pp. 56, 1960.

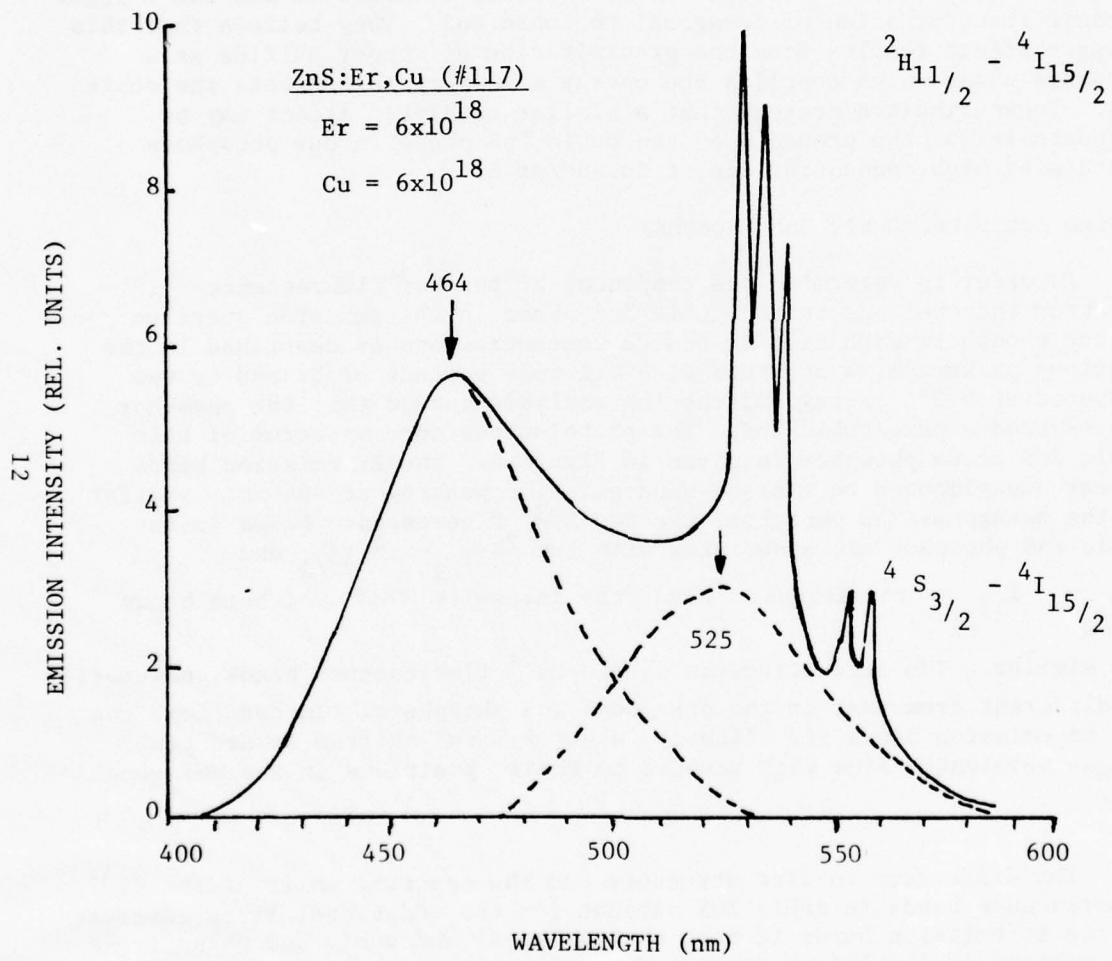


Figure 6. Er^{3+} and Broad-band Emission in Cubic ZnS:Er,Cu Phosphor.

activator and sensitizer concentrations are high or the firing temperatures and quenching rate are low.

Since the presence of both ZnS phases in RE activator ZnS phosphors results in a RE fluorescence spectrum which actually is the spectrum of two, superimposed, it is not surprising that inconsistent literature data on the Er-fluorescence spectrum in ZnS with respect to the number of bands, precise positions, half-width, and line structure of the bands, have been reported.¹⁴

The broad-band emission of the cubic ZnS:Er,Cu phosphor with its peak of 464 nm, as shown in Figure 6, is located at a considerably shorter wavelength than the broad-band emission in the hexagonal ZnS:Er,Cu which peaks at 510 nm. The long wavelength tail of the 464 nm broad-band indicates, however, the presence of a second band located about 525 nm as drawn in by the dashed lines. The change from the hexagonal to the cubic form of ZnS of a conventional Cu-activated phosphor (ZnS:Cu,Cl) is generally marked by an emission band predominately in the blue spectral region and, depending on the Cu concentration, with a weak Cu-green emission band. The same seems to be true for the broad-band emission in cubic and hexagonal ZnS:Er,Cu phosphors. Because the cubic ZnS has a smaller band gap than the hexagonal ZnS, one should expect a slight shift of the broad-band emission band in the cubic ZnS toward the larger wavelength side which actually is found if one compares the corresponding broad-band peaks at 510 nm in the hexagonal ZnS and the 525 nm peak in the cubic ZnS.

The rather strong intensity of the broad-band emission of this cubic ZnS:Er,Cu phosphor indicates that the diffusion rate of the Cu-ions at 990°C is much larger than that of the Er-ions. It required about a 9 hour firing time to obtain an appreciable Er fluorescence spectrum as compared with about 2-4 hours at 1175°C to prepare a hexagonal ZnS:Er,Cu phosphor from the same batch of material.

Effect of Firing Time on the Broad-Band Emission

In order to determine the dependence of the luminescent output of the ZnS:Er,Cu phosphor, specifically that of the broadband emission, on the firing time, a series of identical phosphor mixtures were prepared and fired at 1175°C for various periods of time. The mixtures were prepared to yield a phosphor containing 0.01 mole percent ($6 \times 10^{17}/\text{cm}^3$) of Er and Cu.

14. M. Bancie-Grillot - *ibid*

The firing time varied from one-half to four hours. The photoluminescence spectrum of each fired sample was recorded and the intensities of the ${}^2H_{11/2}$ Er fluorescence band and that of the broad-band component were measured. The data obtained and plotted as a function of firing temperatures are shown on the graph in Figure 7. The intensity of the broad-band decreases very strongly with increasing firing time until, at four hours, it is below the detection limit of the recording instrument. The narrow-band ${}^2H_{11/2}$ Er fluorescence emission increases by a factor of 2.5 for firing times up to two hours and then decreases slightly from two to four hours. After the four hours of firing, the ratio of the Er and broad-band peaks has increased by more than 100 times. The results obtained, show that the undesirable broad-band emission of ZnS:Er,Cu phosphors can be drastically reduced, or even eliminated with increasing firing time and hence can yield a nearly monochromatic phosphor of high contrast.

A similar drastic decrease of the broad-band emission with increasing firing time has been found for the ZnS:Er,Ag phosphor Number 81B of Figure 23.

In order to compare the emission of the narrow-band ZnS:Er,Cu phosphor with that of a conventional broad-band ZnS:Cu,Cl phosphor, the photoluminescence spectra of phosphor Number 72 and a commercial P-2 phosphor were taken under identical conditions and plotted in Figure 8 in relative intensity units. While the total luminous flux of the narrow-band phosphor is only about 30 percent of the broad-band component phosphor, a higher contrast, however, with the narrow-band phosphor is achieved which is important in display devices operating at high ambient radiations. To further increase the contrast, an appropriate narrow-band filter can be used to block out the ambient light except in the narrow wavelength region of the emission band without affecting significantly the total luminance of this phosphor. The broad-band emitting phosphor, on the other hand, using the same filter would not only lose about 70 percent of its luminance but would have half of the intensity only in the wavelength region of the narrow-band phosphor.

