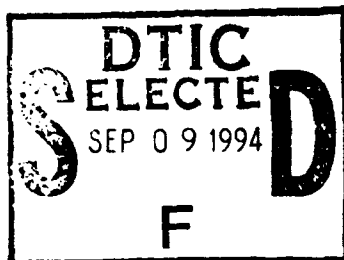


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**PREPARATION AND INVESTIGATION OF IMPROVED LOW
VOLTAGE ELECTRON EXCITABLE PHOSPHORS**

Final Technical Report

by

**A Vecht, D W Smith and S S Chadha
July 1994**

United States Army

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13. ABSTRACT (Maximum 200 words) In the final report, we describe the work carried out on the investigation and development of low voltage phosphors for field emission displays. The standard blue-green ZnO:Zn was improved considerably and now yields very high luminance. New methods were developed which produced good, saturated green zinc gallate phosphor. A novel, narrow band calcium titanate red phosphor has been synthesised, as well as a broader band zinc magnesium oxide blue emitter. The synthesis and characteristics of these materials are described and analysed. Future work is suggested. Samples of all good phosphors were supplied to Fort Monmouth, as well as seven US firms. Keywords: Phosphors; cathode ray; displays; low voltage; zinc gallate; calcium titanate; zinc oxide; tin oxide; thin films; inorganic and organic synthetic processes.			
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ABSTRACT

This final report covers the work carried out in the two years of the contract to investigate new and improved low voltage phosphors for field emission displays (FEDs). The work commenced with a literature survey of relevant papers and patents and attempts to determine suppliers of phosphors, with particular reference to suitable low voltage materials. Not surprisingly, very few manufacturers of low voltage phosphors were unearthed and these only supplied ZnO:Zn. Hence, at the commencement of this contract, only one low voltage phosphor was available.

Our work during this period has concentrated on assessing new lattices, attempting to obtain high surface conductivities from nominally insulating materials, as well as setting up a low voltage, demountable cathodoluminescent rig, together with a spectroradiometer. In addition, our research efforts have been geared towards ensuring that we were not dependent on external suppliers for ZnO:Zn phosphors. Hence, this aspect received considerable attention.

One annual and six interim reports have been issued, together with samples of many types of phosphors prepared in our laboratories. Some of these have been evaluated by our colleagues at Fort Monmouth and the results so far have been very promising. As a result of our efforts, a phosphor system emitting saturated green (ZnGa₂O₄:Mn), a new emitting orange-red (CaTiO₃:Pr) and finally, a blue emitting ZnMgO:Zn, have been successfully produced.

Under 'standard' conditions, the luminance levels in foot lamberts, at the end of the first year, (measured at Fort Monmouth EDTL), are indicated under A. The results at the end of the contract period are under B.

	A	B
ZnO:Zn (blue green)	{2600 (UG) {2700 (commercial)	4650 -
ZnGa ₂ O ₄ :Mn (saturated green)	350	2610
CaTiO ₃ :Pr ('saturated red')	160	576
ZnMgO:Zn (blue)	-	1614

This clearly indicates the improvements made. However, for a RGB system, the colour purity is not yet perfect and filters will still be required.

Samples were supplied to seven US firms.

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I) OBJECTIVES

The cathode ray tube, after a century of development, is still the major display component used in information technology. The extension of its usefulness, from oscilloscope to monochrome and then full colour television, has always been accompanied by improvements in the phosphors used. For example, the advent of the present colour television systems depended on the development of efficient, narrow band red phosphors. Similarly, the recent progress made in field emission/microtip technology will not be exploited to its full potential until the red, green and blue (RGB) phosphors operating at the required conditions have been synthesised.

Although cathode ray phosphors have been optimised to work at high voltages (over 10 eV), and relatively low current densities (a few micrams per cm²), the requirements for field emission displays (FEDs) are totally different. The voltages of operation range from 10 to 1500 eV, but high current densities are needed. Because of the relatively low operating voltages, aluminizing of the phosphor layer to avoid space charge is not possible. At the start of the contract, the only phosphor systems used with any success are the ZnO systems.

For these reasons, the objective of this contract was to produce a new system of phosphors excitable by low energy electrons, capable of saturated R G and B emission with high efficiency. It should be emphasised that although we are dealing with FEDs in a general way, there are many proposed FED systems and each may require a phosphor system designed for it. Every application has specific I-V conditions of operation, resolution and maintenance. These, in turn, will be governed by the size of the display required and the method of address used.

II) LITERATURE SEARCH

A literature search was carried out at the beginning of the contract. Most patents were of Japanese origin. Only a few patents covering phosphor preparation techniques were uncovered. The complete list of references was given in the first interim report. Since then, only a few papers and patents have been found in the literature. These have been listed in the other interim reports.

III) PHOSPHOR SUPPLIERS

A list of phosphor suppliers was appended in the first interim report. All these suppliers were approached for information on any phosphors for low voltage application. Only Kasei, PTL (UK) and Hoechst responded but only Kasei appeared useful.

IV) POWDER PHOSPHOR SYNTHESIS AND RESULTS

1) ZnO:Zn Powder Phosphor*

Throughout the contract, many different methods of preparing ZnO:Zn phosphor have been tried. The original method involved firing ZnO powder in a CO reducing atmosphere. This led to bright ZnO:Zn which was reproducible, but never as bright as the commercial ZnO:Zn. Furthermore, the batch size was limited to around 30g. The introduction of some S into the CO reducing atmosphere improved the PL to near commercial levels, but not much better. More recently, we have experimented with modifying the firing conditions and replacing the CO atmosphere. This led to a significantly improved phosphor vis-a-vis commercial.

Various suppliers (Koch-light, Koch, Merck, Rose Chemicals, Grillo Zinc Oxide and Aldrich) were sourced for fine particle, pure zinc oxide starting material and wide differences in quality of the phosphor so produced were found.

In an alternative route, a variety of zinc oxysalts were precipitated which could then be thermally decomposed to produce ZnO. This route should have the advantage that the purity and possibly the particle size of the zinc oxide can be more closely controlled. The precursor for the preparation of the ZnO phosphor was optimised. Again, showing that results were better if suitable starting materials were selected. The type of furnace used also affects the final results obtained.

The PL of ZnO:Zn is now extremely bright when compared to the commercial phosphor. The procedure now chosen is fairly complex involving several firing stages and very stringent control of the ambient. Details were given in previous reports.

Further improvements, particularly in the reduction of the particle size, were obtained by using a charge of mixed starting materials.

There are some references in the literature where etching has been shown to be beneficial in improving phosphor performance. The improvement may be due to the removal of dead surface layers. We have treated both raw ZnO material and ZnO:Zn phosphors using a range of suitable etchants such as H_2SO_4 , HCl , HNO_3 , $HClO_4$, H_2O_2 , NH_4OH and $N_2H_4H_2O$. Positive results were obtained with some of these etchants. With raw ZnO, the most beneficial etchant was H_2SO_4 (2.5%). This seems to point to S as being a useful (if not the most important) impurity in ZnO:Zn.

* For a description of assessment equipment used see Appendix A & B.

Though some improvements were seen when ZnO:Zn phosphor was etched with H_2SO_4 , far better etchants have been developed, the PL of the etched phosphor being significantly brighter than control.

1a) ZnO:Zn phosphor assessment

The assessment of the phosphors prepared was carried out using material examination techniques such as XRD, SEM, ICP, as well as PL studies using both laser and UV excitation and CL studies using both low and high voltage sources. Table 1 summarizes the results for the types of phosphors we have made, along with the commercial material where available. For reference, the best commercially available ZnO:Zn was used.

