

AD-A214 742

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE September 1982		3. REPORT TYPE AND DATES COVERED Final (Jun 1, 81-May 31 82)
4. TITLE AND SUBTITLE RESEARCH ON ELECTROLUMINESCENCE IN THIN FILM YTTRIA OXYSULFIDE			5. FUNDING NUMBERS 61102F 2306/B1	
6. AUTHOR(S) R.D. Ketchpel				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Microelectronics Research and Development Center Rockwell International Corporation Thousand Oaks, California 91360			8. PERFORMING ORGANIZATION REPORT NUMBER AFOSR-TR-89-1456	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR BLDC 410 BAFB DC 20332-6448			10. SPONSORING/MONITORING AGENCY REPORT NUMBER F49620-81-C-0069	
11. SUPPLEMENTARY NOTES DTIC ELECTE NOV 30 1989				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release distribution unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Thin films of a rare-earth oxysulfide phosphor ($Y_{2O_3}S:Eu$) were evaluated for use in a thin film electroluminescent emitter (TEL). For the first time, emission typical of the rare earth activator was observed in a rare earth host TFEL emitter. The films were characterized for optical spectrum, brightness-voltage characteristic, photoluminescence, crystal structure, and compared to efficient cathodoluminescent power phosphors ($Y_{2O_3}S:Eu$) as well as high efficiency TFEL emitters of $ZnS:Mn$. The present low intensity red emission (fractions of a ft-L) is limited by annealing induced cracks in the emitter structure.				
14. SUBJECT TERMS			15. NUMBER OF PAGES 36	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT
				20. LIMITATION OF ABSTRACT

MRDC41090.1AR

TABLE OF CONTENTS

	<u>Page</u>
1.0 SUMMARY.....	1
2.0 BACKGROUND.....	2
2.1 EL Model.....	4
2.2 Requirement for Thin Film EL Materials.....	8
3.0 MATERIALS FABRICATION.....	11
4.0 PHYSICAL PROPERTIES.....	14
4.1 X-ray.....	14
4.2 SEM.....	15
5.0 ELECTRO-OPTIC MEASUREMENTS.....	18
5.1 Electroluminescence Measurements.....	18
5.2 Photoluminescence Measurements.....	23
6.0 CONCLUSION.....	33
7.0 REFERENCES.....	34

Accession No.	
NTIS	✓
DTIC	✓
Unannounced	
Justified	
By	
Date	
A-1	
Dist	

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1 Cross section electroluminescent device structure.....	5
2 Brightness-voltage for ZnS:Mn thin film emitter showing nonlinear response.....	6
3 One-dimensional model of interface states in presence of large electric field.....	7
4 Plot of $\ln J_{\max}$ vs $1/F$ for thin film emitter.....	9
5 SEM photograph of annealed oxysulfide film on Al_2O_3 showing cracks. Annealed for 1 hour at $900^\circ C$	16
6 SEM photograph of annealed oxysulfide film on 7059 glass showing crazing. Annealed for 1 hour at $600^\circ C$	17
7 Room temperature electroluminescent spectrum of yttrium oxysulfide film doped with Eu^{+3}	19
8 Brightness-voltage curve for $Y_2O_2S:Eu^{+3}$ thin film emitter.....	21
9 Current and voltage waveform showing electronic component (A) Capacitor (B) EL emitter.....	22
10 $\ln J_{\max}$ vs $1/F$ for unannealed $Y_2O_2S:Eu$ films at $250^\circ K$, $300^\circ K$ and $375^\circ K$	24
11 Photoluminescent spectrum of yttrium oxysulfide europium powder used as CRT phosphor.....	25
12 Photoluminescence spectrum of $Y_2O_2S:Eu^{+3}$ film on Al_2O_3 (A) Annealed for 1/2 hour at $900^\circ C$ (B) Annealed for 1 hour at $900^\circ C$ (C) Annealed for 3 hours at $900^\circ C$ (D) Unannealed film.....	27 28 29 30
13 Photoluminescence spectrum of $Y_2O_2S:Eu^{+3}$ film on Al_2O_3 (A) Annealed for 1/2 hour at $600^\circ C$ (B) Annealed for 5 hours at $600^\circ C$	31 32



1.0 SUMMARY

The rare-earth oxysulfide phosphors have proven to be highly efficient phosphor materials for cathode ray tubes (CRT). Thin films of these phosphors have provided the highest brightness for a CRT reported to date.¹ The objective of this program was to evaluate the feasibility of fabricating thin film ac electroluminescent devices using the rare-earth activated oxysulfides. Rare-earth activators were chosen because their spectra covers the visible region and they are in general narrow line emitters. For the first time electroluminescence was observed in a thin film of rare earth host phosphors. Described in this report are the results of characterizing these thin film emitters. The characterization includes: 1) optical spectrum; 2) brightness-voltage curve; 3) photoluminescence; 4) x-ray diffraction; 5) annealing experiments. The characterization also includes comparative data on efficient rare earth cathodoluminescent powder phosphor material as well as high efficiency ZnS:Mn thin film EL emitter.

In summary, the results show that thin film ac electroluminescent devices can be fabricated using rare-earth activated yttrium oxysulfide material. The e-beam fabrication technique used is similar to that used to fabricate high efficiency ZnS:Mn thin film EL emitters at this laboratory. Presently the low observed EL intensity (fractions of a ft-L) is limited by the physical integrity of the film during elevated temperature annealing required for luminescence. Both photoluminescence and x-ray diffraction measurements indicate the optimum anneal temperature and time to be 900°C for one hour compared to the 600°C limit of the present 7059 glass substrate material. Through use of alternate substrate materials and/or an alternate annealing procedure, higher brightness electroluminescence should be achievable in these rare-earth thin film emitters.



2.0 BACKGROUND

The continued improvement in capability of military systems is due in large part to the use of increasingly complex solid state components. Many systems, however, are currently display limited for lack of a solid state replacement for the CRT, particularly where direct sunlight legibility, space, weight and power requirements are severe constraints.

Recent developments in flat panel matrix display technology offer solutions to many of the limitations of the cathode ray tube (CRT). In particular, thin film electroluminescence (TFEL) appears close to duplicating the operating characteristics of the CRT (shades of gray, high resolution, wide temperature range, true electronic mode of operation for long life color capability) while offering a dramatic decrease in weight, display volume and power requirements.

Using state-of-the-art TFEL materials a 20:1 reduction in weight and volume and a 10:1 reduction in power is possible over the conventional CRT terminal. Electro-optic brightness voltage measurements of state-of-the-art material indicate achievable brightness under matrix scan conditions of 200 ft-L when operated at a duty cycle of 1/200 (200 line scan). For higher density displays (500-1000 lines) the duty cycle available for any one line drops proportionately so that the brightness is decreased to below 100 ft-L. Legibility in direct sunlight, which exists in a cockpit, requires at least a 200 ft-L brightness. Therefore, an important extension of the TFEL technology could be achieved if the material exhibited a higher luminous conversion efficiency so that higher peak brightnesses were achievable under such conditions. Current TFEL materials exhibit a luminous conversion efficiency of 5 lu/watt.²

CRT phosphors and fluorescent lamp phosphors yield 50-100 lu/watt.³ A 10-fold improvement in a TFEL efficiency and instantaneous brightness could have a significant impact on high density matrix addressed display panels for cockpit use in direct sunlight.



MRDC41090.1AR

Current TFEL phosphors utilize a zinc sulfide host matrix with various activators in order to produce the desired emission color. Previously, CRT phosphors also used the ZnS host. However, a significant increase in efficiency was made through the use of rare-earth activators. Certain members of the rare-earth oxysulfide phosphor family are among the highest intrinsic efficiency cathodoluminescent materials yet discovered.⁴

The rare earth host materials represent a more rigid crystal lattice as evidenced by the higher melting point of these materials compared with the zinc sulfide. This results in less phonon loss to the crystal lattice during the electron-to-light conversion process within the phosphor system. In addition, the higher temperature melting point characteristic insures a more stable phosphor when exposed to environmental extremes of heat and moisture. Rare earth activators typically exhibit a line spectra rather than a band spectra. This important characteristic allows the emitted light to be confined to the photopic response spectrum of the human eye so that the luminous conversion efficiency is maximized. Also, the line spectra allows one to achieve better color purity in a multi-color display. Rare earth activators are available to provide the full color range (red, green, blue) required for a full-color display. These rare-earth activators are more easily incorporated into the rare-earth host crystal lattice compared with the zinc sulfide lattice.

Previous work by Buchanan¹ has demonstrated that thin films of the lanthum oxysulfide materials can be fabricated which exhibit good cathodoluminescence characteristics. These films were intended for use as the phosphor screen in a cathode ray tube. Additional requirements exist on the material properties in order to provide an electroluminescent display element. In order to elucidate those additional requirements on the thin film phosphor, a model is proposed which describes the light generating process and electro-optic characteristics of our current zinc sulfide manganese activated thin film EL devices.



2.1 EL Model

Figure 1 shows a cross-section of the display structure. A unique characteristic of this structure, using the ZnS:Mn, is the highly nonlinear electro-optic response of the emitter (Fig. 2). A model for this device has been proposed by this laboratory in which the nonlinear response is due to the nature of electron injection into the ZnS phosphor by a tunnel emission phenomenon.⁵ The tunnel emission characteristic is relatively independent of temperature, which implies that a display of this type can be operated over a wide temperature range.

The model attempts to explain the mechanism of initiation of electroluminescence in ZnS:Mn films. The basic assumptions are:

1. Electrons from unidentified donor levels become trapped at the ZnS:oxide interface.
2. The trapped electrons are very long lived and are only released at high (10^6 V/cm) field strength by tunneling.
3. These electrons, when released at high fields, quickly become very energetic and impact excite the active Mn center in the ZnS layer, causing luminescence.
4. The electrons then become trapped again to be re-released on the opposite polarity swing of the voltage cycle.