LUMINESCENCE PROPERTIES OF ZnS:Er,Cu PHOSPHOR

Instrumentation

The experimental set-up used for the investigations of the temperature dependence of the Er^{3+} fluorescence spectrum in ZnS:Er,Cu phosphor, the excitation spectrum, the rise and decay characteristics, and the details of the line structure of the Er^{3+} fluorescence bands, is shown in Figure 9. The phosphor sample is excited by a 5000 watt high pressure Xenon lamp after filtering by two 1/4 meter Ebert monochromators. A small fraction of the excitation light is monitored by the CdSe cell via the beam splitter. The remotely controlled shutter with variable aperture and shutter speed is used for the luminescence build up and decay studies. The phosphor is mounted on a heatable sample holder and placed in a liquid nitrogen dewar. The sample temperature can be maintained anywhere between liquid nitrogen temperature (LNT) and 100°C. For higher temperatures, up to 250°C, the

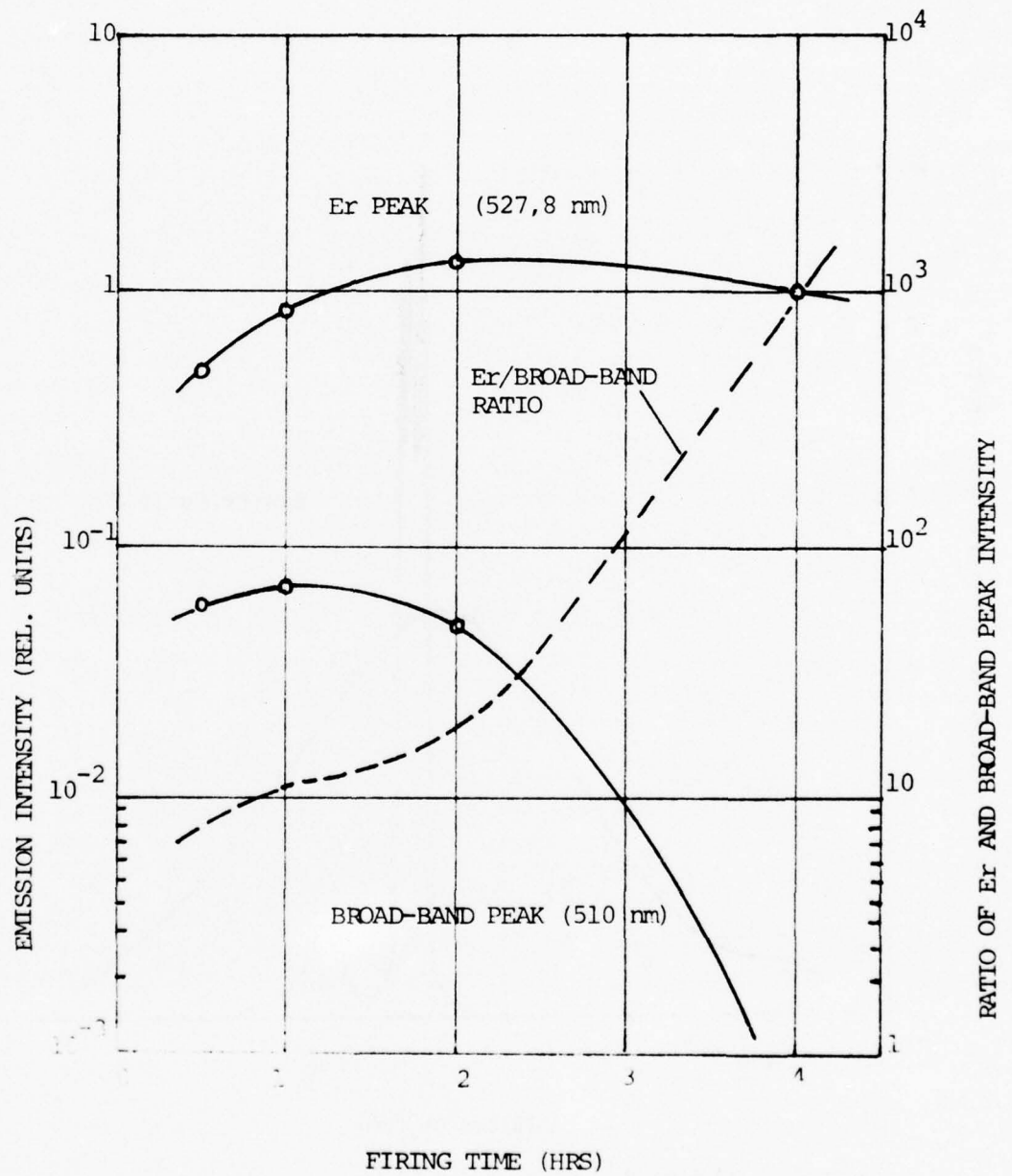


Figure 7. Effect of Firing Time on Er and Broad-band Emission Intensity in ZnS:Er,Cu Phosphor.

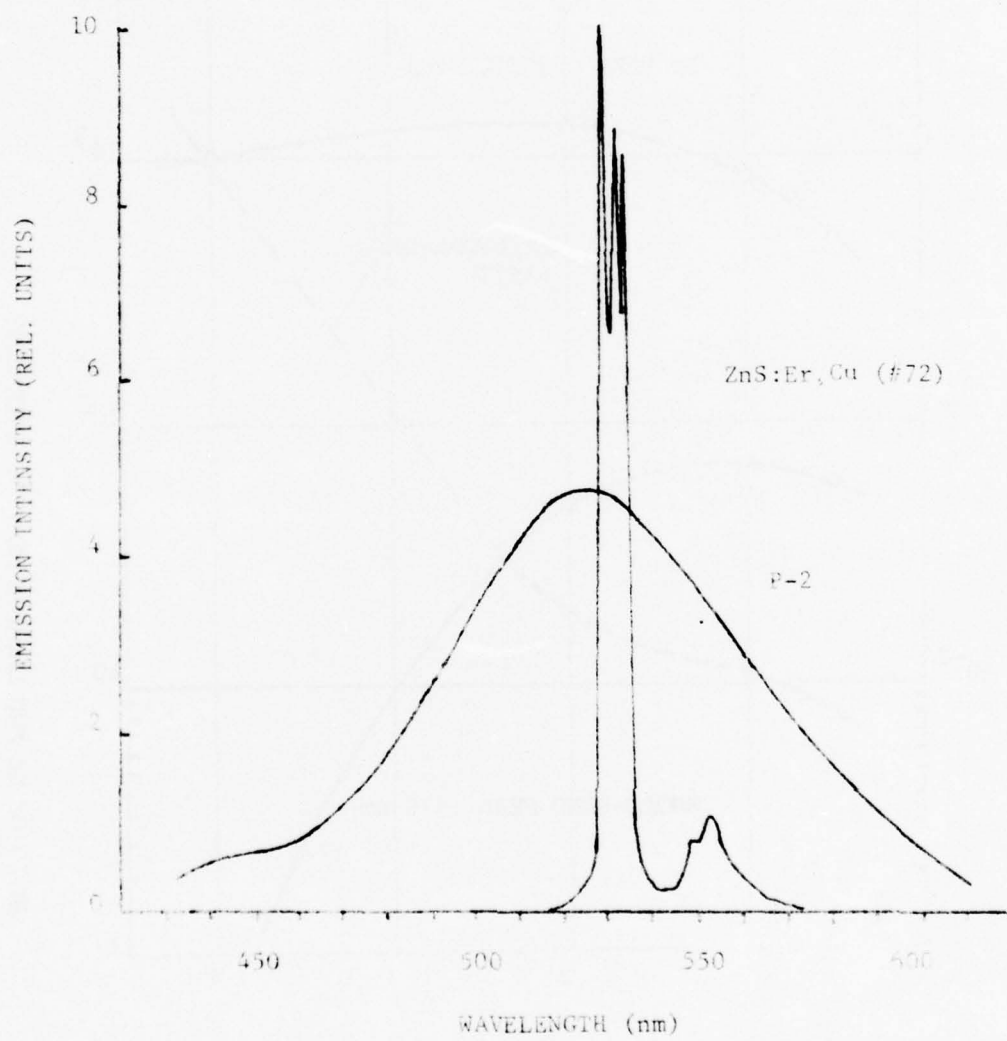


Figure 8. Comparison of Narrow-band and Broad-band Emitting Phosphors.