TABLE 1

Phosphor	Threshold Voltage (V)	Peak (nm)	FtL (1500V 100 μ A)	Luminance 2 hrs (ftL)	CIE X Y	
ZnO:Zn	40	505	9350	4650	0.2268	0.4427
ZnO:Zn (commercial)	40-50	505	7140	1250	"	"
ZnGa ₂ O ₄ :Mn	40	505	3120	2610	0.1087	0.7574
CaTiO ₃ :Pr	90	612	1152	576	0.6799	0.3111
SnO ₂ :Eu	60	596	164	102	0.5873	0.3831
(Zn,Mg)O:Zn	50	476	3250	1614	0.1707	0.2843

1a.i) XRD

XRD examination of ZnO (raw), ZnO with added S and ZnO prepared from a Zn oxysalt precipitated from $ZnSO_4$, revealed no discernible differences (Figs. 1-3).

1a.ii) SEM

SEM examination of ZnO indicated that the particle size was around 1-2 μ m. The commercial material was similar, (Figs. 4 and 5) both in size and in morphology.

1a.iii) Inductively Coupled Plasma

Chemical analysis to determine the impurity level in some of the phosphors prepared from commercial ZnO samples, ZnO:Zn prepared via the chemical methods, as well as commercial ZnO:Zn, was carried out using inductively coupled plasma spectroscopy. The results of this exercise are tabulated below:

Phosphor sample	Elements (ppm)						
	Cd	Ni	Ca	Cu	Fe	Pb	Mn
Commercial ZnO:Zn	0.965	0.760	0.082	0.028	0.138	4.67	0.054
BDH-ZnO	0.944	0.752	0.102	0.074	0.012	5.11	0.052
Rose Chemical-ZnO	1.4	0.761	0.074	0.039	0.074	5.66	0.053
ZnSO ₄ -Zn oxalate-ZnO	0.906	1.19	0.433	0.203	0.326	4.18	0.065
ZnAc ₂ -Zn oxalate-ZnO ZnAc ₂	0.932	0.751	0.496	0.171	0.153	4.35	0.074

As can be seen, most impurities levels are very similar. The major differences are in the levels of Ca, Cu and, in one instance, Fe. Hence, overall, it is difficult to judge why some materials yield a good phosphor, whilst another yields a poor phosphor. The major problem with ZnO is that, unlike other phosphors which require activators and/or co-activators, it is self-activated. This imposes very severe restrictions on the preparation conditions. The Zn-O dissociation plot is shown in Fig. 6.

1a.iv) Photoluminescence

Gradually, over the last two years, the PL of ZnO:Zn phosphors prepared in-house, first approached, then exceeded, that of the commercial material. Under UV excitation, ZnO:Zn emitted as intense green luminescence. The excitation and emission spectra are shown in Fig. 7. The broad emission peak of the ZnO:Zn is centred around 505nm (FWHM 120nm). The decay time t was very short, $\sim 0.3\mu\text{s}$ (where t is defined as the time for the initial PL intensity to decrease by a factor $1/e$ (Fig. 8).

1a.v) Cathodoluminescence studies

CL studies have been carried out both at ETDL, Fort Monmouth, and the University of Greenwich. The phosphor layers for evaluation were prepared by either doctor blading or electrophoresis. In the initial tests when no baking was used, the stability was very poor. After removal from the vacuum test chamber, a heavy browning (burning?) was observed at the point where the e-beam impinged on the phosphor.

When the layers were baked the stability was improved dramatically. The browning was almost eliminated.

The results obtained were as follows:

Phosphor	Luminance (ftL) at 1500V 50 μ A	
	<u>1993</u>	<u>1994</u>
ZnO:Zn (Greenwich)	2600	4650
ZnO:Zn (commercial)	2700	-

Hence, the in-house ZnO:Zn is significantly better than the commercial material.

The luminance measurements undertaken at UG are summarized in the L/V, L/I and L/t curves of Fig. 9, a), b) and c), and the broad band emission spectrum in Fig. 10, where it is compared with the spectra of other low voltage phosphors.

2) (Zn,Mg)O:Zn Powder Phosphor

Various dopants were used in an attempt to shift the emission peak or enhance the PL emission of ZnO:Zn.

The addition of large concentrations of Mg oxysalts to ZnO followed by reduction in CO shifted the emission by about 30nm towards the blue, but at a much reduced intensity. No improvement was gained by using co-precipitated Zn and Mg.

However, by using selected precursors which underwent complex exothermic reactions at the mixing stage, the emission was considerably intensified. As a result, a (ZnMg)O:Zn phosphor was produced with bright blue PL or CL emission.

2a) (ZnMg)O:Zn phosphor assessment

The phosphor was assessed using many of the methods described for ZnO:Zn.

2a.i) SEM

The particle size appeared slightly smaller than ZnO:Zn (Fig. 11) but the morphology was similar.

2a.ii) Photoluminescence

Compared with ZnO:Zn, the peak was shifted by 30nm toward the blue and, like ZnO:Zn, was a broad band emission.

2a.iii) Cathodoluminescence

The emission peak at 476nm compared with 505nm for ZnO:Zn and, again, the broad band spectrum was retained (Table 1, Fig. 10).

Emission was detected at 50V (V_{th}) and the luminance after 2 hours continuous operation at 1500V, 50 μ A approached 2000 ftL. Typical L/V, L/I and L/t curves are shown in Fig. 12 a), b) and c).

3) ZnGa₂O₄:Mn Powder Phosphor

We have had considerable success with the synthesis of ZnGa₂O₄:Mn phosphors. The initial samples were synthesised by the solid state reaction of the specific oxides at elevated temperatures. The mixtures were prefired at lower temperatures in order to properly dehydrate the oxides and to provide a more homogeneous mixture. The final firing was always in an atmosphere such that the manganese was reduced to the Mn^{II} state. The reduction of the manganese to the +2 state was accomplished by firing in an atmosphere of carbon monoxide. This led to a phosphor with a long PL persistence. Covering the phosphor layer surface with a layer of powdered charcoal during firing led to a significantly reduced persistence. However, recently, it was found that reduction using gas mixtures gave more reproducible results.

ZnGa₂O₄:Mn has been prepared with up to 1% Mn. A range of temperatures up to 1300°C was used, though, in order to restrict the particle growth, no fluxes have been added. The higher temperature gave more consistent results. Attempts to substitute Ga with Al led to poor phosphor so this route of investigation was not pursued.

3a) ZnGa₂O₄:Mn Phosphor Assessment

(N.B. methods used as above).

3a.i) XRD

XRD spectra have been obtained for both the long and short UV persistence material. However, no structural differences were found (Figs. 13 and 14).

3a.ii) SEM

The SEM for ZnGa₂O₄:Mn presented a complex picture (Fig. 15). The powder consisted of a mixture of particles from 1-10µm mixed with large, flat, rectangular plates. EDAX examination revealed no chemical differences between these plates and the rest of the particles.

3a.iii) Photoluminescence

The ZnGa₂O₄:Mn emits a purer green luminescence than ZnO:Zn. The excitation and emission spectra are shown in Fig. 16. The narrow band emission peak is centred around 505nm with a decay time (1/e) of around 4mS (Fig. 17).

3a.iv) Cathodoluminescence

The emission spectra is almost identical with the PL spectrum (Table 1, Fig. 10) showing the same narrow band, saturated green.

The threshold for emission at 40V was similar to ZnO:Zn. The L/V, L/I and L/t data is illustrated in Fig. 18. No burn-in problems were experienced and the emission was very stable.

4) Calcium Titanate:Pr (CAT) Powder Phosphor

This phosphor is not available commercially. A pinkish-red emission with a substantial afterglow is obtained when excited by either long (366nm) or short (254nm) wavelength UV.