Figure 3 illustrates schematically the one-dimensional model for the interface states in the presence of a large electric field. This simple one-dimensional model assumes that electrons vibrate in a one-dimensional well with frequency $\nu(E)$ and that they can tunnel with a probability of tunneling given approximately by the WKB approximation:

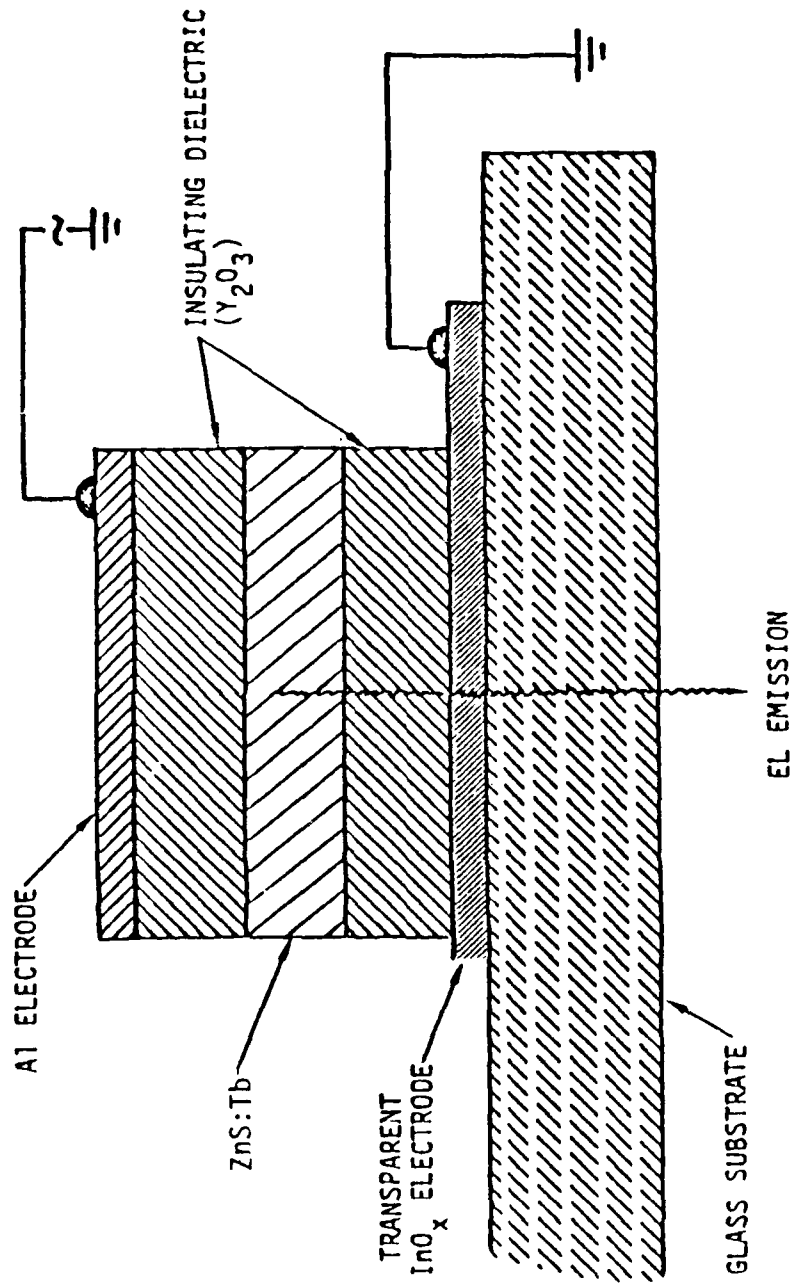


Fig. 1 Cross section electroluminescent device structure.

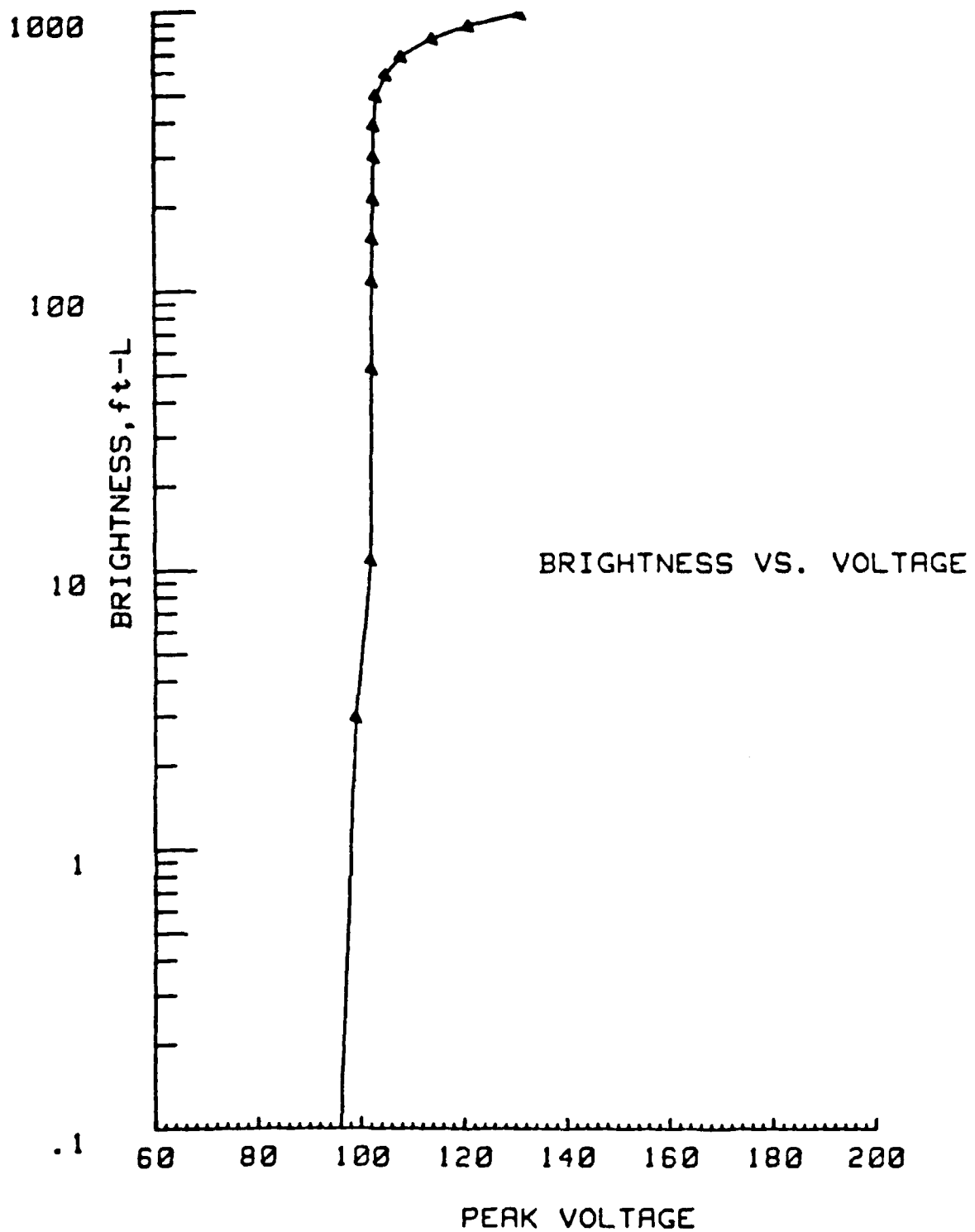


Fig. 2 Brightness-voltage for ZnS:Mn thin film emitter showing nonlinear response.

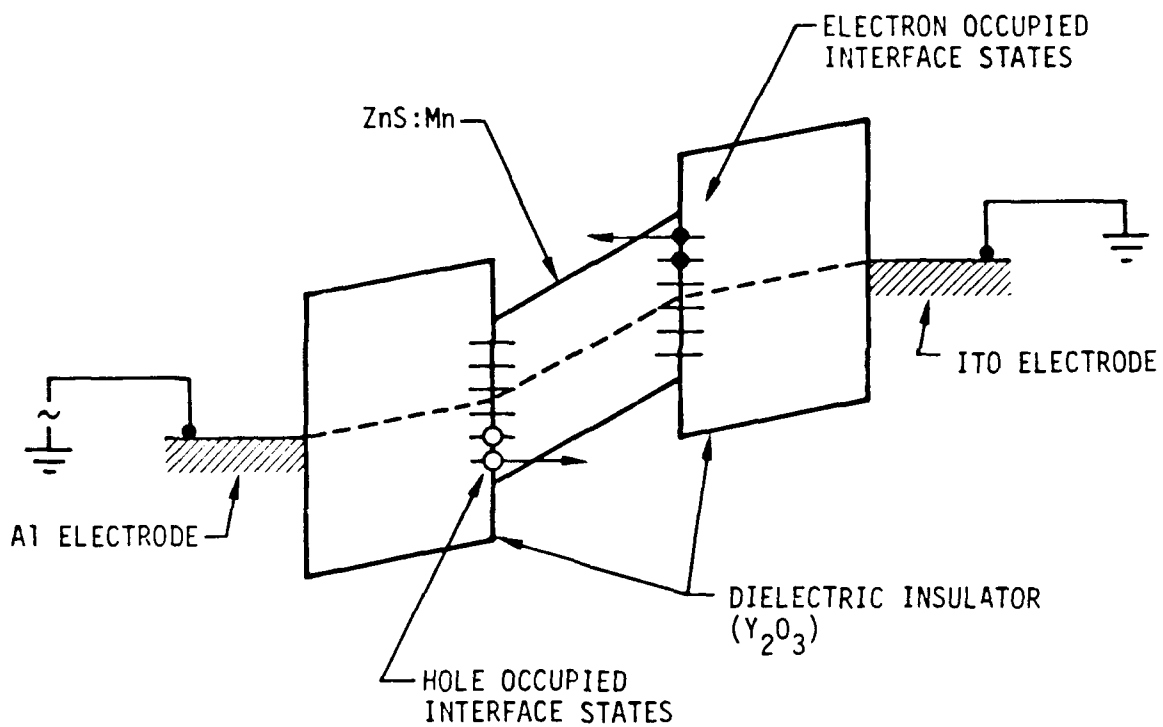


Fig. 3 One-dimensional model of interface states in presence of large electric field.