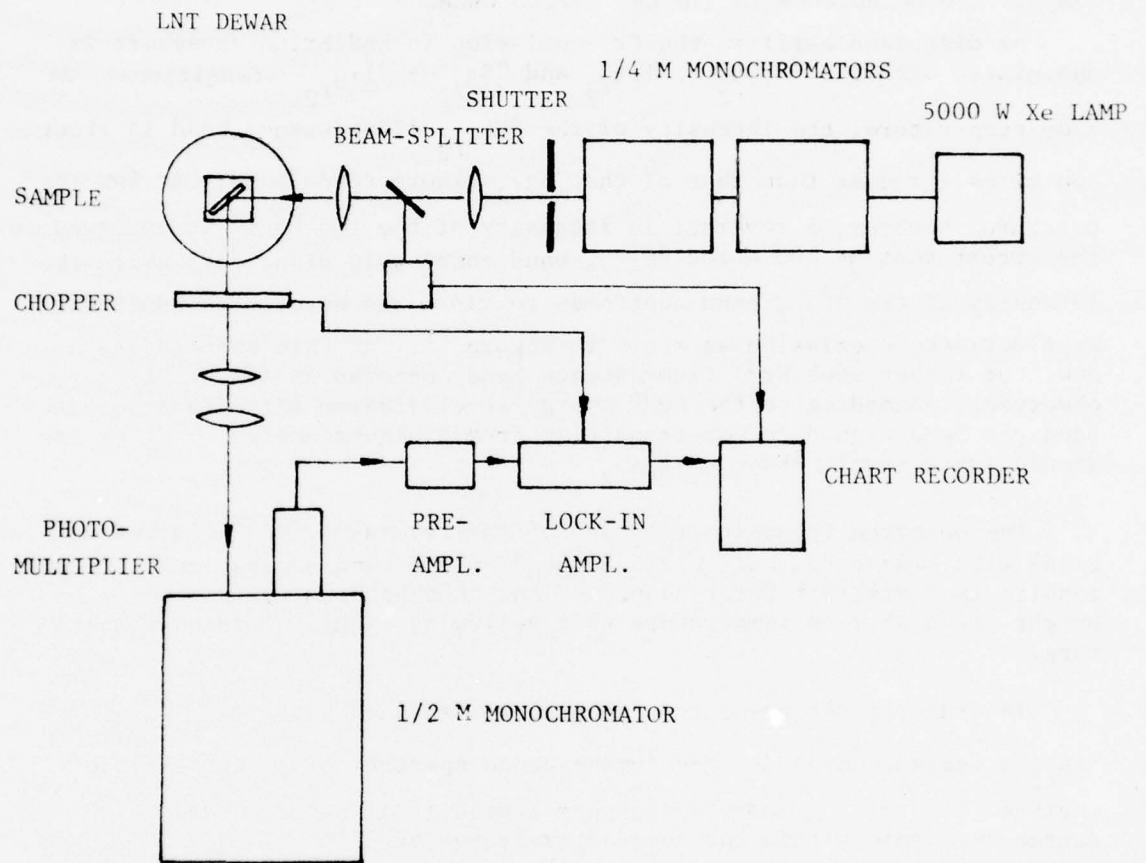


Figure 9. Diagram of Spectrometer System for Measuring of the Phosphor Properties.

phosphor sample was placed on a temperature controlled heating plate.

The phosphor luminescent output is chopped by the PAR chopper to provide an AC signal for the electronic metering and a reference signal for the signal processing amplifier and then received by the photomultipliers via the 1/2 meter Ebert monochromator. The photomultiplier output is amplified and displayed on a two-channel brush recorder together with the output from the monitor.

Temperature Dependence of the Er^{3+} Fluorescence

As discussed earlier, the Er emission in ZnS:Er,Cu phosphors is associated with the ${}^2\text{H}_{11/2} - {}^4\text{I}_{15/2}$ and ${}^4\text{S}_{3/2} - {}^4\text{I}_{15/2}$ transitions. At room temperature, the intensity of the ${}^2\text{H}_{11/2}$ fluorescence band is about ten times stronger than that of the ${}^4\text{S}_{3/2}$ fluorescence band. At low temperature, however, a reversal in intensity of the two bands is observed to the extent that at 100°K the ${}^2\text{H}_{11/2}$ band completely disappears while the intensity of the ${}^4\text{S}_{3/2}$ band continues to rise and becomes the dominant Er fluorescence emission as shown in Figure 10. At this temperature a new, but rather weak Er^{3+} fluorescence band centered at 465 nm, is observed. According to the Er^{3+} energy level diagram this fluorescence band can be assigned to the transition from a higher energy level to the ground state level, ${}^4\text{F}_{5/2} - {}^4\text{I}_{15/2}$.

The observed intensity reversal of the two narrow Er^{3+} fluorescence bands with a spectral half-width about 8 nm and band separation of 21 nm results in a distinct color change of the phosphor luminescence from a bright green at room temperature to a yellow at liquid nitrogen temperature.

In order to determine the temperature dependency of the ${}^2\text{H}_{11/2}$ and ${}^4\text{S}_{3/2}$ fluorescence bands, the luminescence spectrum of an ultra-violet excited (365 nm) ZnS:Er,Cu phosphor sample (#21) was recorded at 20 degree intervals within the temperature range of $77^\circ\text{K} - 500^\circ\text{K}$. For each temperature, the areas under the two fluorescence bands were measured and plotted as a function of temperature, Figure 11. The results show that the intensity of the ${}^2\text{H}_{11/2}$ reaches a maximum slightly below room temperature, at 275°K , and decreases rapidly with decreasing temperature. The intensity of the ${}^4\text{S}_{3/2}$ band, on the other hand, continuously increases with decreasing temperature and reaches a maximum at 80°K . Above room temperature the intensities of both fluorescence bands are decreasing rapidly, and approach zero at elevated temperature, which is 400°K for the ${}^4\text{S}_{3/2}$ band and 500°K for the ${}^2\text{H}_{11/2}$ band.

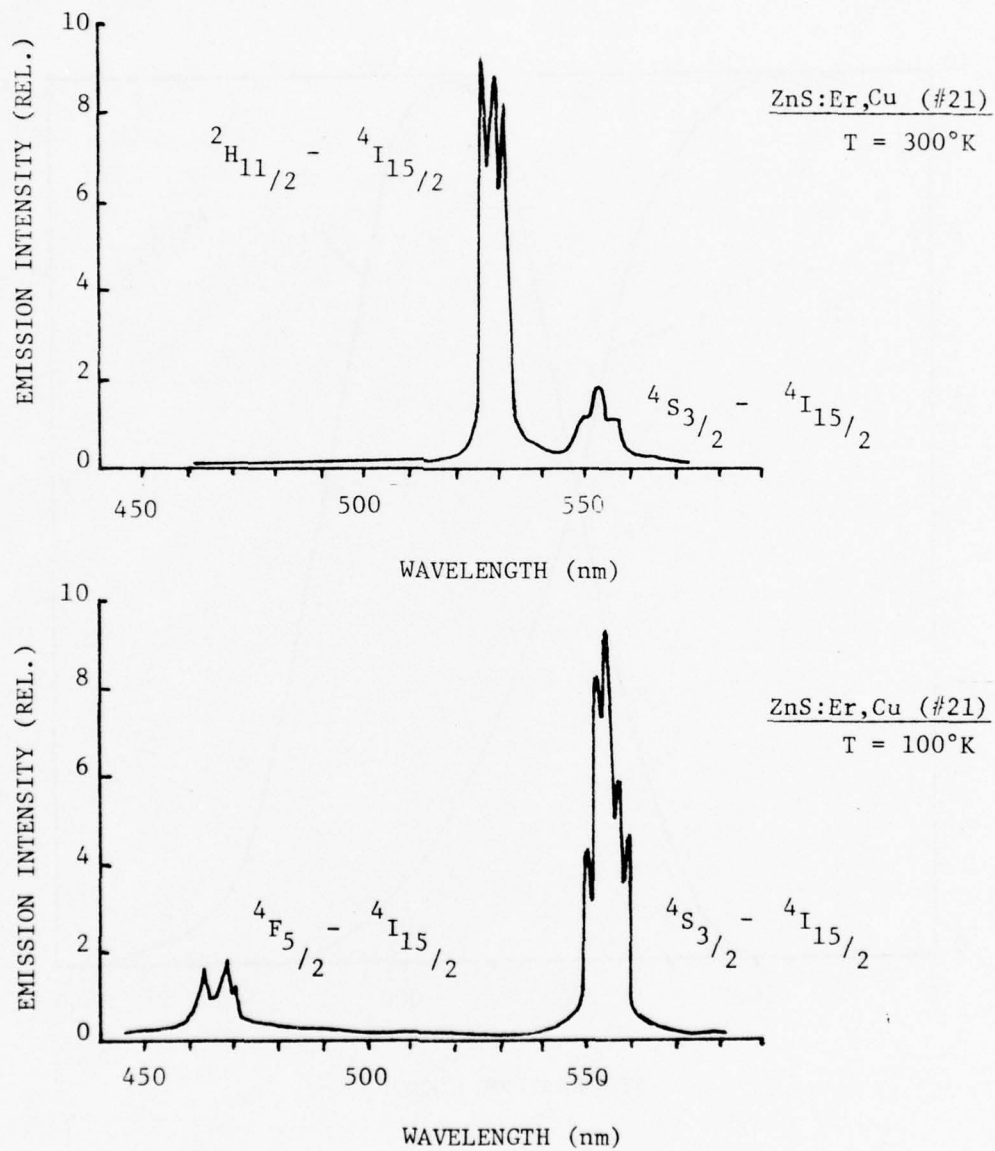


Figure 10. Er^{3+} Fluorescence Spectrum in ZnS:Er,Cu at RT and at Low Temperature.