The emission of the system was optimised for firing temperature and time, Ca:Ti ratio and activator concentration. A total of three hours firing in four stages at 1000°C and 1100°C was necessary, the last firing being in a slightly reducing atmosphere. The best results were found with relatively low (<0.2 at. %) concentrations of praseodymium in a matrix with a very slight excess of Ti. Praseodymium was replaced by 12 other rare earths at 0.1 at. % and 0.5 at. % concentrations in the optimised formulations, but the PL of the Pr activated phosphor was at least an order of magnitude more intense than any of the others.

Other group II elements, both IIA and IIB, were partially substituted for calcium, with mostly detrimental effects on the photoluminescence. The emission colour was unchanged. However, substitution of up to 50% of the calcium by strontium gave a brighter phosphor under UV with a much shorter afterglow.

4a) Calcium Titanate Phosphor Assessment

4a.i) XRD

The XRD spectrum of $\text{CaTiO}_3\text{:Pr}$ is shown in Fig. 19. It is a typical Perovskite structure as expected.

4a.ii) SEM

The micrograph (Fig. 20) illustrates the very characteristic feature of this powder, the particle appearing to consist of fine hexagonal crystals of 1 μm or less collected in distinct approximately spherical agglomerates of 5 μm or more.

4a.iii) Photoluminescence

The emission spectrum for a $\text{CaTiO}_3\text{:Pr}$ under laser excitation is shown in Fig. 21, and that for the calcium/strontium phosphor is identical.

4a.iv) Cathodoluminescence

In contrast to the PL, the partial substitution of calcium by strontium does not increase the CL intensity either at low or high loading. Indeed, the CL intensity of the substituted phosphor was lower. As under UV excitation, the peak emission is at 615nm (Table 1, Fig. 10). The L/V, L/I and L/t curves at 1500V, 50 μ A are shown in Fig. 22, a), b) and c).

5) Tin Oxide:Eu Powder Phosphor

The starting material was pure SnO_2 powder and the Eu was added as the chloride. The unfluxed material, even when fired at 1600°C, only gave weak PL emission. Fluxes such as NaCl, BaCl_2 and NH_4F were therefore introduced either singly or as mixtures in proportions up to 40%. After firing, the powder was washed in nitric acid to remove excess flux. The most intense PL was obtained using 20% of mixed NaCl/ BaCl_2 flux in a single firing at 1550°C at an Eu concentration of 0.5-1.0%.

5a) Tin Oxide Eu Phosphor Assessment

5a.i) XRD

The XRD spectrum of the phosphor is shown in Fig. 23.

5a.ii) SEM

A SEM micrograph (Fig. 24) shows a large variation in particle size in the range $>1\mu\text{m}$ - $6\mu\text{m}$ with well defined particles.

5a.iii) Cathodoluminescence

Only weak CL was achieved with a pink emission centred on a double peak around 590nm (Table 1, Fig. 10). The L/V, L/I and L/t curves are shown in Fig. 25.

6) Zinc and Cadmium Stannate Powder Phosphors and Assessment

This possible phosphor system may have certain advantages, if Eu activation is possible, over the $\text{SnO}_2\text{:Eu}$ system. In particular, Cd_2SnO_4 is a known conductor and, if efficient luminescence could be obtained, it should be suited to excitation by low voltage cathode rays.

The synthesis of $\text{Zn}_2\text{SnO}_4\text{:Eu}$ was carried out via a standard phosphor route by firing the mixed oxides of zinc and tin at temperatures up to 1500°C for periods from half-an-hour to three hours in an oxidizing (air) atmosphere. A range of Eu from 0% to 5% was added, as well as a flux consisting of equal parts of sodium and barium chlorides, up to 20% by weight. The fired powder was washed free of flux.

The best activated phosphor contained 2 at. % Eu but showed only very weak orange-yellow PL under 366nm UV and an even weaker pink emission under 254nm. Substitution of all or part of the zinc by cadmium gave powders with intense body colours which were not luminescent. The zinc compounds were insulating while the cadmium compounds were, not unexpectedly, conducting.

The brightest phosphor, a zinc stannate, contained no added europium, giving a whitish emission under 254nm and a stronger greenish-yellow under 366nm. The intensity, although still rather weak, was at least an order of magnitude greater than from $\text{Zn}_2\text{SnO}_4\text{:Eu}$.

The particle size and morphology of both unactivated and Eu activated phosphor were similar when studied under the SEM. Unactivated Zn_2SnO_4 is shown in the microphotograph in Fig. 26. The XRD spectra of the two types were also similar (Fig. 27), showing evidence of unreacted ZnO and SnO_2 . This was still true even after firing for 16 hours. So far, this system has shown little promise.

V) THIN FILM PHOSPHOR

1) The Synthesis of Thin Films - General

These oxide films were prepared by organometallic vapour deposition (OMCVD) using the method of aerosol spray pyrolysis (ASP). A sketch of the apparatus used is shown in Fig. 28. A solution of an organometallic precursor of the desired metal is dissolved in an appropriate solvent, usually organic. It is pumped to the nebulizer at the top of the 3-necked flask. A fine mist is thus formed in the flask, any larger drops falling out to waste. A second inlet in the flask enables the ratio of the gases to the carrier gas, e.g. $\text{N}_2\text{:O}_2$ to be simply varied. The fine mist is delivered to the reaction chamber, comprising a rectangular section tube, into which the platform bearing the substrates has been inserted. The platform is held at an elevated temperature, usually $430^\circ\text{--}480^\circ\text{C}$, the mist decomposing at, or near to, the substrate surface.

Glass quartz and sapphire substrates were employed, the latter enabling annealing temperatures exceeding 1500°C to be used. The deposition rate is approximately $1\mu\text{m/hr}$. The

approximate film thickness was rapidly estimated from UV/Vis spectra by the application of the formula

$$t = \frac{\lambda_2 \lambda_1}{2n (\lambda_2 - \lambda_1)}$$

where λ_2 , λ_1 are the wavelengths of successive nodes and n is the refractive index of the film. A UV/Vis spectrum for ZnO:Zn is shown in Fig. 29.

2) ZnO:Zn Thin Films

The precursor solution was prepared from zinc organometallic compounds in a mixed solvent and the films were deposited in a N₂/O₂ atmosphere. Initially, they were prepared on Corning 7059 borosilicate glass but later, sapphire substrates were used.

The as-deposited films were not photoluminescent. An SEM micrograph of such a film, about μm thick, is shown in Fig. 30. Weak orange PL was obtained from the glass based films when reduced at temperatures just above the MP of the glass. Substantial blue-green PL and CL was not obtained until the sapphire based films were annealed at temperatures greater than 900°C in a carefully controlled reducing atmosphere. As can be seen from the XRD spectrum in Fig. 31, the film shows strong preferential orientation. From a SIMS analysis (Fig. 32) a film on Si was shown to be fairly uniform. The annealed films were also shown to exhibit cathodoluminescence.

3) (ZnMg)O:Zn Thin Films

Attempts were made to incorporate Mg in the ZnO lattice in order to shift the colour towards the blue as in the respective phosphor powders. With organometallic Zn and Mg precursors, no satisfactory common solvent system could be found. Mg(NO₃)₂ was therefore used along with zinc organometallic precursor. Deposition appeared satisfactory but no colour change in the PL was effected, even when high concentrations of Mg were used.

4) Zinc Gallate:Mn Thin Films

The precursor solution was a mixture of organometallic compounds of zinc, gallium and Mn^{II} in a molar ratio of 1:1:0.01 respectively in a mixed organic solvent. The sapphire substrates were held at temperatures of 430-470°C.

The as-deposited films were pale brown and not photoluminescent. Because of their opacity, an estimate of the thickness of the films could not be obtained from a simple UV/Vis spectrum (Fig. 33). However, the spectrum did demonstrate that the band edge had been shifted to 275nm

compared with 371nm for ZnO, indicating the probable formation of zinc gallate at the substrate surface before annealing.