$$T(E,F) \sim \exp - \frac{AE^{3/2}}{F}$$

where E is measured from the top of the conduction band, and F is the field across the ZnS. It is assumed that all the surface state density is concentrated in a level E_1 . The current density is given by

$$j(t) = n_1 v(E_1) T(E_1, t)$$

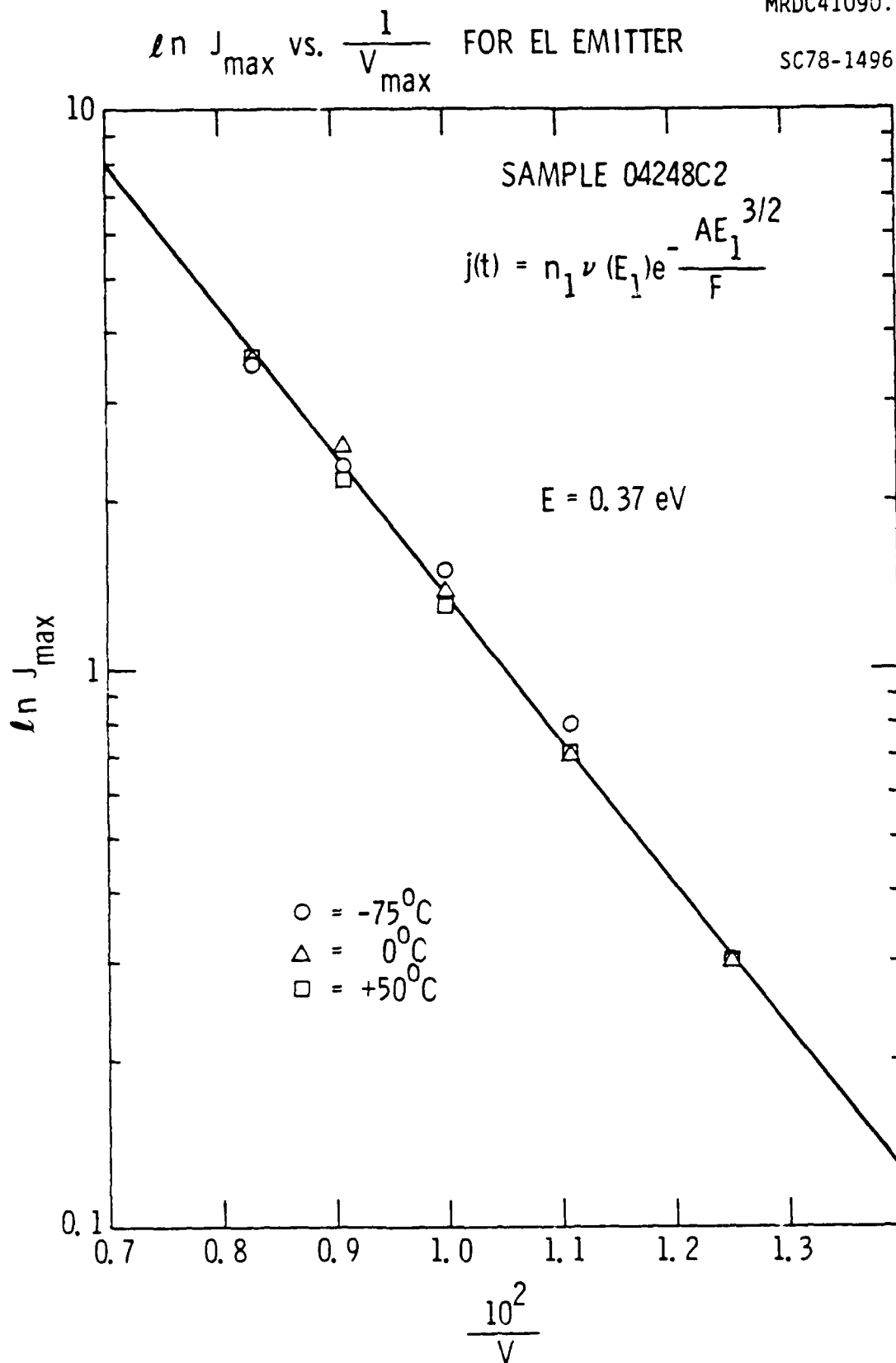
where n_1 is the number of electrons at E_1 , $v(E_1)$ is the vibrational frequency of the electron, and $T(E_1, t)$ is the tunneling probability. The current rises steeply with field so that most of the charge is transported at $j = j_{\max}$ corresponding to $F = F_{\max}$. A plot of $\ln j_{\max}$ versus $1/F_{\max}$ should give a value for E_1 the interface level.

Figure 4 is a plot of $\ln j_{\max}$ vs $1/F_{\max}$ for an EL device made at this laboratory. The interface level of 0.4 eV was obtained from the slope of the curve. In addition, the invariance of the tunneling current as a function of temperature is also shown.

It should be stressed that we are discussing tunneling field emission, not the Frenkel-Poole effect. The latter is the field induced lowering of the thermal emission barrier. In the Frenkel-Poole effect the log of current density is proportional to $V^{1/2}$. However, the Frenkel-Poole effect is strongly temperature dependent while the tunneling emission is not.

2.2 Requirements for Thin Film EL Materials

The luminescent property requirements are similar to those for cathodoluminescence films. That is, efficient absorption of hot electrons by the activator sites, efficient radiation of this energy in the optical wavelength visible to the human eye. However, in the case of the electroluminescent film, electron injection and transport to the activator site must be provided by the electrode structure on the film rather than from external

Fig. 4 Plot of $\ln J_{\max}$ vs $1/F$ for thin film emitter.



MRDC41090.1AR

high velocity electrons injected from an electron beam source. The requirements for a transparent host crystal are similar so that the light generated reach the observer's eye with minimum attenuation. The film should be stable with exposure to heat and moisture conditions so that the display panel can be fabricated by normal photolithographic techniques. The film should have a minimum of impurity ions that would tend to drift under electric field application. The material should be capable of being fabricated in a continuous form so that high electric fields can be applied to the device without breakdown through the film. The material must be compatible with conductive electrodes so that the electric field can be applied to the phosphor film. An electron injecting contact is required, particularly of the tunnel emitter type so that the threshold type response can be preserved for matrix panel addressing. The film must be capable of electron transport of hot electrons so that the injected electrons can reach the activator site. The activator itself must be stable under high electric field so that no drift within the crystal lattice occurs that would distort the electric field or destroy the electroluminescence of the film.

MRDC41090.1AR

3.0 MATERIALS FABRICATION

Presently, the high brightness, high efficiency ZnS activated electroluminescence films are fabricated using a "hot wall" electron beam evaporation system which is microprocessor controlled. The activator is introduced by co-evaporation from a resistance-heated boat. The thickness of the film is monitored using an optical monitor during film growth. The substrate is maintained at an elevated temperature through the use of quartz lamps in the vacuum chamber. The advantage of this type of system is that the films produced tend to be more crystalline, where films produced by sputtering tend to be more amorphous. The crystallinity of the thin film EL emitters improves their performance since one of the parameters that determine the intensity and power efficiency is the product of the electric field and the mean free path of the electron. The E-beam evaporator system allows the activator concentration and the necessary background gasses to be controlled or varied in a simple manner. This is extremely important in trying to optimize the various parameters. The films are fabricated on Corning glass 7059 coated with indium tin oxide (ITO). The emitter structure shown in Fig. 1 consists of a transparent conductor, a layer of dielectric followed by the appropriate host material (ZnS, oxysulfide) doped with the appropriate activator. A second dielectric layer is followed by a conductor such as aluminum.

To obtain optimum performance of the ZnS:Mn electroluminescence films, it has been found necessary to anneal the films at an elevated temperature for about an hour. Films which are not annealed have a lower brightness and higher threshold voltage. Electron spin resonance (ESR) experiments performed by this laboratory have shown that annealing does tend to sharpen the ESR lines indicating that the localized Mn^{+2} ions are diffusing so that they are more homogeneously distributed in the lattice.

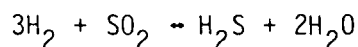
Previous workers have investigated RF sputtering and thermal evaporation of rare-earth metals with subsequent conversion to oxysulfide.⁶ In these



MRDC41090.1AR

investigations, it was found necessary to add H_2S to the Ar in order to compensate for the loss of sulfur during deposition. In addition, it was reported that the brightness of the sputtered films was improved significantly if the films were treated in a hydrogen and sulfur dioxide atmosphere at about $1000^\circ C$.⁶ It appears that the deposited films contain sulfur vacancies which become filled during the H_2 plus SO_2 treatment. The treatment is effective in converting La_2S_3 films to La_2O_2S and also converting La_2O_3 to La_2O_2S . Thus it has the unique capability for restoring both sulfur deficient and oxygen deficient materials to the stoichiometric composition.

Hydrogen and sulfur dioxide can react at elevated temperatures according to the equation:



It is the H_2S which supplies the sulfur and the water vapor which supplies the oxygen to correct the deficiencies.

Additional consideration must be given to the substrate material when treating films at $1000^\circ C$. The thermal coefficient of expansion must be matched to the film and the substrate must be capable of withstanding the high temperature. Clear sapphire (Al_2O_3) was found to be an excellent material. Films deposited on Corning glass 7059 required that the post deposition treatment temperature be reduced to about $700^\circ C$. The lower anneal temperature required a significantly longer time. The ultimate brightness of these films was lower than those treated at the higher temperature. The thermal coefficient of expansion of the 7059 glass matched that of the La_2O_2S films.

In the present investigation $Y_2O_2S:Eu$ films were produced by electron beam evaporating Y_2O_3 in an H_2S atmosphere and coevaporating EuF_3 for the activator. The H_2S pressure was varied to determine its effect on the films. Films were deposited on both 7059 glass and ceramic (Al_2O_3) plates.

The electroluminescent devices were fabricated by first E-beam evaporating a layer of Y_2O_3 , (1000Å) on ITO coated 7059 glass. The ITO had



MRDC41090.1AR

been etched into a conductor pattern. The activated oxysulfide layer (3900Å) was then deposited as described above. The Al_2O_3 plates were fabricated in the same manner except there was no conductor.

The devices fabricated on 7059 glass were annealed in an atmosphere containing 90% H_2 plus 10% SO_2 at 600°C for various lengths of time.

After anneal, a second layer of Y_2O_3 (1000Å) and then the rear Al electrode was deposited. On some devices the second dielectric layer was Al_2O_3 .



4.0 PHYSICAL PROPERTIES

4.1 X-ray

In evaluating the rare-earth oxysulfide thin films, measurements were made on their physical properties and compared to the CRT powder phosphor material. X-ray diffraction measurements were made in order to determine whether the Y_2O_3 had been converted to Y_2O_2S . In addition SEM measurements were made to determine the ratios of yttrium to sulfur and yttrium to europium as a function of the depositions and anneal process. These SEM results were compared to the standard CRT powder phosphor material.

The films, which were produced by electron-beam evaporation from a Y_2O_3 pellet in a sulfur background, were subjected to several different anneal time-temperature profiles. Some films were annealed in an argon atmosphere at 600°C for one hour. After anneal these films turned black and the film appeared crazed. The crazing appears to be caused by the mismatch in thermal expansion between the glass and oxysulfide films.

All other films were annealed in an atmosphere of 10% SO_2 and 90% H_2 . The films appeared pale yellow before anneal and were colorless after anneal. During each deposition both 7059 glass and ceramic (Al_2O_3) were used as substrates. Those films deposited on the 7059 glass were annealed at 600°C for 1 hour. In order to make them into electroluminescent devices, a second dielectric layer was deposited and finally the rear Al electrode.

The films on the Al_2O_3 substrate had both the first dielectric (Y_2O_3) and the oxysulfide film. These films were subjected to a series of time-temperature profiles in the hydrogen plus sulfur dioxide atmosphere. Some were annealed at 900°C for 1/2, 1, 3 hours. Others were annealed at 600°C for 1/2, 1, 3, 5 hours.

The X-ray diffraction patterns of these films indicate that the optimum time and temperature is 900°C for 1 hour. The films annealed at 600°C for 5 hours had a diffraction pattern that was similar to the unannealed



film. From this data it is difficult to determine whether the films are predominantly Y_2O_3 or Y_2O_2S . This will be discussed further in the section on photoluminescence.