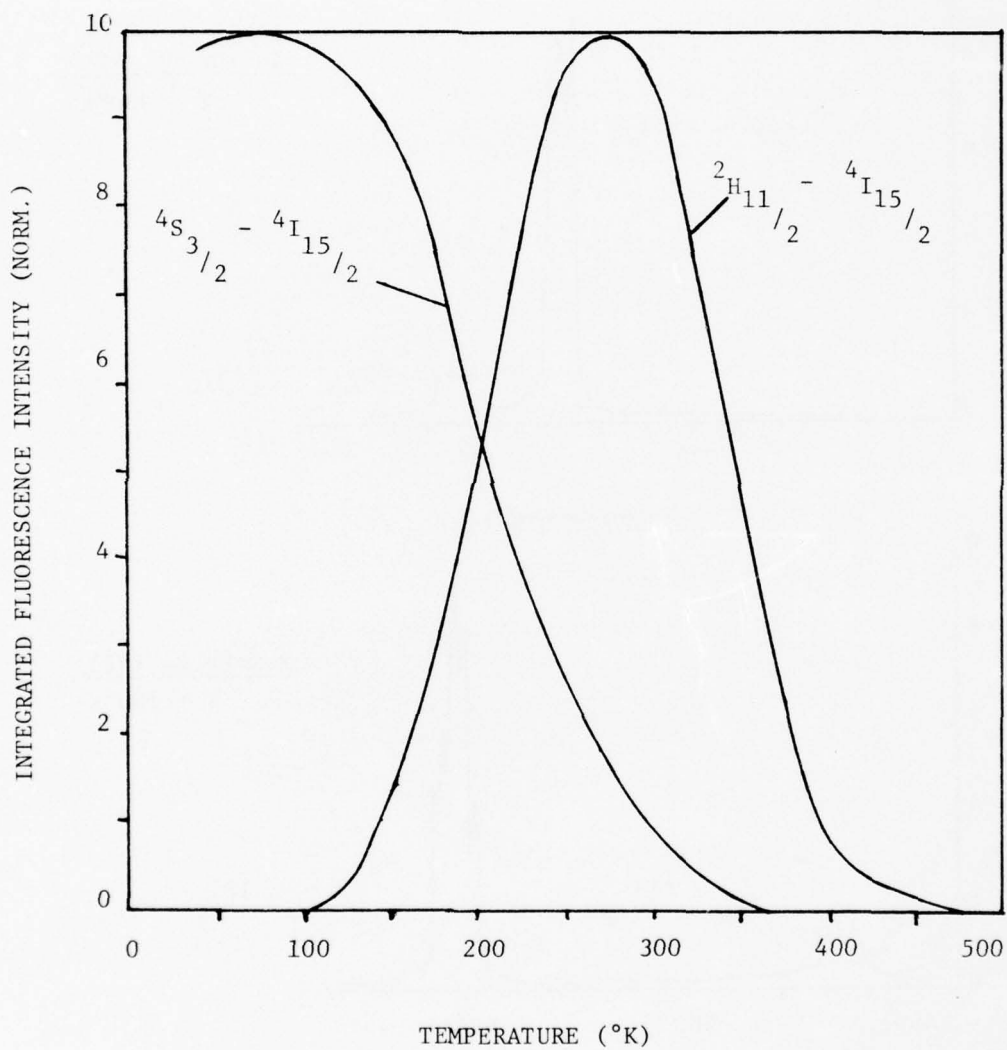


Figure 11. Temperature Dependence of the Er³⁺ Fluorescence Bands in ZnS:Er,Cu Phosphor.

The quenching of both Er^{3+} fluorescence bands at temperature above room temperature can be explained by the familiar thermal quenching process in ZnS type phosphors. The thermal activation energies which control this quenching correspond approximately to the depths of the donor and acceptor levels from the conduction and valence band respectively. At elevated temperatures, localized electrons and holes at the donor-acceptor pairs are liberated into the conduction and valence band. This in turn reduces the electron-hole recombination probability of the donor-acceptor pairs and hence the energy transfer to the Er^{3+} ions.

The decrease of the $4\text{S}_{3/2}$ fluorescence and simultaneous enhancement of the $2\text{H}_{11/2}$ fluorescence in the temperature range of $100^\circ - 300^\circ\text{K}$ suggests that the quenching of the $4\text{S}_{3/2}$ band is associated with the small energy separation between the $2\text{H}_{11/2}$ and the lower lying $4\text{S}_{3/2}$ energy level of Er^{3+} .¹⁵ If this intensity change of the two fluorescence bands is controlled by a thermal activation energy, its value should correspond to the energy difference (0.087 eV) between these two levels. Taking into account the crystal field splitting of the Er^{3+} energy levels, one can assume that the lower split levels of the $2\text{H}_{11/2}$ manifold are sufficiently close to the upper split levels of the $4\text{S}_{3/2}$ manifold to be substantially populated thermally even at room temperature to observe a strong $2\text{H}_{11/2}$ fluorescence when the $4\text{S}_{3/2}$ level is excited.

The quenching mechanism can be described by the equation for the dependency of the luminescence intensity I_T on the temperature T by;

$$\frac{I_T}{I_0} = I_n = \frac{1}{1 + A \exp(-E_T/KT)} \quad (1)$$

where I_n is the normalized luminescence intensity, E_T the thermal activation energy in eV and A is a constant. The equation can be written in the form

$$\ln \left(\frac{1}{I_n} - 1 \right) = \ln A - E_T/KT \quad (2)$$

The expression on the left side, if plotted as a function of $1/T$, can be approximated by a straight line. From the slope of this straight line the thermal activation energy E_T can be determined. Replotting the

15. G. H. Dieke and M. H. Crosswhite - Ibid

data of Figure 11 in the above described manner, E_T has been calculated for three temperature regions. The results are given in Table 1.

TABLE 1.

THERMAL ACTIVATION ENERGIES DERIVED FROM
THE TEMPERATURE DEPENDENCE OF THE Er^{3+}
FLUORESCENCE BANDS IN $ZnS:Er,Cu$ PHOSPHOR

Er ³⁺ Fluorescence	TEMPERATURE REGION (°K)		
	100° - 260°	300° - 400°	400° - 500°
${}^2H_{11/2} - {}^4I_{15/2}$	0.088 eV	0.416 eV	0.96 eV
${}^4S_{3/2} - {}^4I_{15/2}$	0.077 eV	0.418 eV	--

The data obtained shows that the temperature variation of the two Er^{3+} fluorescence bands and can be associated with three different activation energies within the temperature range investigated. In the temperature range between 100°K and 260°K where the intensities of both bands change in opposite directions, the calculated value for $E_T \sim 0.08$ eV is comparable to the value for the energy spacing $\Delta E = 0.087$ eV between the ${}^2H_{11/2}$ and ${}^4S_{3/2}$ levels. It can be reasonably assumed, therefore, that the increase in intensity of the ${}^2H_{11/2}$ band (and subsequent decrease in intensity of the ${}^4S_{3/2}$ band) with increasing temperature in this temperature range is governed by a thermal population of the ${}^2H_{11/2}$ energy level by electrons from the lower lying excited ${}^4S_{3/2}$ level.

In the higher temperature range, 300° - 400°K, where the intensity of both fluorescence bands decreases with temperature, the calculated value of the thermal activation energy, $E \sim 0.42$ eV, seems to be consistent with the value of 0.3-0.5 eV for the position of trivalent ion donor levels below the conduction band of the ZnS energy diagram.¹⁶ It can be assumed

16. R. H. Bube, Photoconductivity of Solids, John Wiley & Sons, New York, N.Y., pp. 100, 1960.

therefore, that thermal release of localized electrons of the donor level into the conduction band is the controlling factor for the quenching of both fluorescence bands in this temperature region.¹⁷ At higher temperatures (400 - 500°K range) the thermal activation energy is sufficiently high to release localized holes from the acceptor levels into the valence band, destroying completely the donor-acceptor pair entity and hence to totally quench the Er³⁺ fluorescence.