Photoluminescence was induced in the films by annealing at 1000°C for short periods, mainly in reducing atmospheres. The PL was far more intense than that found in the ZnO:Zn films and of a colour typical of ZnGa₂O₄:Mn powder phosphor. The XRD spectrum of the film was also identical to that of the powder although the ratio of the peak intensities differed (Fig. 34).

The CL of these films did not match that of ZnO:Zn. It is probable that the optimum thickness has not been found. Indeed, the films were thicker than ZnO:Zn, up to 2.5µm, and a SIMS analysis indicated a large variation in thickness in a single film (Fig. 35).

5) CaTiO₃:Pr and SnO₂:Eu Films

Initially, attempts were made to produce red luminescent films of CaTiO₃:Pr. This was abandoned because of the incompatibility of the available precursors both in terms of mutual solubility and decomposition temperature. The simpler SnO₂:Eu was therefore investigated. The Sn precursors contained up to 1% Eu as the acetate, again in a mixed organic solvent. Deposition was carried out at 430-470°C on sapphire substrates with subsequent annealing at temperatures up to 1500°C. The films were white and opaque with a strong orange PL.

Photograph 1 shows the PL emission from ZnGa₂O₄:Mn, SnO₂:Eu and ZnO:Zn films.

VI) CONDUCTING ITO POWDER

For use in low voltage devices, cathode ray phosphors must either be intrinsically conducting, as in ZnO:Zn, or may be made so by forming a conducting layer on the particles. Alternatively, the phosphors may be mixed with a conducting powder. We investigated both methods. Indium oxide powder was doped with tin and indium then fired and milled. The pale yellow powder exhibited a bulk conductivity several orders of magnitude higher than ZnO:Zn phosphor.

A graph showing the change in resistance as a function of varying the Sn concentration in ITO powder is shown in Fig. 36. As can be seen, there is a minimum resistance at concentrations of ~6% in the ITO powders. Firing in a reducing atmosphere leads to a doubling of conductivity of the ITO powder.

Early attempts to make layers of InBO₃:Tb phosphor with ITO powder for use in the CL system led to indifferent results.

The body colour became darker. The change in the threshold voltage, V_{th} , is shown in the table below, where V_{th} refers to the point at which visible luminescence appears.

% In_2O_3	V_{th}
0	>1500
5	1500
10	1000
20	600

VII) CONDUCTING SURFACE COATINGS ON POWDER PHOSPHOR

As an alternative to mixing an insulating phosphor with a conducting powder, a conducting layer can be formed in situ on the phosphor powder surface. Slurries of the phosphor with solutions of indium and tin complexes were dried then fired at moderate temperatures.

Various phosphors were used and the effect on $InBO_3:Tb$ is typical. The surface did become conductive but the PL intensity was reduced possible because of the absorption of UV by the ITO film.

The optimum concentration of Sn in the In_2O_3 was around 4% as shown in the table below. $CaTiO_3:Pr$, which is not completely insulating, was used.

% Sn in In_2O_3	R (k ohms)
0	180
0.2	130
0.4	21
0.9	15
1.7	6
4.2	2
8.1	12
11.2	50
15.0	25
Uncoated control	12000

VIII) INTERACTION WITH OTHER US ORGANISATIONS

We have attended many informal and formal meetings with most companies interested in FED manufacture. Phosphors have been supplied to many of these companies and on-site help has been provided to six of these. In most cases, our phosphors have been well received and said to deposit acceptably and behave under low voltage electron excitation. However, we have not been supplied with any quantitative data on the performance of the phosphors in return.

IX) MEETINGS, VISITS AND PUBLICATIONS

Apart from the various US FED manufacturers, many visits have been paid to the ETDL Labs, Fort Monmouth. This included a two-week visit by S S Chadha to teach electrophoresis (EP) to the personnel at Fort Monmouth and to learn the usage of the low voltage rig. Many phosphors were evaluated after EP deposition of these materials. Due to the fact that the phosphor layers were not baked, lifetime maintenance characteristics were poor. Some bakeout was attempted which improved the stability somewhat. A return visit has been paid by Dr D C Morton. This is resulting in an extensive exchange of information involving the synthesis and assessment of phosphors.

A outline of the work carried out on this programme was presented at the Sixth International Vacuum Micro-electronics Conference in July 1993 and at SID in June 1994, (see Appendix C).

X) EDUCATIONAL

We have, as yet, not been asked to take part in the US educational programme of the Phosphor Center of Excellence. We have, however, presented two short courses at SID. These were:

- 1) Display Phosphors - May 1993
- 2) Emissive Displays - June 1994

Copies of the notes of these courses are available on request. A further seminar will be presented in October 1994 at the IRDC in Monterey and a half-day course on phosphors will be given at the SPIE meeting in San Jose in February 1995.

XI) CONCLUSIONS

The objectives of the programme were the synthesis of low voltage RGB phosphor and the supply of these phosphors to US industry. These objectives have, to a large extent, been achieved.

At the start of the project only ZnO was available, which emits with broad band blue-green emission.

We have in two years developed:

- a) a much improved and brighter ZnO phosphor (~9000 ftL at 1500V 100 μ A),
- b) a saturated red-green based on zinc gallate (~3000 ftL at 1500V 100 μ A),
- c) a good red based on calcium titanate (~1000 ftL at 1500V 100 μ A),
- d) a blue (ZnMg)O:Zn phosphor (~3000 ftL at 1500V 100 μ A).

Other powder phosphors investigated were SnO₂:Eu and Zn₂SnO₄Eu. The PL of SnO₂:Eu appears orange-red but the emission from Zn₂SnO₄Eu was very weak. Further studies of these systems are still required.

In addition, techniques were developed permitting fabrication of very small particle size (<1000) conducting powders, such as In₂O₃, ITO and SnO₂, for phosphors where sufficient conductivity was not achieved.

Experiments engineered to provide surface conduction to normally insulating phosphor have also been successful and conductive InBO₃:Tb phosphor has been made.

Thin film phosphors were synthesised for the first time so that the possibility of very high resolution FEDs was established. Photoluminescent thin films of ZnO:Zn, SnO₂:Eu and ZnGa₂O₄:Mn have been made by a novel aerosol spray pyrolysis method. Considerable further development is required for making good low voltage screens, but promising initial results have been obtained with the above compounds.

Stability measurements under low voltage CRT excitation were made on ZnO:Zn, ZnGa₂O₄:Mn, (ZnMg)O:Zn and InBO₃:Tb phosphors. The stability of these phosphors varied. At this early stage it would appear that ZnGa₂O₄:Mn shows most promise. It should be noted that the zinc oxide made at the University appeared more stable than those commercially available. Clearly, far more assessment is still required, more especially in completed devices.

We have supplied phosphors and thin film samples to seven US firms. We are now supplying 100 gram samples for evaluation. (N.B. 100 grams could cover 100 sq ft of display or 14,400 sq in samples).

XII) FUTURE WORK

Although good, three-colour displays can be made from the phosphors we have produced so far, further work is required to prepare phosphors with saturated emission. The blue emission from the (ZnMg)O:Zn phosphor still requires filtration and the emission from the CaTiO₃:Pr requires a slight shift to the red. The emission from the ZnGa₂O₄:Mn is ideal from the point of view of colour saturation but clearly, as always, improved efficiency is still called for. Although considerable progress has been made in the preparation of fine particle phosphors, we believe the new techniques that are being investigated will still yield far better results.

It has become quite clear that various industrial firms are working with FEDs operating over a range of voltages. Thus, phosphors operating below 500V, or even below 50V, are required, as well as those operating at about 1000V and above 2000V. A separate optimisation for each voltage range will be required.