4.2 SEM

Films deposited on 7059 glass and ceramic (Al_2O_3) substrates were examined both before and after anneal at $900^\circ C$, using the scanning electron microscope (SEM). Figure 5 is an SEM photograph at 1×10^4 magnification of the annealed film. The large particles are the Al_2O_3 substrate. After annealing the films appear to have cracked along crevices of the Al_2O_3 substrate. SEM photographs of the annealed films on 7059 glass are shown in Fig. 6. The area analyzed was the phosphor area with the ITO and first dielectric layer underneath. The crazing of the film is probably due to the mismatch in thermal expansion of the glass and the Y_2O_2S film.



MRDC82-18755



Fig. 5 SEM photograph of annealed oxysulfide film on Al_2O_3 showing cracks. Annealed for 1 hour at 900°C .



MRDC82-18756

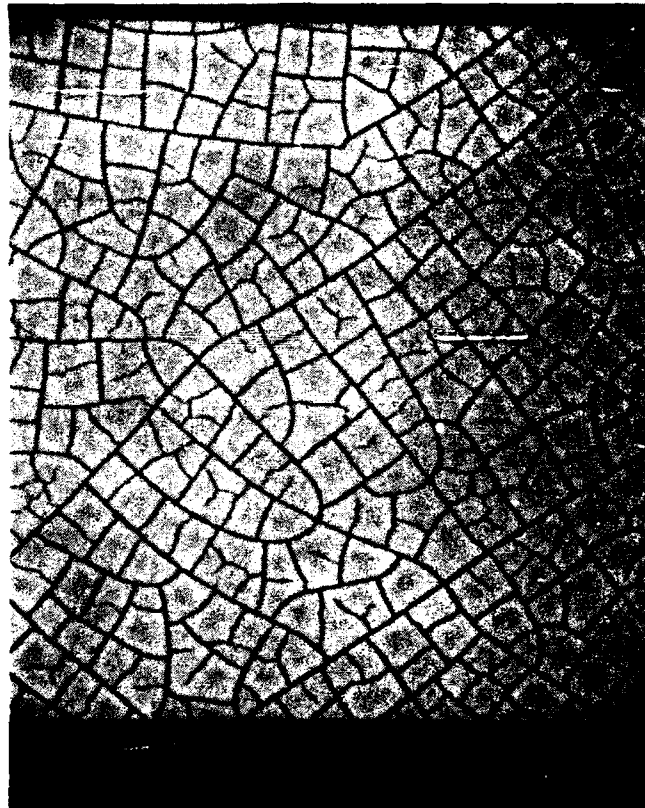


Fig. 6 SEM photograph of annealed oxysulfide film on 7059 glass showing crazing. Annealed for 1 hour at 600°C.

5.0 ELECTRO-OPTICS

5.1 Electroluminescence Measurements

Several electro-optic measurements were performed on the $(Y_{1-x}, Eu_x)_2O_2S$ thin films. These consisted of: 1) emission spectra; 2) photoluminescence spectra; 3) brightness-voltage curves. The emission spectra were obtained using a Jarrel-Ash 0.5m monochromator and a PAR lock-in amplifier.

The room temperature electroluminescent emission spectrum of the $(Y_{1-x}, Eu_x)_2O_2S$ thin films is shown in Fig. 7. A GaAs photomultiplier was used because of its flat spectral response in the visible region. The dominant lines are due to the following transition, $^5D_1 \rightarrow ^7F_2$ (5656 Å), $^5D_0 \rightarrow ^7F_1$ (5960 Å), $^5D_0 \rightarrow ^7F_2$ (6720 Å) and $^5D_0 \rightarrow ^7F_4$ (7070 Å). These films were deposited on 7059 glass and were annealed for one hour at 600°C.

The crystal field establishes in part the oscillator strengths of the $4f^5$ transitions. With the free ion, all the $4f^5$ transitions have the same parity; therefore, only the magnetic dipole and quadrupole transitions can occur. In this case, electric dipole transitions are forbidden. When the symmetry of the crystal field lacks a center of inversion, electric dipoles are allowed.⁸ The transitions observed with the $(Y_{1-x}, Eu_x)_2O_2S$ films are the $^5D_1 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ both magnetic dipole transitions ($J=1$) and the $^5D_1 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_4$ which are electric dipole transitions. This is to be expected since the Y_2O_2S structure is hexagonal. Each metal ion is bonded to four oxygen ions and three sulfur ions.

The unannealed $Y_2O_2S:Eu$ devices showed no electroluminescence although they showed some photoluminescence. Because the energy of the 5D_3 level of the europium ion appears to coincide with the conduction band of the oxysulfide host,⁹ energy transfer between the electronic band system of the host and the sharp electronic band systems of the europium becomes very efficient. Therefore, it may be expected that there would be some photoluminescence even in unannealed films. However, for electroluminescence to occur, the electrons in the host must be accelerated to energies sufficient to

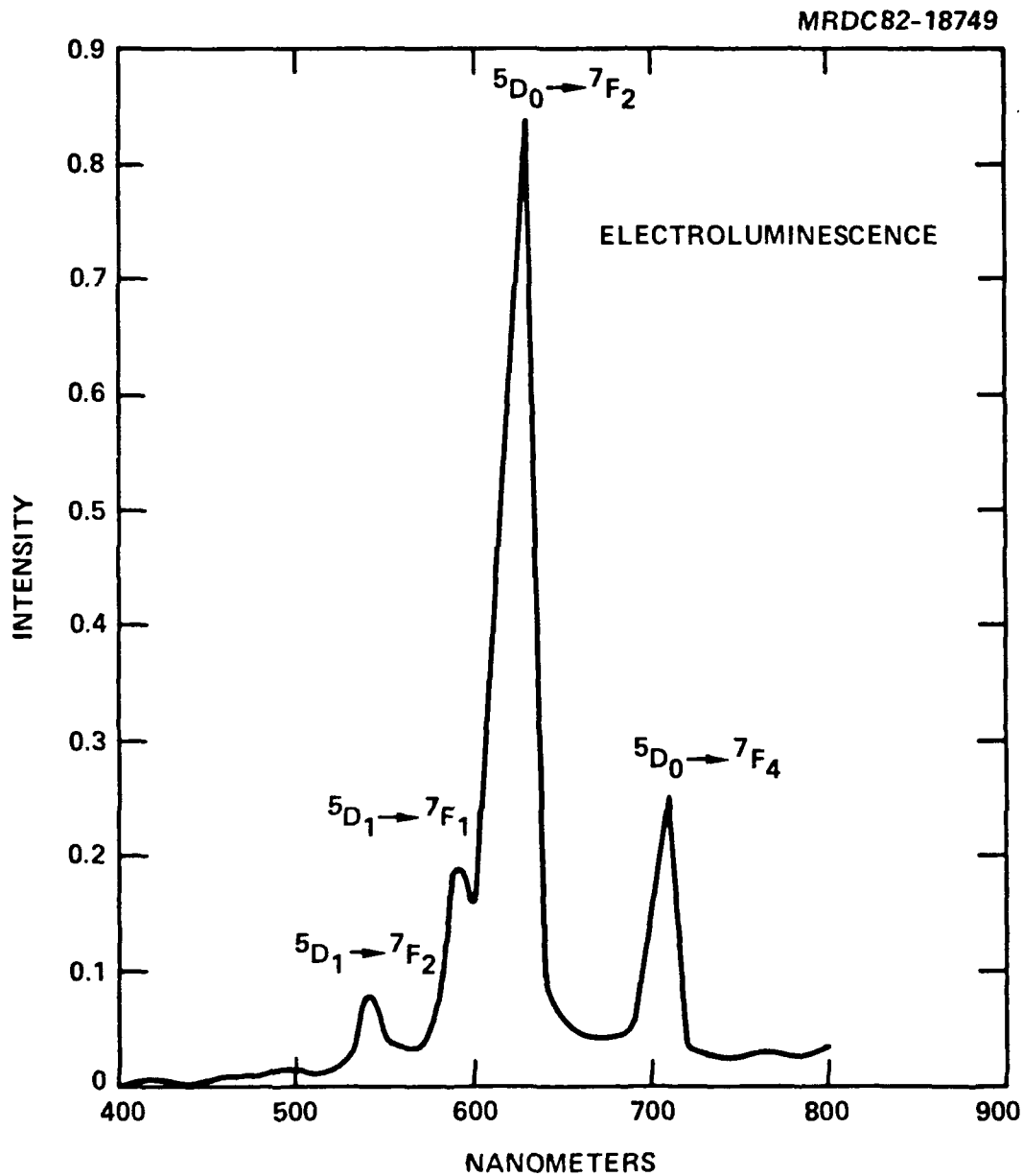


Fig. 7 Room temperature electroluminescent spectrum of yttrium oxysulfide film doped with Eu^{+3} .



MRDC41090.1AR

excite the activator. X-ray data indicates that the unannealed films are not very crystalline. It may be expected then, that the electron will give up much of its energy to the lattice through inelastic collisions.

Electroluminescent devices fabricated using ZnS as a host exhibit a steep nonlinear response of brightness as a function of voltage. The mechanism responsible for this nonlinear response can be explained as follows:⁵ charges from deep trap within the active layer are field ionized and swept to the interface between the dielectric and the ZnS layer where they are trapped. In the next voltage cycle they remain in their traps until the field reaches a sufficient level to allow the charges to tunnel through the barrier and become "hot electrons" very fast. These energetic electrons then impact excite the activator causing luminescence and are trapped at the opposite interface where they remain until the next half cycle of the voltage waveform. The process then repeats itself. It is this tunneling field emission which explains the steep nonlinear characteristics of these thin film emitters. Figure 8 shows the brightness-voltage characteristics of the Y_2O_2S films developed under this program. It can be seen from the plot that the slope is very shallow indicating poor charge injection from the interface. Previously the electronic current responsible for generating light was measured by placing a triangular voltage across the device and measuring the current. For a capacitor which exhibits no tunneling, the current waveform is a squarewave. However, for a device in which there is a tunneling current, this current is superimposed on top of the squarewave displacement current (see Fig. 9). For a constant change in voltage the current is a constant until threshold is reached then the electronic current increases rapidly. With oxysulfide devices, the electronic component appears to continually increase during a greater portion of time that the voltage is increasing. The total number of charges available for excitation is about 10^{11} , which is comparable to the ZnS devices. However, since the current starts at a much lower voltage, many of the electrons do not reach energies sufficient to impact excite the europium activator. Measurements of the current density of the annealed devices was extremely difficult because of cracks due to the