Excitation Spectra

The room temperature and low temperature excitation spectra of the two Er fluorescence bands in ZnS:Er,Cu phosphor were obtained by scanning the phosphor sample with monochromatic light from the high pressure Xenon lamp in the wavelength region of 300 - 500 nm. The intensity of the fluorescence bands which were monitored at its peak wavelength was recorded as a function of the excitation wavelength. Simultaneously, the spectrum of the Xenon lamp was recorded and used to adjust the excitation spectrum for constant excitation intensity at each wavelength. The results are shown in Figure 12A. For comparison, the excitation spectra of the blue and green luminescence bands of a P-2 (ZnS:Cu,Cl) phosphor taken under identical conditions are included and shown in Figure 12B.

The excitation spectra of the Er fluorescence bands are composed of a single band located at $\lambda_{\text{EXC}} = 360 \text{ nm}$ (3.44 eV) and of a smaller band located near the fundamental absorption edge of ZnS at $\lambda_{\text{EXC}} = 335 \text{ nm}$ (3.7 eV) at room temperature and at $\lambda_{\text{EXC}} = 327 \text{ nm}$ (3.8 eV) for the low temperature spectra. Except for the intensities at different temperatures, the excitation spectra of both the $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ fluorescence bands are identical. The absence of a line structure in the excitation spectra implies that the Er³⁺ ions are not excited directly, but by an energy transfer process involving the host lattice.

It is known that the addition of copper (Cu) to ZnS leads to the formation of various Cu-luminescent centers depending on the kind and relative concentration of the coactivator. Among them are the so-called "Blue-Copper" (B-Cu) and the "Green-Copper" (G-Cu) emitting centers which are responsible for the blue and green broad-band and luminescence in ZnS:Cu,Cl phosphors. As can be seen in Figure 12B, besides the peak at the fundamental absorption edge, which is characteristic of all ZnS phosphors, both luminescence bands exhibit a distinctively different excitation spectrum. The B-Cu excitation spectrum shows a single narrow-band at about 360 nm (3.44 eV). The G-Cu excitation spectrum on the other hand, is broad and extends significantly towards the longer wavelength region and shows an additional band at about 400 nm (3.1 eV.) The 360 nm and the 400 nm excitation bands are regarded as the direct excitation into the B-Cu and G-Cu luminescent centers, respectively. The

17. S. Larach, "Group II-VI Phosphors with Rare-Earth Activators," Proc. Int. Conf. Luminescence, Budapest, pp. 1549, 1968.

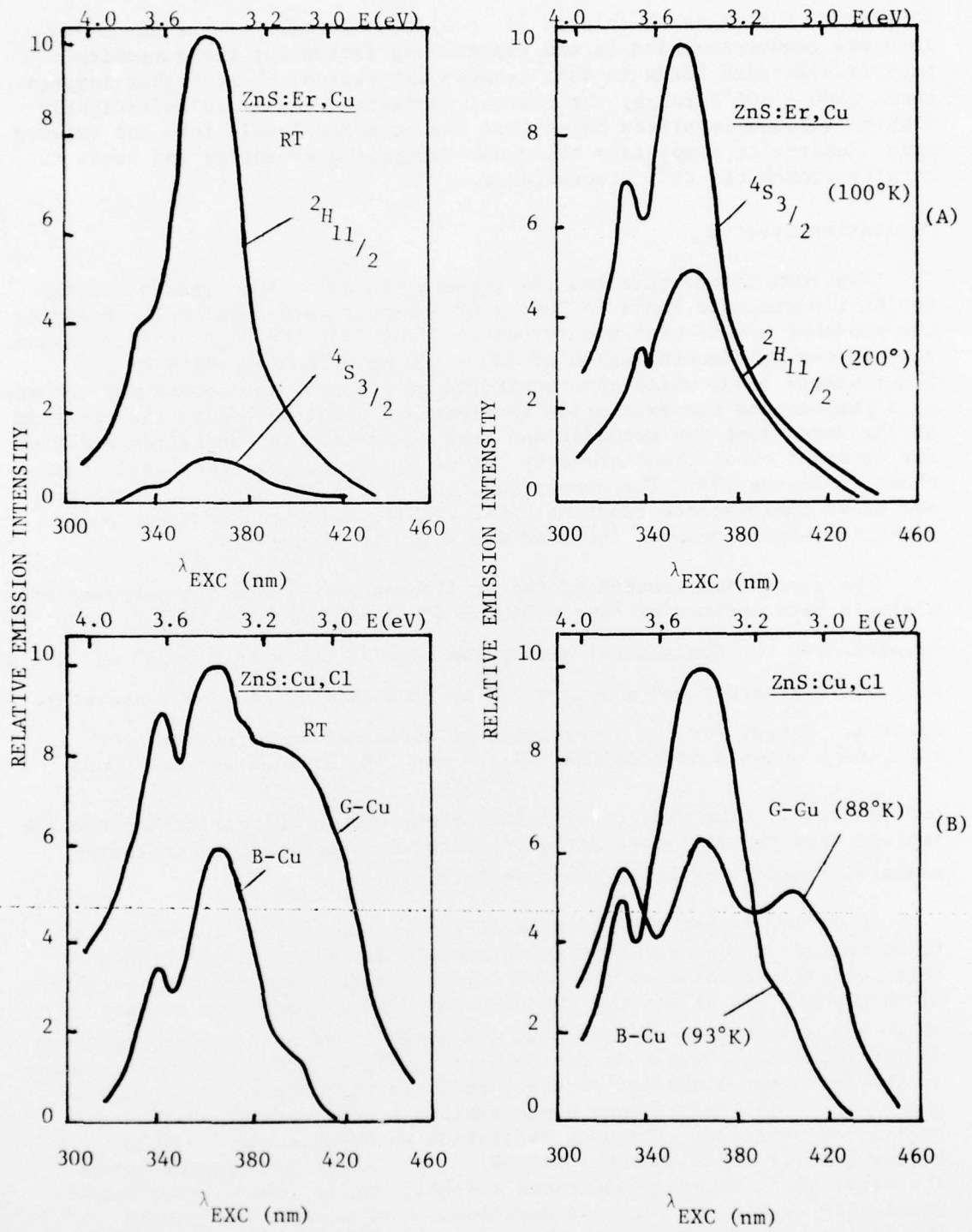


Figure 12. Excitation Spectra of the Er Emission in ZnS:Er,Cu, and the Green-Cu and Blue-Cu Emissions in ZnS:Cu,Cl at Room-and Low Temperatures.

presence of the 360 nm band in the G-Cu excitation spectrum indicates that a large portion of the excitation energy absorbed by the B-Cu center is transferred to the G-Cu center.

Comparing the excitation spectra of both phosphors, one observes a similarity between the spectrum of the Er and that of the B-Cu. Based on numerous investigations of the atomic structure of the B-Cu luminescence center in ZnS,^{18,19} there is a strong indication that this center is formed by the close association of a substitutional Cu^+ ion at the Zn^{2+} site with an interstitial Cu^+ ion and that the luminescent transition be probably between two localized levels of this center.

Applying this model to the luminescent center in ZnS:Er,Cu, several coordinations of the Er^{3+} and Cu^+ ions are possible. For example, if both dopants are present in approximately equal concentrations, the Er luminescence center can be formed by an interstitial Er^{3+} ion symmetrically surrounded by Cu^+ ions substituting for the four nearest neighbor Zn^{2+} sites in the ZnS lattice. Such centers have a net effective charge of -1 and introduce acceptor levels within the ZnS band gap. The remaining Er^{3+} ions located at Zn^{2+} sites at next-nearest or larger neighbor distances away from the acceptor center form donor-type defects and introduce the donor levels. Excitation of the phosphor creates electrons and holes which localize on donors and acceptors respectively. Following their recombination at closely associated donor-acceptor pairs, the transition energy is transferred radiationless by a resonance process to the 4f electron configuration of the interstitial Er^{3+} ion which is part of the acceptor center. In the case of the broad-band emitting ZnS:Cu,Cl phosphor, the electron-hole recombination within the donor-acceptor pairs is radiative and contributes directly to the luminescence of this phosphor.

Build-up and Decay of the Er^{3+} Fluorescence in ZnS:Er,Cu

The transient behavior of the ZnS:Er,Cu phosphor at room temperature was determined from the build-up and decay curves of the intensity of the ${}^2\text{H}_{11/2}$ fluorescence band under various levels of ultra-violet excitation

intensities. The wavelength of the excitation light was 365 nm, closely corresponding to the maximum of the excitation spectrum (see Figure 12A.) The excitation intensity was adjusted by the discharge current of the Xenon arc lamp and measured with an Eppley thermopile. The incident light on the phosphor sample was controlled by means of an electronic-shutter. Before recording the build-up and decay curves at the various excitation levels, the phosphor was de-excited for approximately 5 minutes by irradiating it with light from an infrared lamp.