The effort on the preparation of phosphor thin films has been limited and much work still has to be done in the optimisation of thin films. New methods of synthesis still have to be evaluated.

As a result of the studies that have just been completed we have definite ideas on the investigation of new phosphor systems for low voltage application, more particularly for blue emitting phosphors.

We hope that in the coming years we will be able to collaborate far more strongly with other US firms, as well as the Phosphor Center of Excellence. It is imperative that an assembly system for the assessment of small, sealed devices be set up so that maintenance characteristics under realistic conditions can be obtained.

We hope that, in the future, we can take part in the educational/research programmes of US educational establishments.

We will continue to supply ETDL and other US organisations with phosphors as and when requested.

XIII) ACKNOWLEDGMENT

We would like to put on record our thanks for the guidance given on this project by Dr D Slobodin, Mr M R Miller and Dr D C Morton.

APPENDIX A

Monochromator

A fully automated Bentham Spectroradiometer system has been acquired. Data storage and manipulation is via a 486/33MHz IBM clone with output to a HP laserjet. The basic system is shown in Figs. 37 and 37a.

The M300A is a high quality, general purpose grating monochromator (1200g/mm) with a 300mm focal length. A built-in stepping motor and sine drive allows wavelength scanning to be completely controlled from a remote stepping motor drive unit (SMD3B). The SMD3B in turn is controlled by a PC via its IEEE 488 bus interface. Light collection is via a close focus telescope accessory and fibre optic probe. The operation of the whole system is computer controlled permitting the measurement of spectral output, CIE co-ordinates and colour temperature, amongst others.

APPENDIX B

Low Voltage Cathodoluminescent System Measurements

Based on a Kimball Physics Gun (EFG-7), the demountable CL rig was made fully operational. This is shown in Figs. 38 and 39. As noted in the previous report, this gun is capable of 50-5000eV excitation. Prior to any measurements, the system is baked and the phosphor layer given a low electron density burn-in at 1500eV for 30 mins. Typically, the threshold voltage, V_{th} , and the L-V and L-I characteristics are measured first. For L-V characteristics, the emission current is fixed at 50 μ A for a 1.41mm radius spot, and for L-I, the voltage is fixed at 1500eV. The luminance readings are acquired using a Gamma Scientific Telephotometer, IC2000. Accelerated life testing is carried out at 1500eV and 50 μ A for two hours.

Most phosphors prepared in-house and the commercial controls have been assessed.

XRD spectrum of: Fig. 1) Zinc oxide, raw material;
Fig. 2) Zinc oxide phosphor;
Fig. 3) Zinc oxide phosphor with
added sulphur.