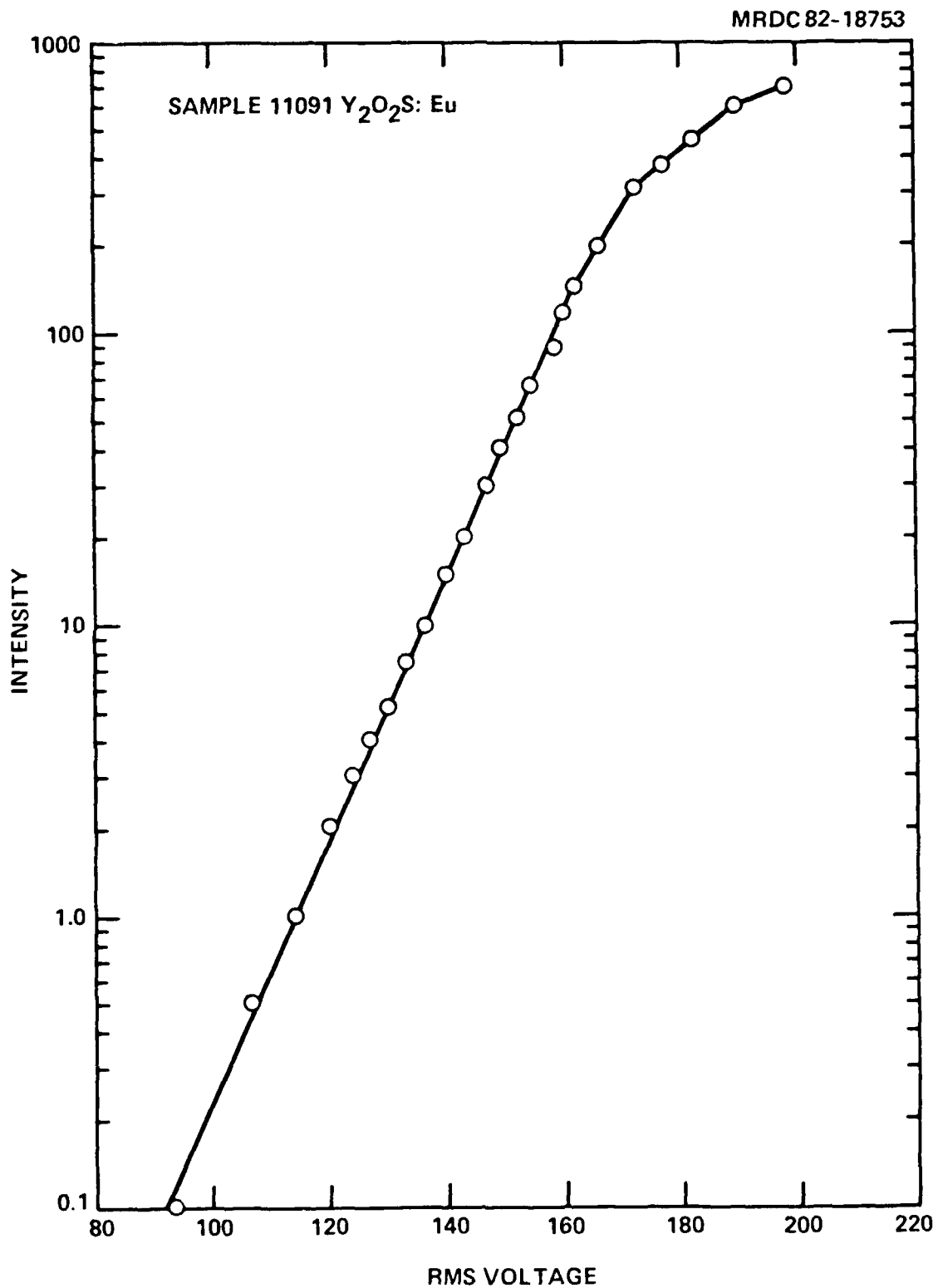


Fig. 8 Brightness-voltage curve for $\text{Y}_2\text{O}_2\text{S:Eu}^{+3}$ thin film emitter.



MRDC80-9475

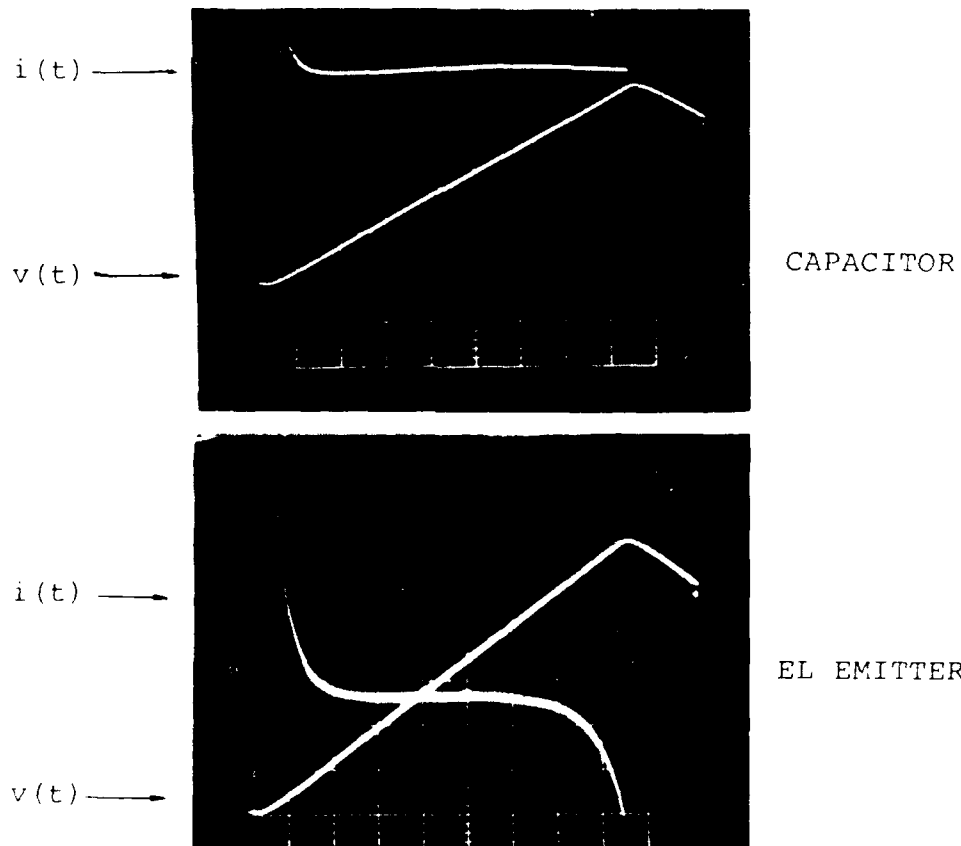


Fig. 9 Current and voltage waveform showing electronic equipment.
(a) Capacitor.
(b) EL emitter.



MRDC41090.1AR

anneal which caused electrical failures. Current measurements made on unannealed samples, which were not crazed, are shown in Fig. 10. It is seen that these devices show a strong temperature dependence. A similar behavior is observed for unannealed ZnS films. However, the Y_2O_2S films started conducting at very low voltages for the higher temperatures. The interface trap depth as determined from the slope of the $\ln j_{\max}$ vs $1/F$ curves are about 0.2 eV as compared to 0.5 eV for the ZnS:Mn films. The conductivity observed with the unannealed Y_2O_2S films appears to have an inverse temperature dependence. This type of behavior can be explained by either Schottky or Poole-Frenkel mechanism. The important observation is that the mechanism for unannealed ZnS films is different than for annealed ZnS films. The annealed ZnS films are temperature independent. Similar results may be true for Y_2O_2S films.

5.2 Photoluminescence Measurements

Photoluminescence measurements were performed on the $Y_{1-x}Eu_x)_2O_2S$ thin films as a means of determining the transitions of the europium activator. In addition, photoluminescence was used to determine the optimum heat treatment. Previous work with ZnS:Mn thin films indicated that in general photoluminescence increased significantly after the anneal procedure as did the electroluminescence. For the oxysulfide films produced on Al_2O_3 it was not possible to perform electroluminescent measurements since no electrodes were included.

Photoluminescence of $Y_2O_2S:Eu$ shows the sharp line europium emission. Figure 11 shows the emission spectrum of a $Y_2O_2S:Eu$ CRT powder phosphor which was used as a reference. The dominant lines are at 6270Å ($^5D_1 \rightarrow ^7F_2$) and 7070Å ($^5D_0 \rightarrow ^7F_4$) both electric dipole transitions. There are several weaker lines most of which are magnetic dipole transitions. The ones of interest which also appear in the thin films are at 5960Å ($^5D_0 \rightarrow ^7F_1$) and 5600Å ($^5D_1 \rightarrow ^7F_1$).