18. H. Blinks, N. Riehl and R. Sizmann, "Reversible Leucht-zentren-Umwandlungen in ZnS Phosphoren," Z. Phys., 163, pp. 594, 1961.

19. K. Urabe, S. Shionoya and A. Suzuki, "Polarization of the Blue-Copper Luminescence in ZnS Crystals," J. Phys. Soc., Japan, 25, pp. 1611, 1968.

The build-up and decay curves obtained at different excitation levels are shown in Figure 13. For comparison, the rise and decay curves of a conventional ZnS:Cu,Cl (P-2) phosphor are included. The build-up of the Er fluorescence intensity (Figure 13A) is fairly slow and reaches its steady-state intensity after 1-3 seconds during continuous exposure to the excitation light. After turning-off the excitation, the phosphor emission decays at a fast rate followed by a long persistent decay. Increasing the excitation intensity causes a faster build-up but does not significantly alter the decay characteristic. The time constant of the decay, about 15 millisecond (ms), is much larger than the intrinsic fluorescence decay of directly excited RE ions. The lifetime of the $^4S_{3/2} - ^4I_{15/2}$ transition in Er^{3+} has been reported to be in the order of 1 ms.²⁰ It can be concluded, therefore, that the rate determining step of the Er fluorescence decay in ZnS:Er,Cu is controlled by decay processes in the ZnS host lattice.

The G-Cu luminescence intensity in ZnS:Cu,Cl, Figure 13B, shows a similar slow build-up and excitation intensity dependence as the Er fluorescence in ZnS:Er,Cu. In contrast to the fast decay of the Er fluorescence, however, the decay of the G-Cu luminescence is very slow and strongly dependent on the excitation intensity. As compared to the relatively slow rise and decay of the G-Cu luminescence, the B-Cu luminescence in the same ZnS:Cu,Cl phosphor rises and decays very rapidly. This difference in the transitional behavior can be understood by the different nature of the G-Cu and B-Cu centers and their electronic transitions, as discussed in the previous section of this report.

The important aspect of the experimental data is the observation that the build-up characteristic of the Er fluorescence is similar to that of the G-Cu luminescence. The long-period build-up of emission in both phosphors can be explained by the presence of electron traps. During the excitation period these traps are filled first by the excited electrons before they are being "trapped" at the donor levels from which they recombine with holes at the acceptor levels of the donor-acceptor pair system. The long decay time of the G-Cu luminescence has been shown to be the result of electron-hole recombinations at donor-acceptor pairs with large intra-pair separations of up to 200 Å, thus extending over more than 50 atomic distances. As the pair separation increases, the photon energy emitted decreases, and the recombination process subsides slowly with time. In the case of the ZnS:Er,Cu phosphor, where pair transition energies are transferred radiationless by resonance to the 4f energy level system of the Er^{3+} ion, it can reasonably be assumed that transitions within donor-acceptor pairs of selected intra-pair distances only contribute to the decay of the Er fluorescence. Consequently, a significantly faster decay is observed as compared with the decay of the G-Cu luminescence in ZnS:Cu,Cl.

20. G. E. Barach and G. E. Dieke, "Fluorescence Decay of Rare-Earth Ions in Crystals," J. Chem. Phys. 43, pp. 988, 1965.
21. K. Era, S. Shionoya and Y. Washizawa - Ibid.

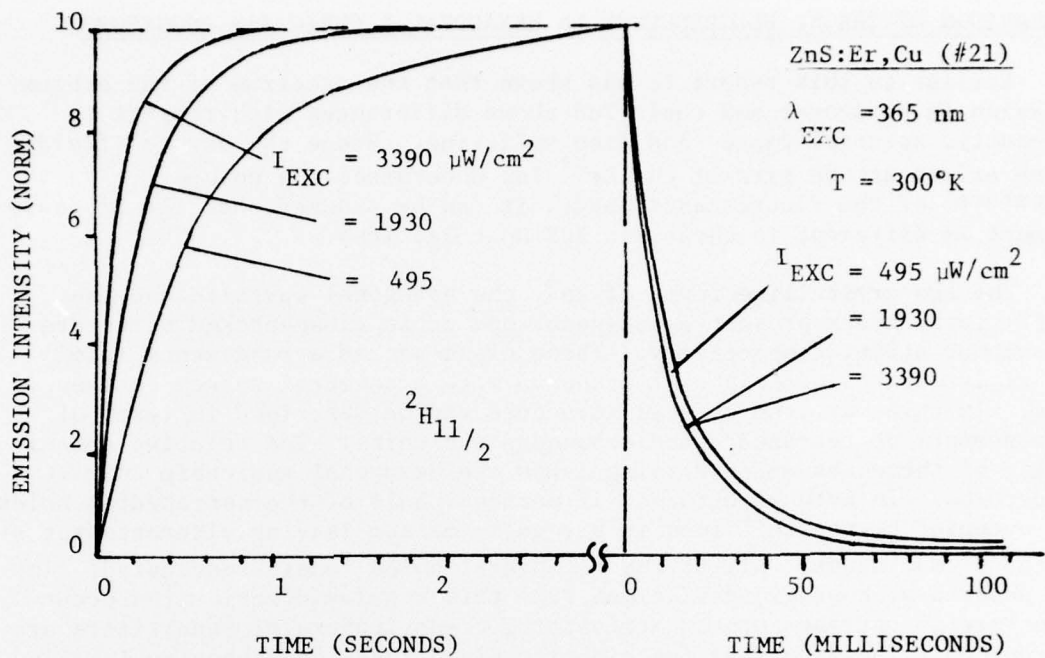


Figure 13A.

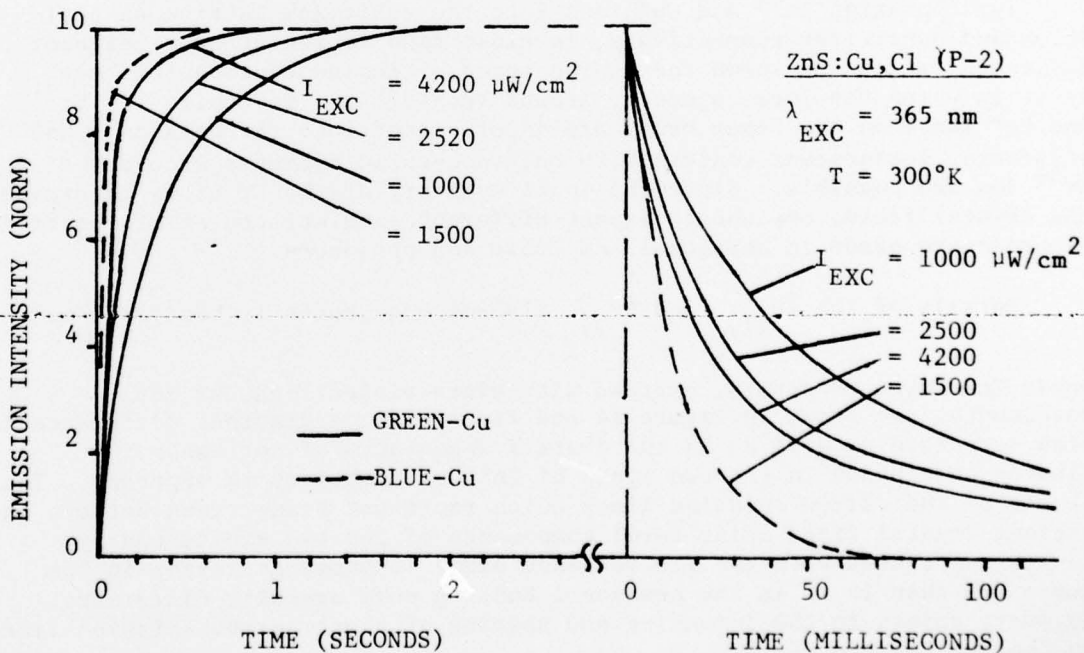


Figure 13B.

Figure 13. Build-up and Decay of Emission at Different UV Excitation Intensities of (A) ZnS:Er,Cu Phosphor, (B) ZnS:Cu,Cl Phosphor.

COMPARISON OF THE Er FLUORESCENCE IN HEXAGONAL & CUBIC ZnS PHOSPHORS

Earlier in this report it was shown that the spectrum of the erbium emission in hexagonal and cubic ZnS shows differences with respect to intensity, spectral range and line splitting. Since the crystal field which exists at the site of the Er^{3+} ion determines the unique signature of the fluorescence bands, it can be assumed that the Er environment is different in these two ZnS host lattices.