Fig. 1



Fig. 2

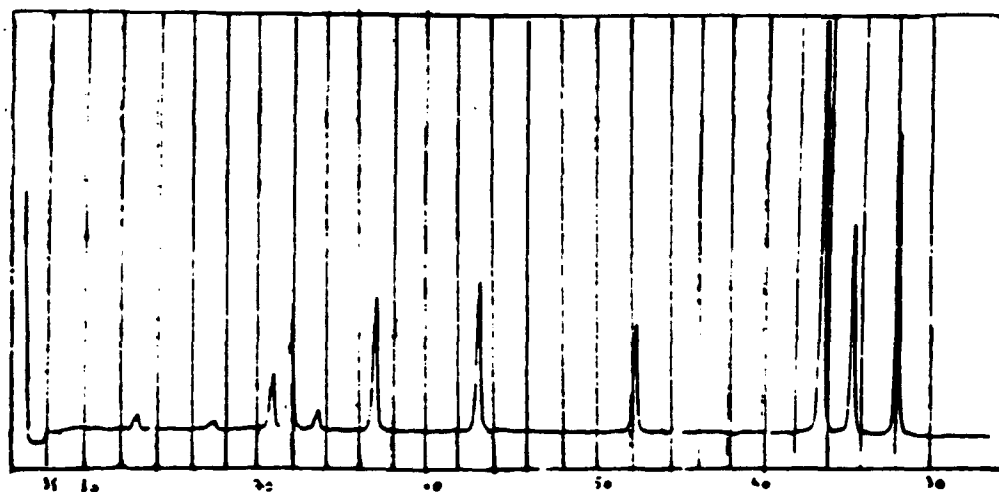


Fig. 3

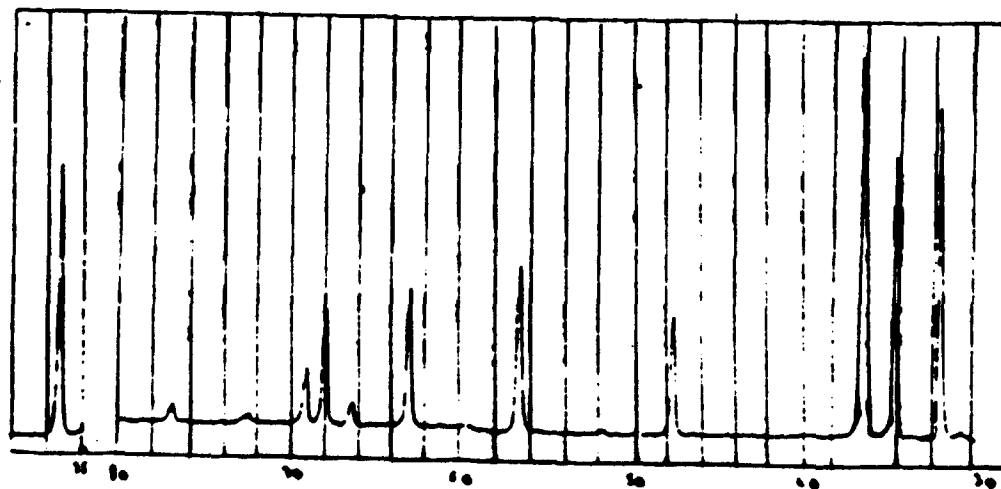


Fig. 4 SEM micrograph of commercial ZnO:Zn phosphor

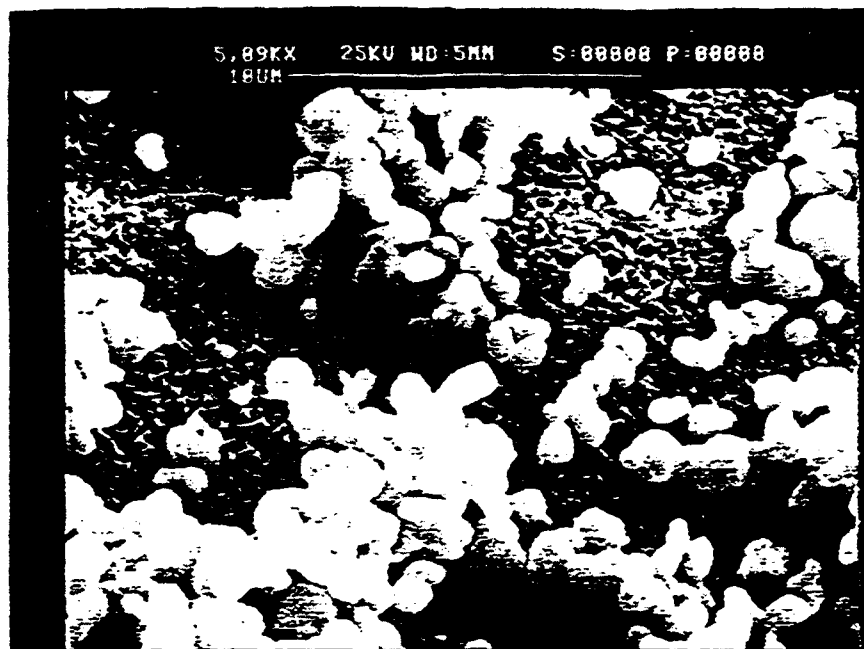


Fig. 5 SEM micrograph of UG ZnO:Zn phosphor

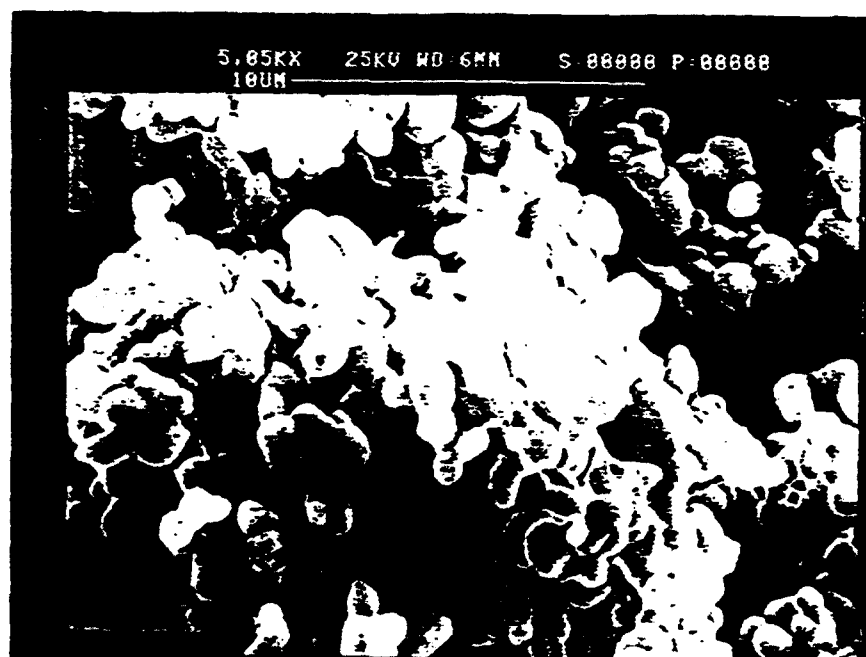


Fig. 6 Dissociation plot for Zn-O

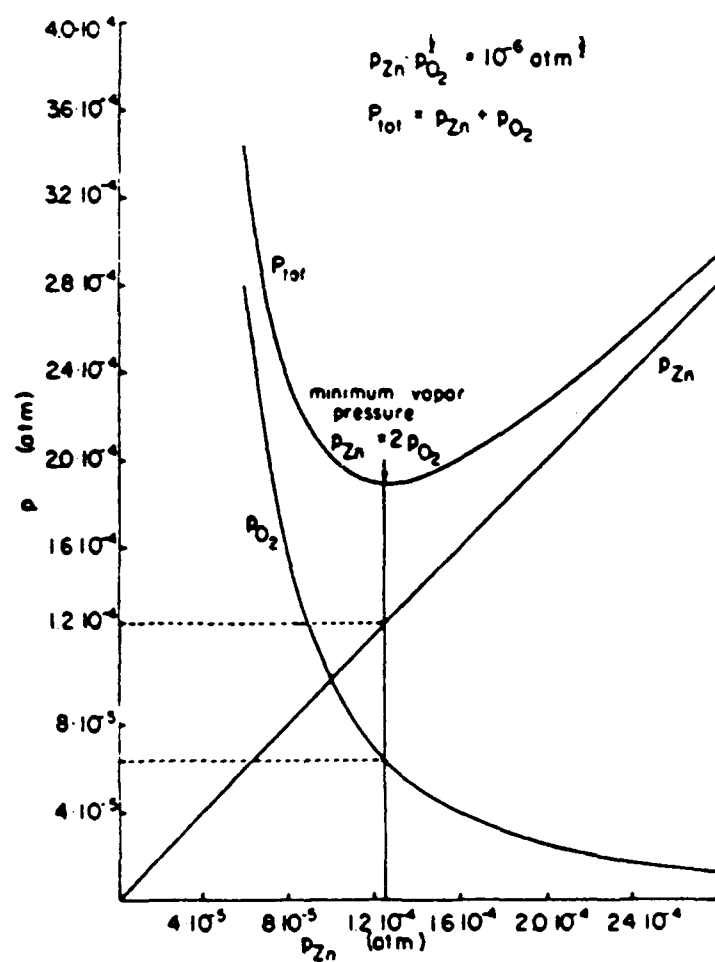
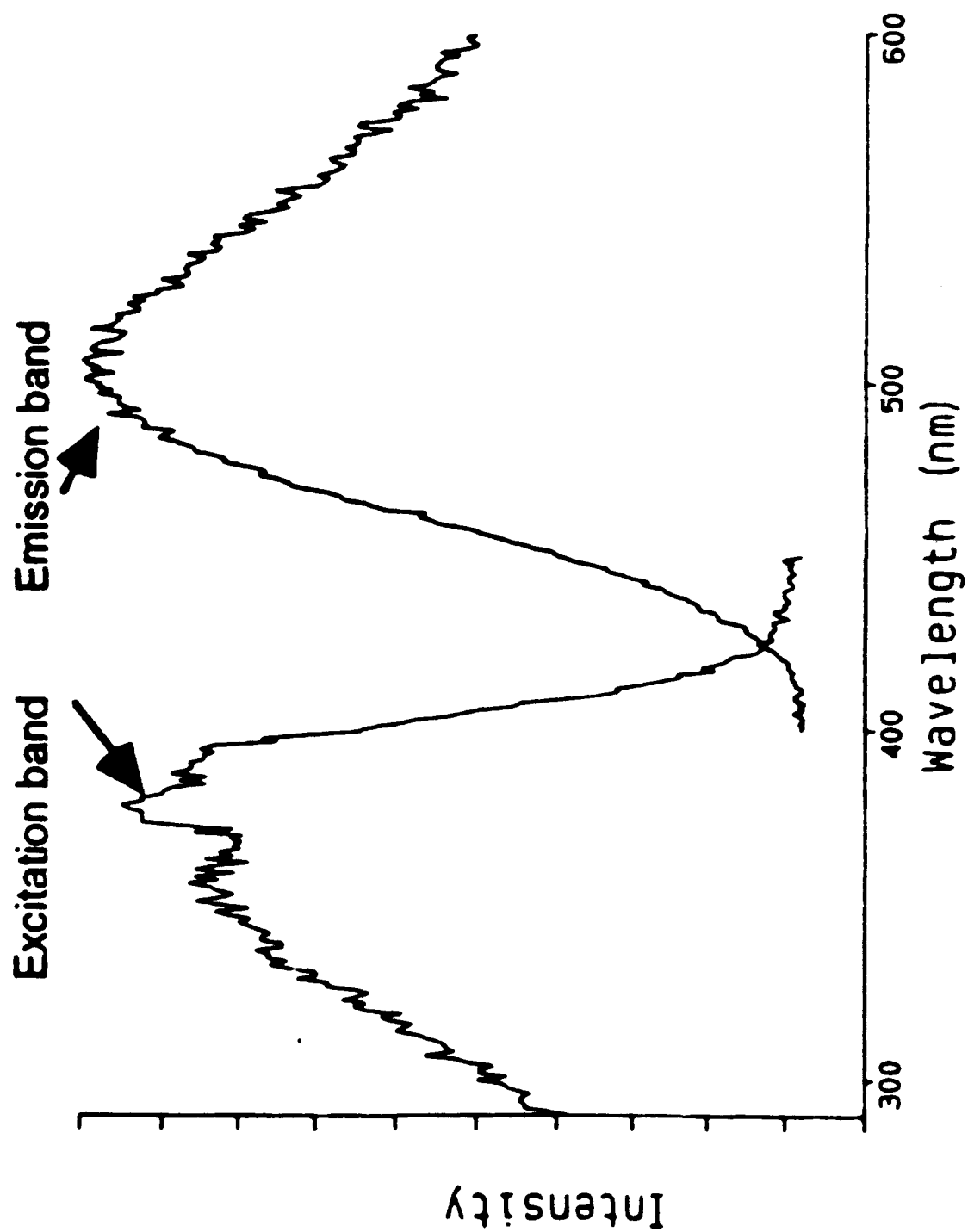