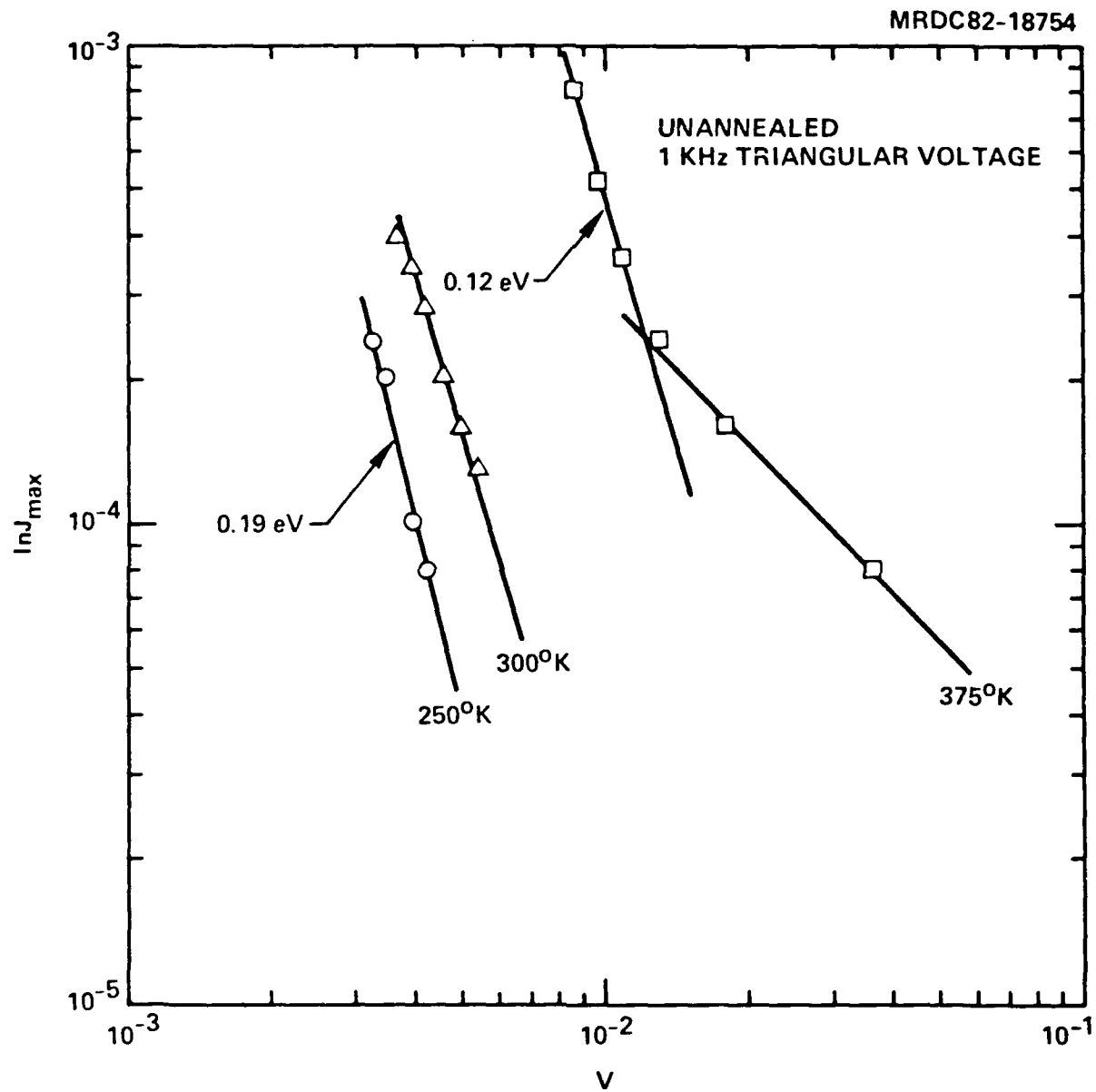


Fig. 10 $\ln J_{\max}$ vs $1/F$ for unannealed $Y_2O_2S:Eu$ films at 250°K, 300°K and 375°K.

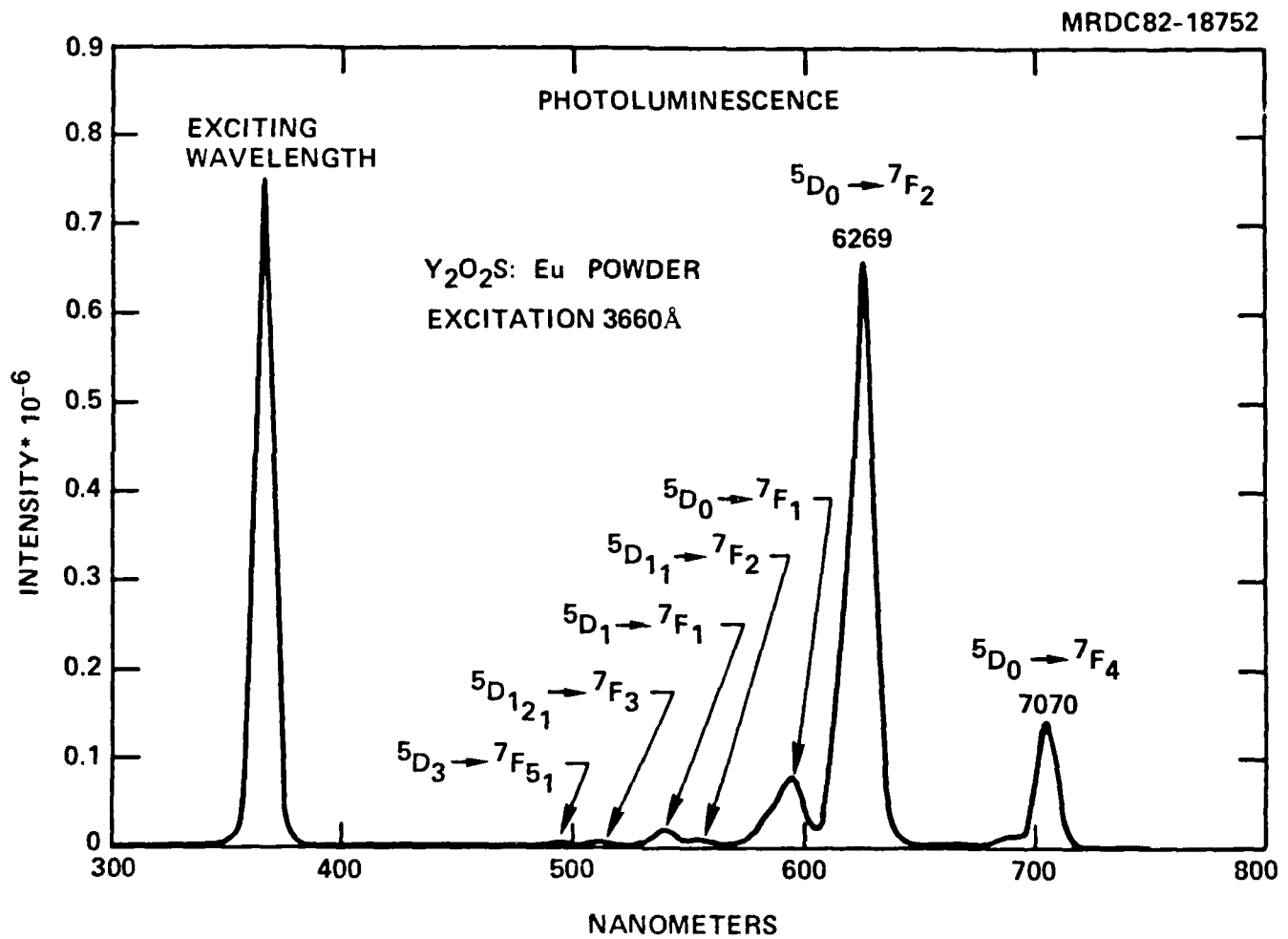


Fig. 11 Photoluminescent spectrum of yttrium oxysulfide europium powder used as CRT phosphor.



Figure 12a, b, c, are photoluminescence spectra showing the effect of annealing the thin films at 900°C for various times. The unannealed film (Fig. 12d) has major line at 6160Å ($^5D_0 \rightarrow ^7F_2$), 5600Å ($^5D_1 \rightarrow ^7F_2$) and a broad unresolved peak at about 5000 angstroms. The shift in the major peak at 6160Å could be due to the influence of the crystal field of the amorphous films or it could be that the films are sulfur deficient and appear like Y_2O_3 . The X-ray diffraction patterns are too weak to be able to differentiate. The EDAX data seems to indicate that the sulfur to yttrium ratio is close to that of the CRT powder. This would seem to indicate that the films are Y_2O_2S and that the shift in frequency is due to the disorder in the films.

As the anneal temperature is increased the intensity of the major peak at 6260Å appears to go through a maximum at one hour. The absolute photoluminescence intensity at 6260Å for the CRT powder is about 200 times as great as that of the Y_2O_2S films. Possible reasons for this are: 1) excess activator concentration in the film so that the light is being concentration quenched; 2) internal light trapping due to the thin film nature of the emitter that only a small portion is emitted perpendicular to the film; and 3) greater phosphor volume of the powder sample compared with the thin film so that most of the exciting radiation is absorbed in the phosphor rather than in the substrate. It should be noted that in the case of an efficient zinc sulfide manganese activated film the ratio of 1000 to 1 exists when comparing an equivalent powder phosphor photoluminescence with the evaporated thin film form.

The photoluminescence spectra of the films which were annealed at 600°C for various times (1/2, 1, 5 hours) are shown in Fig. 13a and b. The data shows that there is some improvement in the crystallinity as evidenced by the narrowing of the linewidth and increase in intensity. However, the improvement is about four times lower than the one hour anneal at 900°C. This important result seems to indicate that it will be difficult to make the most efficient electroluminescent devices from the oxysulfide films on 7059 glass.

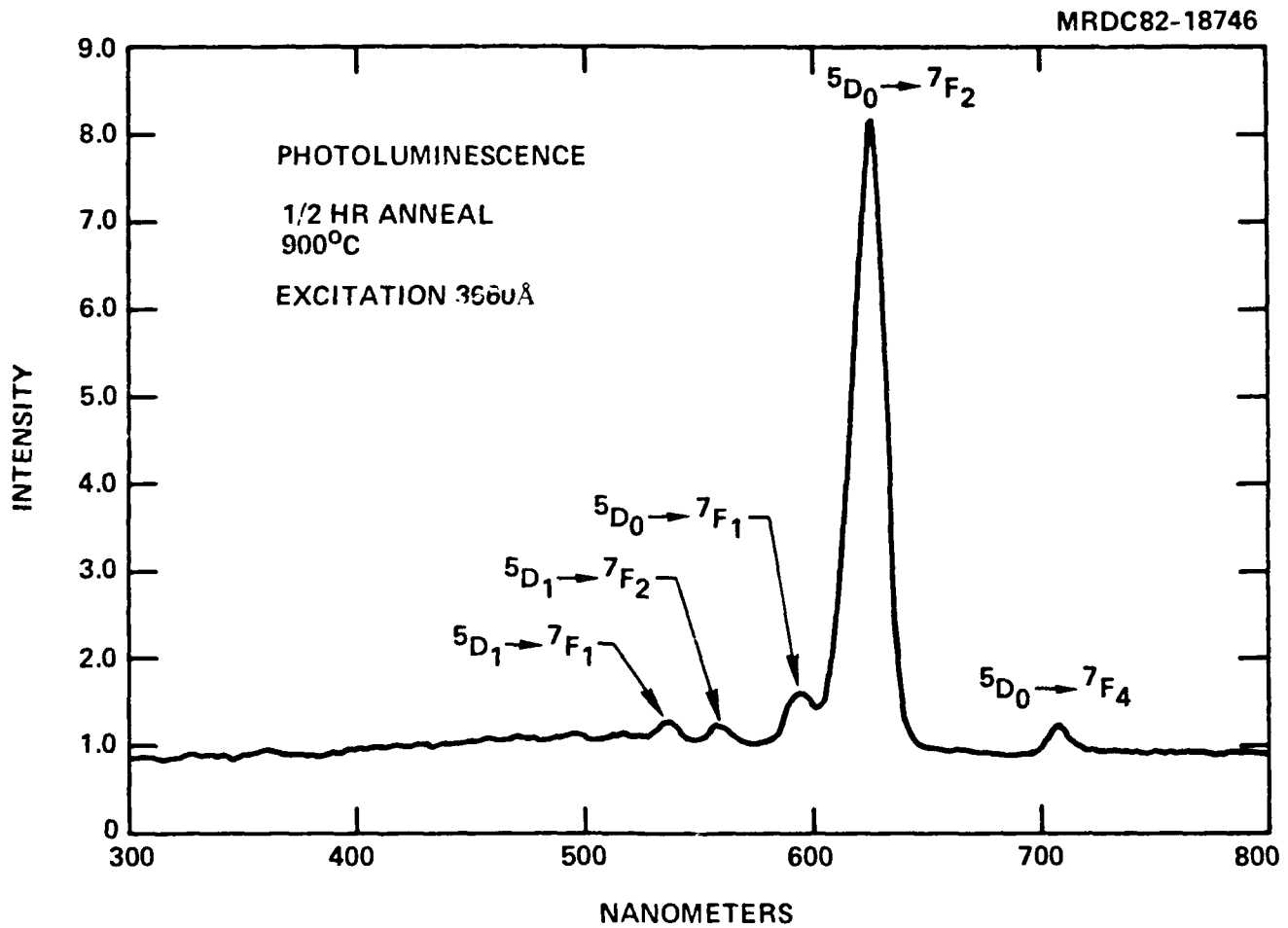


Fig. 12 Photoluminescence spectrum of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{+3}$ film on Al_2O_3
(A) Annealed for 1/2 hour at 900°C