The two crystalline forms of ZnS, the hexagonal wurtzite and the cubic zincblende represent a hexagonal and cubic close-packed structure of sulphur atoms, respectively. These close-packed arrangements form repetitive arrays of sulphur tetrahedra with octahedral spaces between them. In this way, the crystal structure can be described in terms of arrangements of tetrahedra and octahedra sub-units. The relative coordination of these sub-units distinguishes the hexagonal and cubic ZnS structures. In both structures, if perfect, half of the tetrahedral holes are occupied by the Zn^{2+} ions in a regular manner leaving alternate tetrahedral sites vacant. All of the octahedral holes remain unoccupied. In ZnS phosphors, however, deviations from this regular distribution occur when foreign cations such as activators, co-activators or sensitizers are introduced. These cations can either replace Zn^{2+} ions substitutionally or occupy vacant tetrahedral or octahedral holes.

Incorporating Er^{3+} and Cu^+ ions into the cubic ZnS lattice as activator and sensitizer respectively, in close association at near-neighbor distances, it can be shown that three types of luminescent centers can exist in which the local symmetry around the Er^{3+} ion is cubic. If Er^{3+} and Cu^+ ions, on the other hand, are incorporated into the hexagonal ZnS structure, luminescent centers with only non-cubic symmetry around the Er^{3+} ion are possible. Since the local symmetry at the Er sites determines the crystal field, one should expect different line structures of the Er^{3+} fluorescence bands in hexagonal and cubic ZnS phosphors.

Details of the $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ fluorescence bands in hexagonal and

cubic ZnS:Er,Cu phosphors, excited with ultra-violet light of 365 nm wavelength, are shown in Figure 14 and Figure 15. A distinct difference in line structure as well as in the overall appearance of corresponding fluorescence bands in the two types of ZnS host lattices is apparent. The number of the narrow emission lines which represent transitions between the various crystal field split level components of the two erbium energy levels associated with the fluorescence band, is somewhat larger in the cubic ZnS than it is in the hexagonal ZnS. A more dramatic difference, however, exists in the intensity and spacing of these narrow emission lines in the two ZnS hosts.

The half-width of the strongest lines of the $^4\text{S}_{3/2}$ fluorescence band,

Figure 14, is about $3 \overset{\circ}{\text{A}}$ at 77°K. The half-width of the line in the $^2\text{H}_{11/2}$ fluorescence band, Figure 15, which was obtained at higher

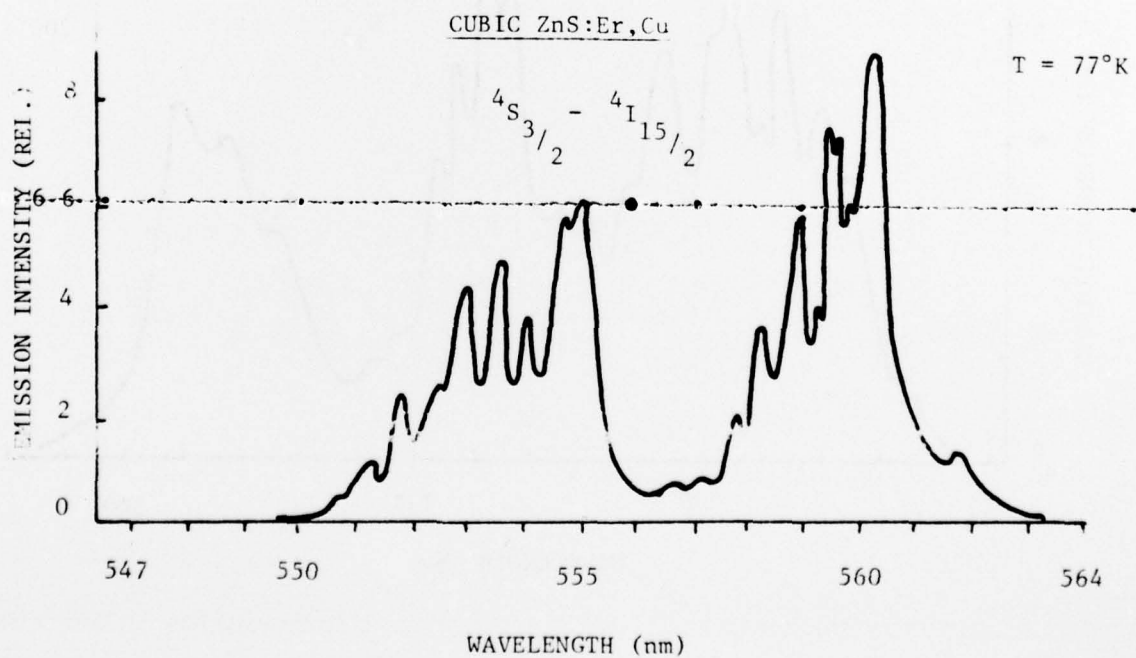
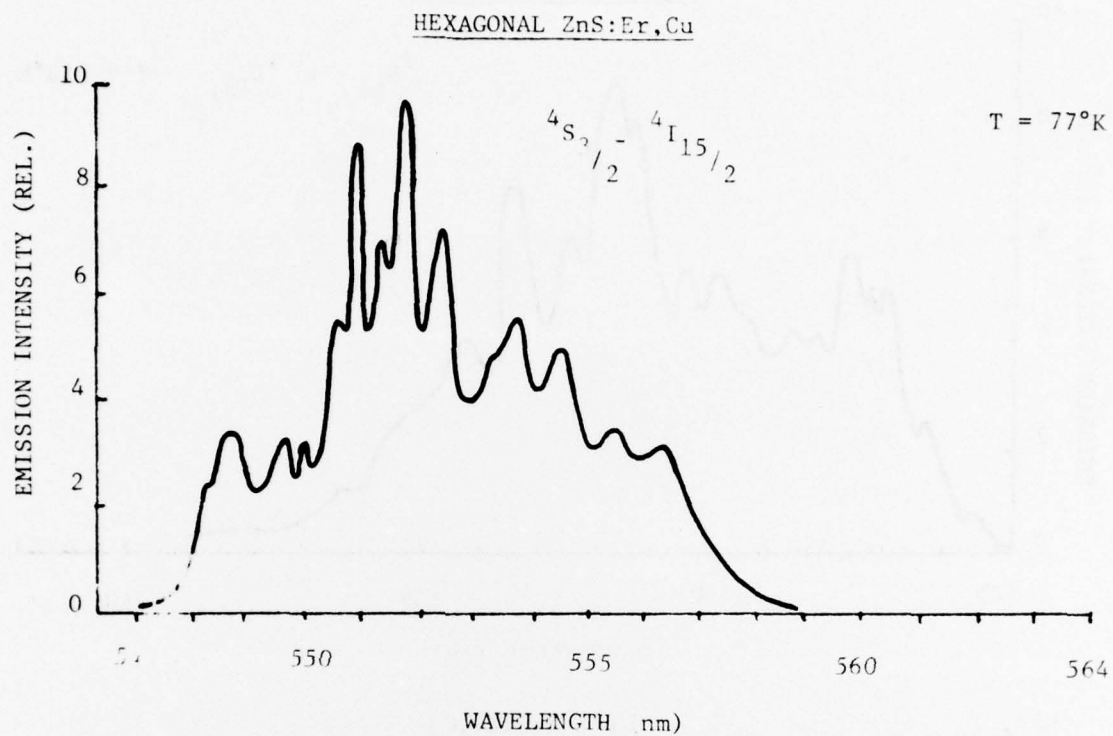


Figure 14. Details of the $4S_{3/2} - 4I_{15/2}$ Er^{3+} Transition in Hexagonal and Cubic ZnS:Er,Cu Phosphor.