Fig. 7 Excitation and emission spectra of ZnO:Zn



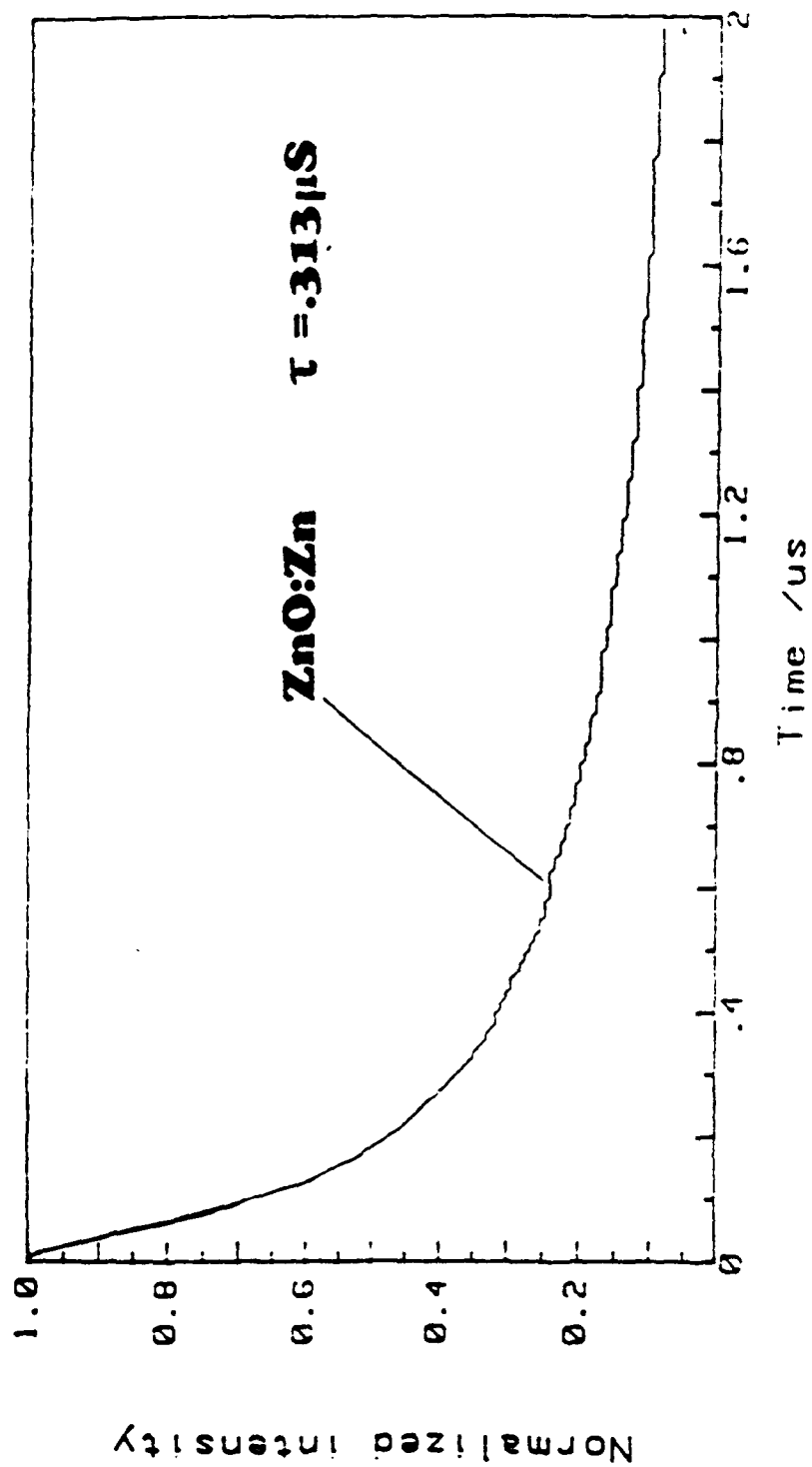
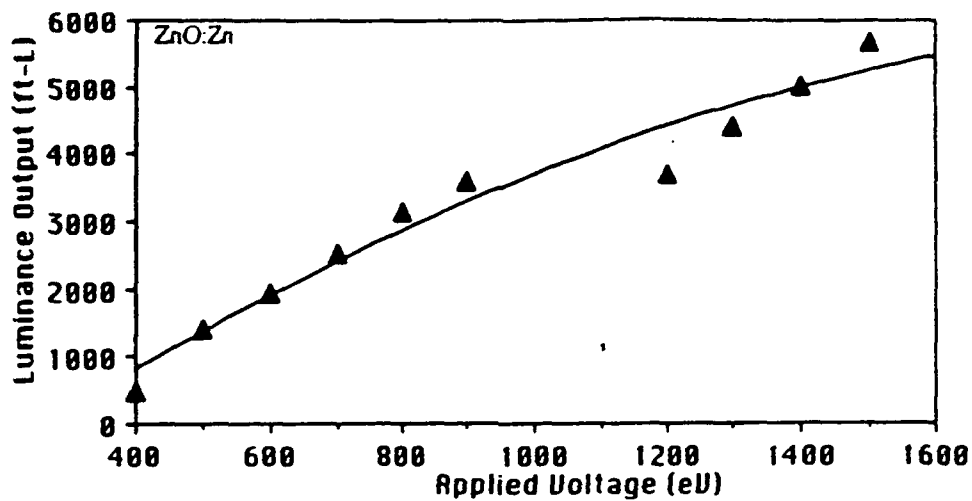
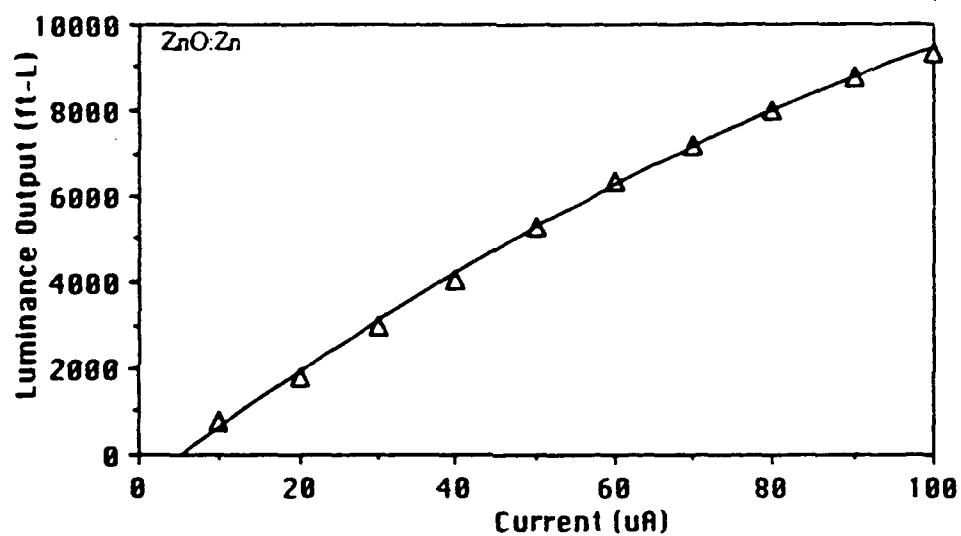