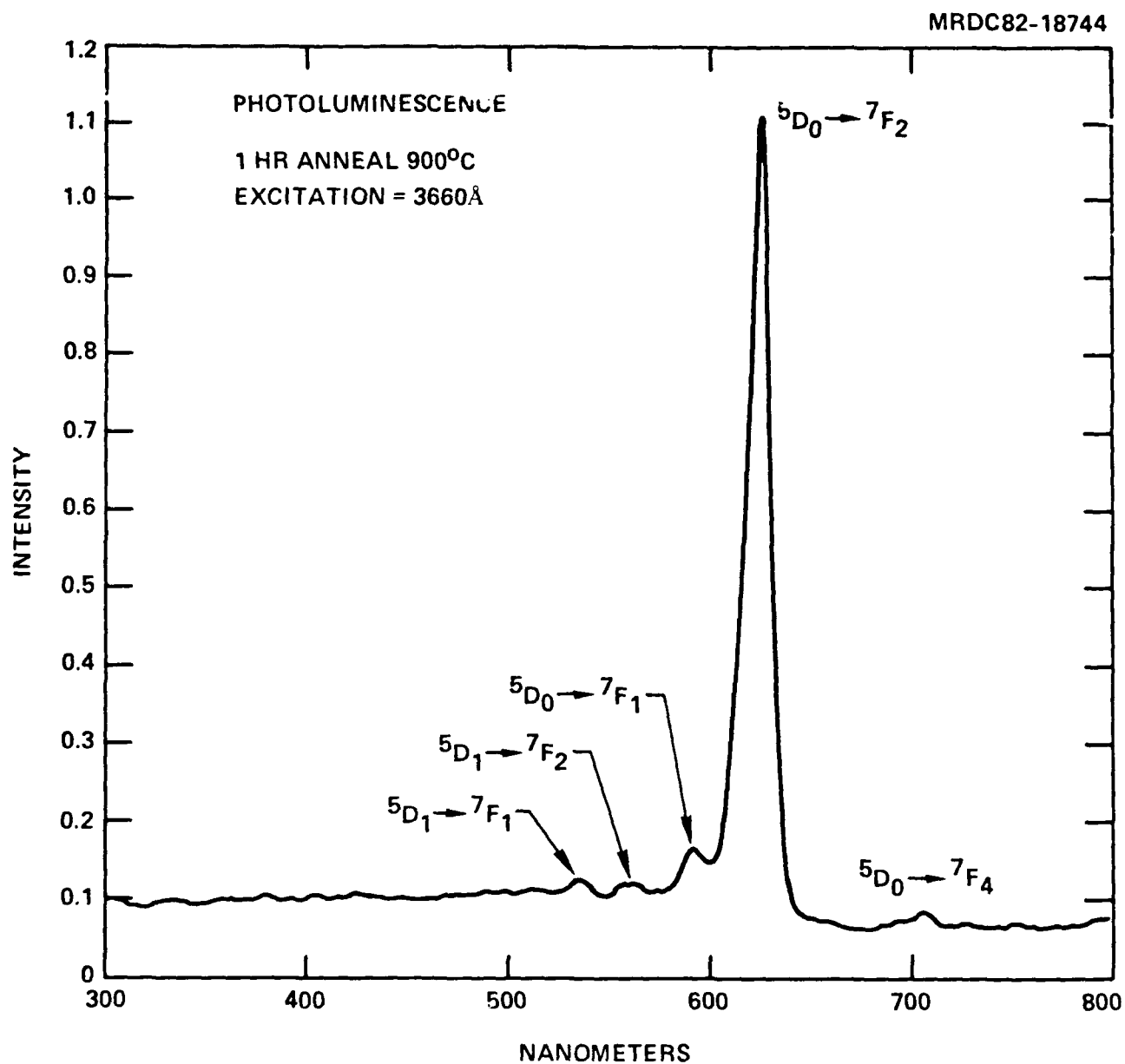


Fig. 12 Photoluminescence spectrum of $Y_2O_2S:Eu^{+3}$ film on Al_2O_3
(B) Annealed for 1 hour at 900°C

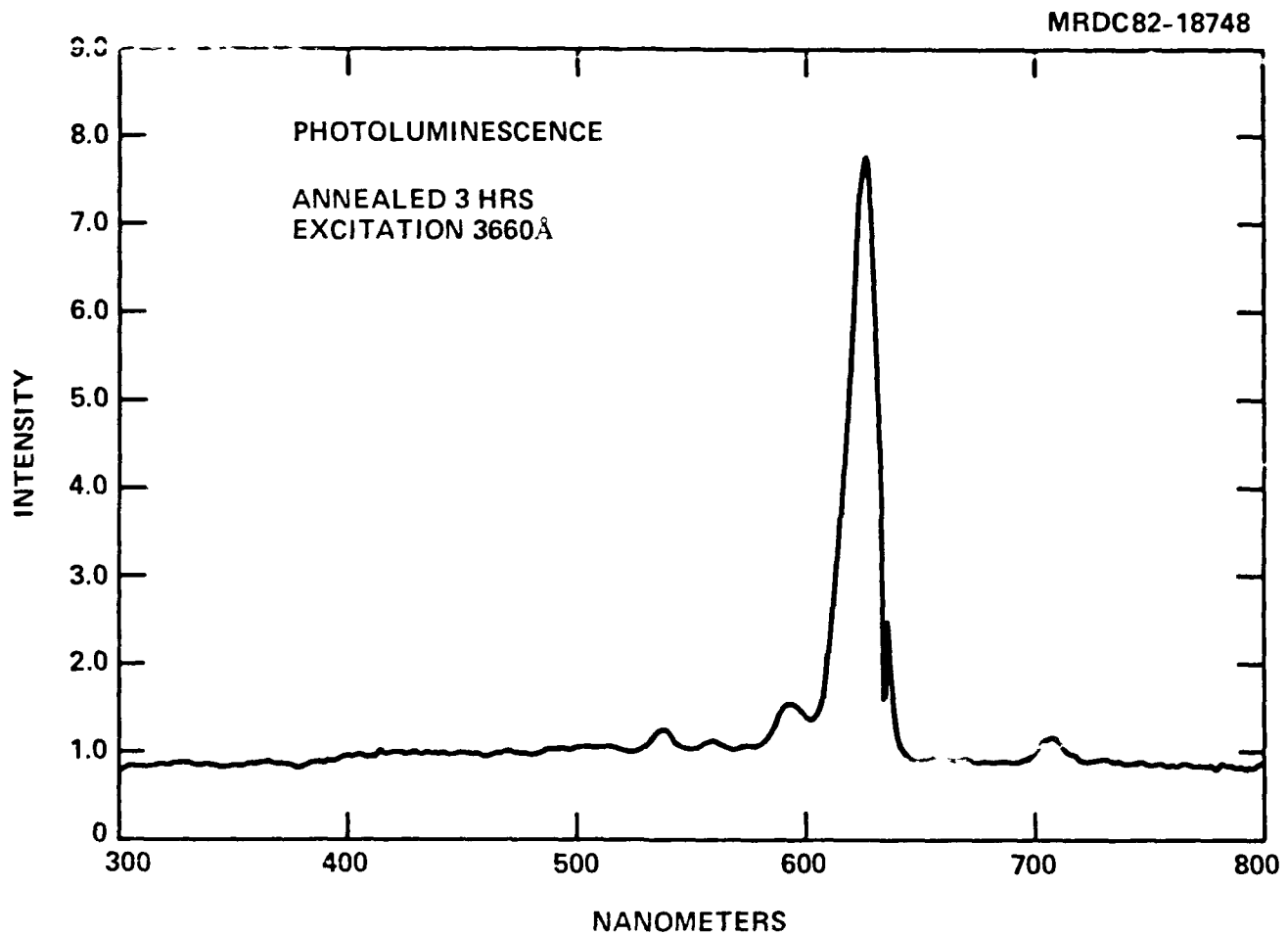


Fig. 12 Photoluminescence spectrum of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{+3}$ film on Al_2O_3
(C) Annealed for 3 hours at 900°C

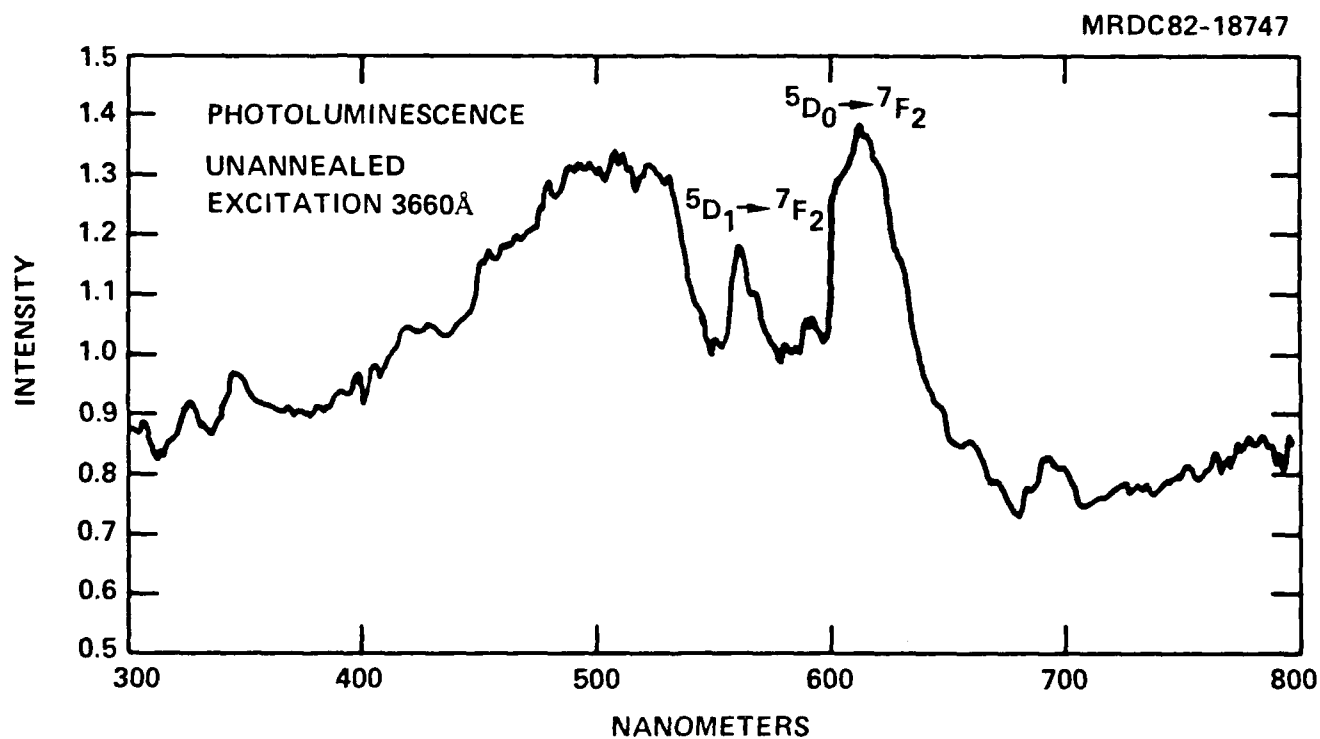


Fig. 12 Photoluminescence spectrum of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{+3}$ film on Al_2O_3
(D) Unannealed film.