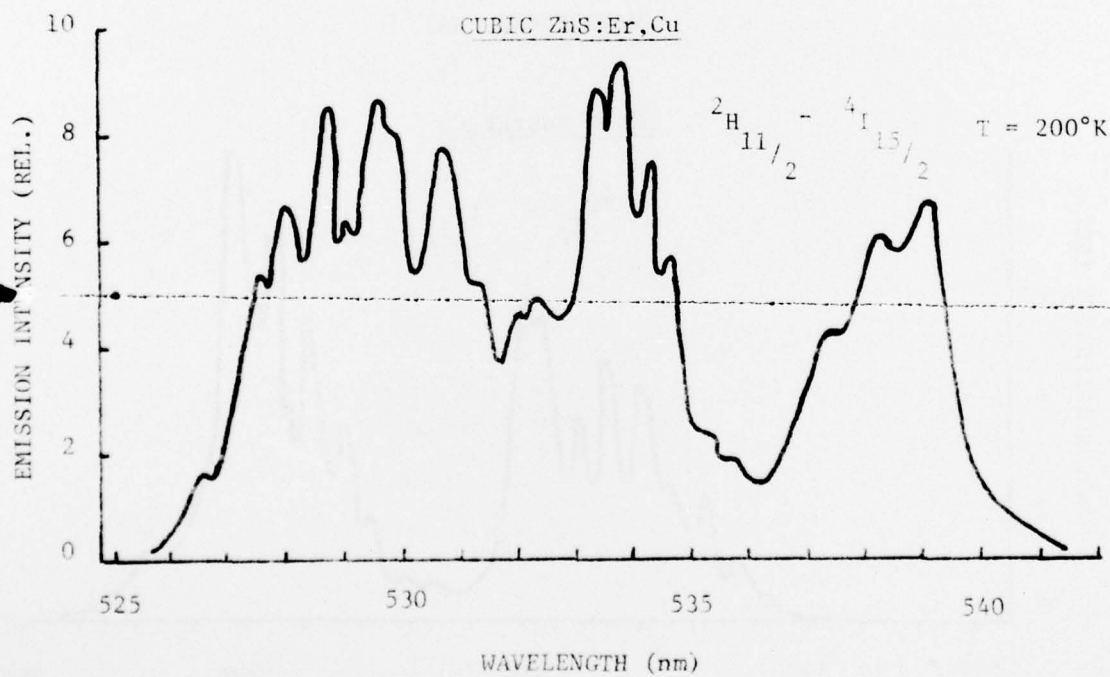
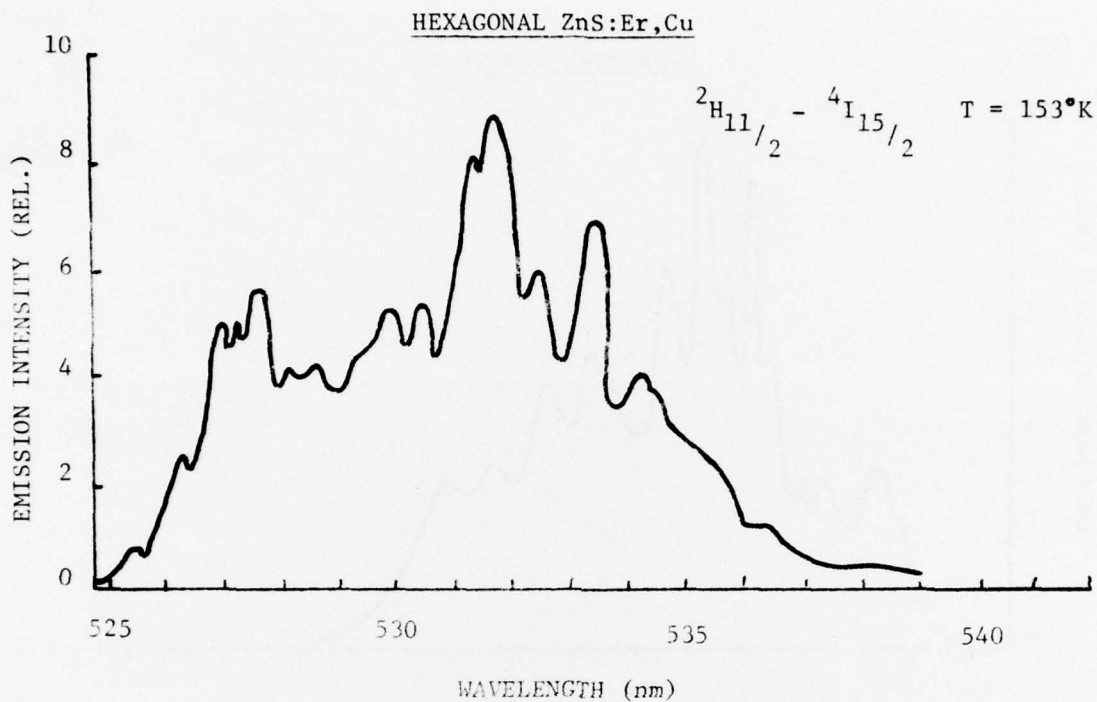


Figure 15. Details of the ${}^2H_{11/2} - {}^4I_{15/2}$ Er^{3+} Transition in Hexagonal and Cubic ZnS:Er,Cu Phosphor.

temperatures because of the rapid decrease in intensity at low temperature, is about 6 Å. These values for the half-width are 3 - 5 times larger than those reported for trivalent RE ions in single crystal hosts. Strain and crystal imperfections in the individual grains of the phosphor powder material are probably the cause for the additional broadening of the emission lines.

For the $^4S_{3/2}$ fluorescence band, 14 lines have been resolved in the hexagonal ZnS, and 19 lines in the cubic ZnS. In view of the limited resolution of the spectrum due to the line broadening, it can be reasonably assumed that the actual number of the lines is larger than determined from the recorded spectra. It can be shown from crystal field selection rules that a maximum of 5 emission lines should be allowed for the $^4S_{3/2} - ^4I_{15/2}$ transition if the crystal field symmetry at the

Er^{3+} site is cubic, and a maximum of 16 emission lines if the crystal field symmetry is non-cubic. Since more lines have been found in the $^4S_{3/2}$ fluorescence spectrum for both the hexagonal and cubic ZnS:Er,Cu

phosphors, one must conclude that the spectrum represents the superposition of sets of lines from different Er luminescence centers. Therefore, it is very difficult to determine which set of lines arises from the different Er sites in these two ZnS structures. Such sets of emission lines belonging to Er sites of different crystal field symmetry however, can be visualized in the fluorescence bands in Figure 14 and Figure 15.

CONCLUSIONS

Conventional broad-band and RE activated narrow-band ZnS type phosphors, in particular ZnS:Er,Cu phosphor, have been discussed with respect to their emissions and energy transfer mechanisms. A transition and energy transfer model for the ZnS:Er,Cu phosphor has been proposed. It has been demonstrated that the frequently observed broad-band component accompanied with the Er fluorescence spectrum in ZnS:Er,Cu is associated with the sensitizer ion. Phosphor preparation parameters have been derived to eliminate this broad-band emission. It has been shown that high concentrations of Er and Cu in ZnS host lattices result in a phosphor of mixed hexagonal and cubic ZnS phases. Such phosphor exhibits a complex Er fluorescence spectrum which has been identified as being a superposition of spectra arising from the two ZnS phases. The Er emission in cubic ZnS is less "monochromatic" and less efficient than it is in hexagonal ZnS. The hexagonal ZnS:Er,Cu phosphor compares favorably to the P-2 phosphor having a peak intensity of the dominant Er fluorescence band more than twice that of P-2 and having a half-width of 1/10 that of the broad-band luminescence in P-2. It has been found that the two Er fluorescence bands in ZnS:Er,Cu undergo an intensity reversal of low temperatures that causes a change in the color of the excited phosphor from a bright green to yellow. The excitation spectra of the dominant and the weak Er fluorescence band in ZnS:Er,Cu is identical and comparable to that of the

blue-copper luminescence band in P-2 phosphors. This implies that the Er emission center is associated with an acceptor level. Several atomic structures of the center can be conceived by which the Er^{3+} ion is surrounded by Cu^+ ions at next-nearest neighbor distances. Build-up and decay characteristics of the Er fluorescence in ZnS:Er,Cu phosphor strongly indicates that the transition within donor-acceptor pairs, in contrast to the broad-band luminescence in P-2 phosphors, is restricted to pairs with selected intra-pair distances only. It has been shown that the line structure of the Er fluorescence bands in both the hexagonal and cubic ZnS:Er,Cu phosphors, represents a superposition of sets of lines associated with Er^{3+} ions at different crystal field symmetry sites.

The results obtained in this study have provided a better understanding of the critical factors involved in the synthesis, and the emission properties of sensitized RE activated ZnS phosphors. The unique, nearly monochromatic emission of the ZnS:Er,Cu phosphor shows promise for display devices where resolution and contrast are stringent requirements. It is felt that the luminous output of this phosphor can be improved further by optimizing the efficiency of the energy transfer to the Er ions in reducing the numbers of Er^{3+} site symmetries by annealing the phosphor in sulphur atmosphere, by adjusting the energy gap using zinc sulfide-cadmium sulfide (ZnS-CdS) solid solution host materials, or by selecting sensitizer ions other than copper.

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