MRDC41090.1AR

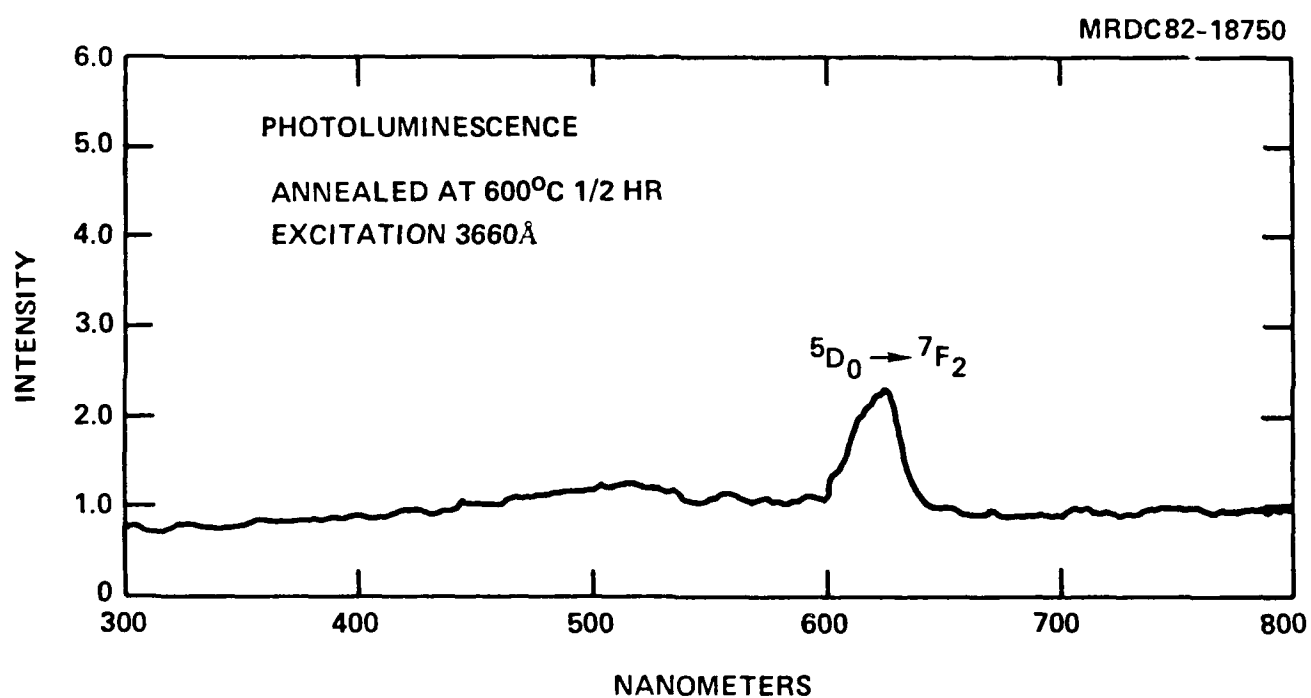


Fig. 13 Photoluminescence spectrum of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{+3}$ film on Al_2O_3
(A) Annealed for 1/2 hour at 600°C.

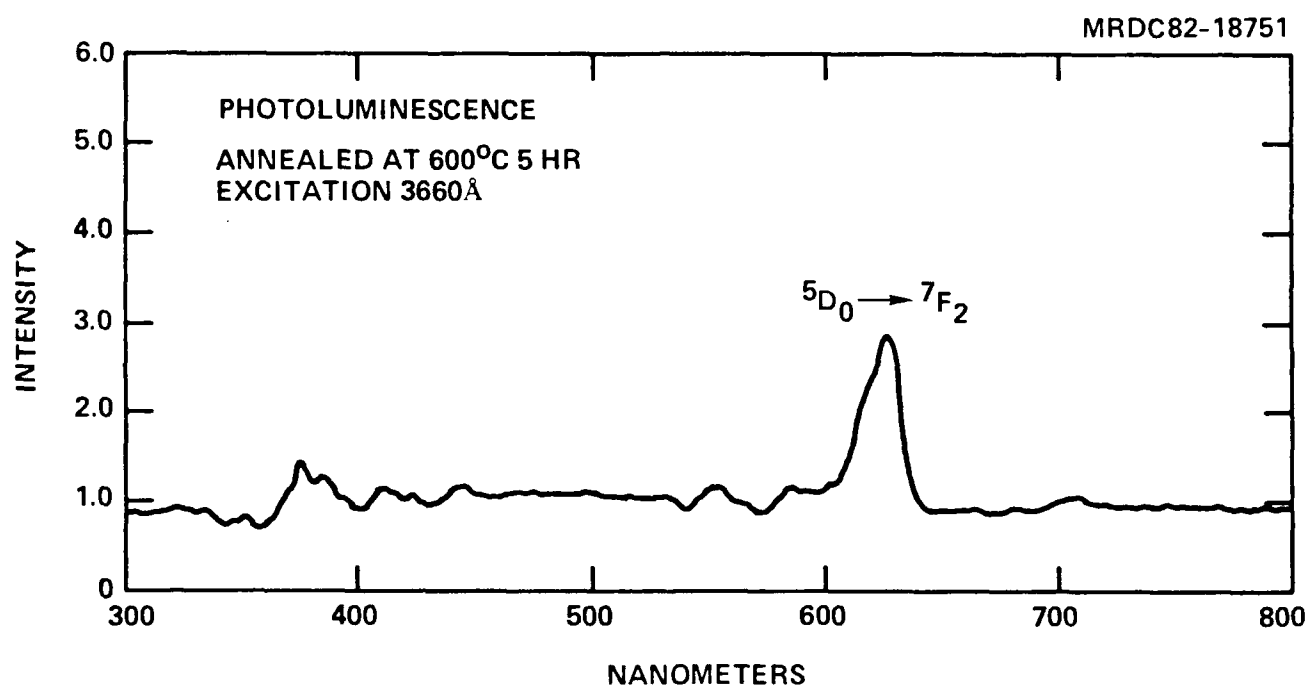


Fig. 13 Photoluminescence spectrum of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{+3}$ film on Al_2O_3
(B) Annealed for 5 hours at 600°C.



6.0 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The objective of this program was to investigate the feasibility of fabricating $Y_2O_2S:Eu$ thin film ac electroluminescent devices. For the first time, electroluminescence was observed in thin films of rare-earth host phosphors. As a result of this work it has been determined that efficient cathodoluminescent thin films can be fabricated using E-beam deposition techniques similar to that required for high quality dielectric films used in conventional electroluminescent emitters. These films exhibited a desirable narrow band emission associated with the europium activator. However, the EL intensity was low (fractions of a ft-L) due to the physical limitations of the film so that a high electric field could not be applied to the final device. Prerequisite for cathodoluminescence in these films was in an annealing step at elevated temperature. Films consistently crazed after this annealing step when they were fabricated on 7059 glass. The crazing in turn induced cracks in the film so that a high electric field could not be applied across the film. Annealing studies at various times and temperatures conducted with an aluminum oxide (Al_2O_3) substrate material indicated that a 4-fold improvement in brightness could be obtained in the photoluminescence if temperature of $900^\circ C$ were used instead of the $600^\circ C$ as limited by the glass substrate typical of the conventional thin film EL emitter.

Future work will focus on lowering the anneal temperature requirements and/or finding substrates which are compatible with the high temperature anneal process. Also, a cathodoluminescence test set-up will be utilized to rapidly evaluate the luminescent properties of the phosphor films. An important application of this test system is the ability to inject electrons into the phosphor system independent of the contact material. By varying the energy of the electron beam, the penetration of the injected electrons can be changed across the interface area where the dielectric film contacts the phosphor films to determine the efficiency of the electron injection.



7.0 REFERENCES

1. T. G. Maple and R. A. Buchanan, "f Sputtered Luminescent Rare-earth Oxysulfide Films," J. Vac. Sci. Technol. Vol. 10 #5, Sept/Oct 1973, p. 616.
2. L. Hale, R. Ketchpel and W. Hale, "Efficiency of Thin Film ac EL Emitters," Tech. Digest, IEDM, Washington, D. C., 1979.
3. A. Vecht, "Electroluminescent Displays," J. Vac. Sci. Technol., Vol. 10, #5, Sept/Oct, 1973.
4. P. N. Yocum and R. E. Shrader, "Cathodoluminescent Power Efficiency of Some Rare-earth Oxysulfide Phosphor Systems," Proc. Seventh Rare-earth Research Conf., Oct. 1968, Coronado, CA pp. 601-608.
5. J. A. Cape, R. D. Ketchpel and L. G. Hale, "A Possible Model for Thin Film ac Electroluminescent Devices," 1978 Device Research Conf., Santa Barbara, CA.
6. R. A. Buchanan, T. G. Maple, H. N. Bailey and R. V. Alves, "Luminescent Applications of Rare-earth Materials," Final Report ARPA Contract DAHC-15-71-C-0138.
7. M. Koskenlkinna, M. Leskela and L. Niinisto, "Synthesis and Luminescence Properties of Europium-Activated Yttrium Oxysulfide Phosphors," J. Electrochem Soc., Jan 1976, p. 75.
8. G. Blasse and A. Bril, "Characteristic Luminescence," Phil. Tech. Rev. Vol. 31 #10, 1970, pp. 304.
9. K. A. Wickersheim and R. A. Buchanan, "Position of the Energy Levels of Trivalent Rare-earth Activator Ions Relative to the Electronic Energy Bands of Lanthanum Oxysulfide: A New Picture of Excitation and Relaxation," App. Phys. Lett. Vol. 17, #5, 1 Sept 1970, pp. 184.