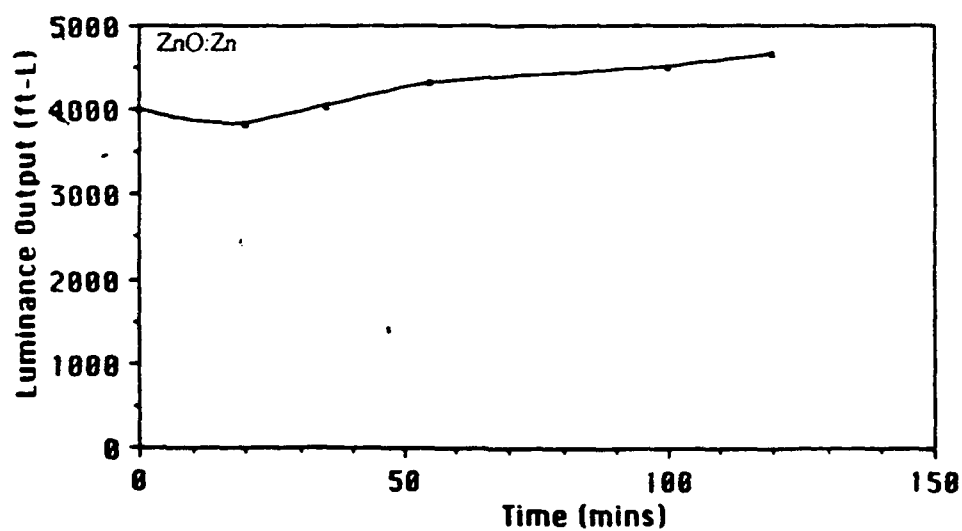
Fig. 8 PL decay profile of ZnO:Zn



a)



b)



c)

Fig. 9 a) L/V b) L/I c) L/t
curves for ZnO:Zn

Emission spectra of various low voltage phosphors

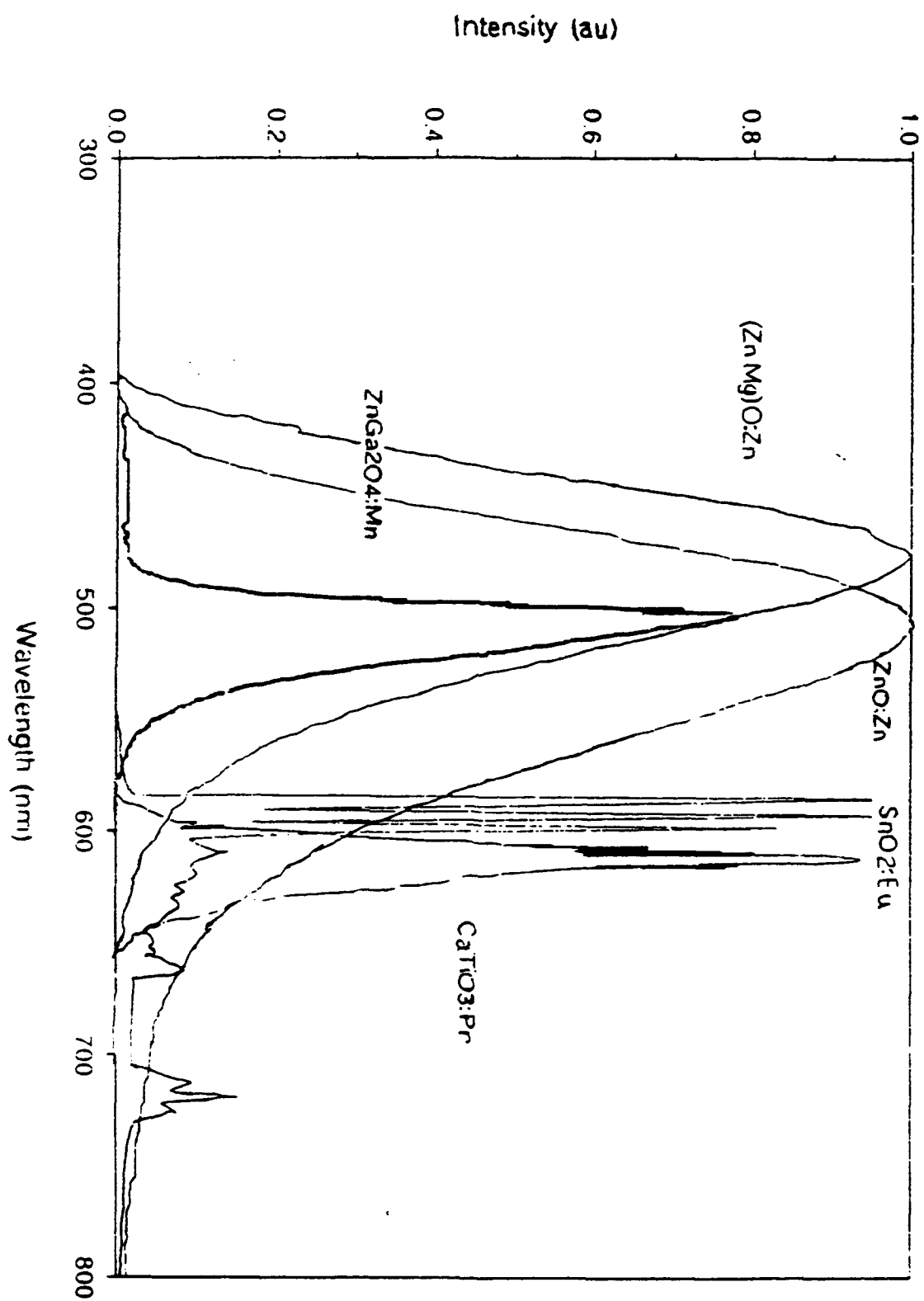
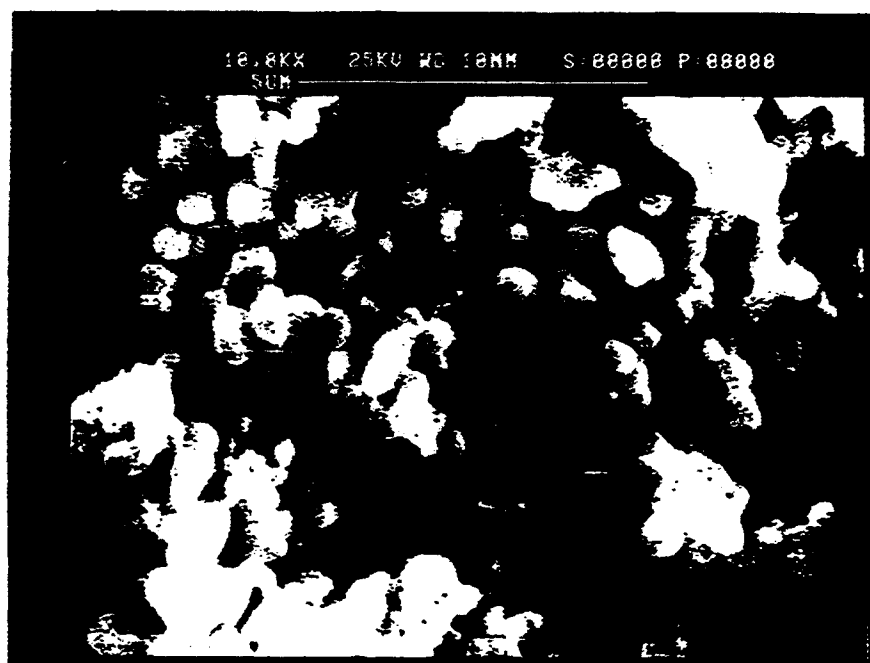
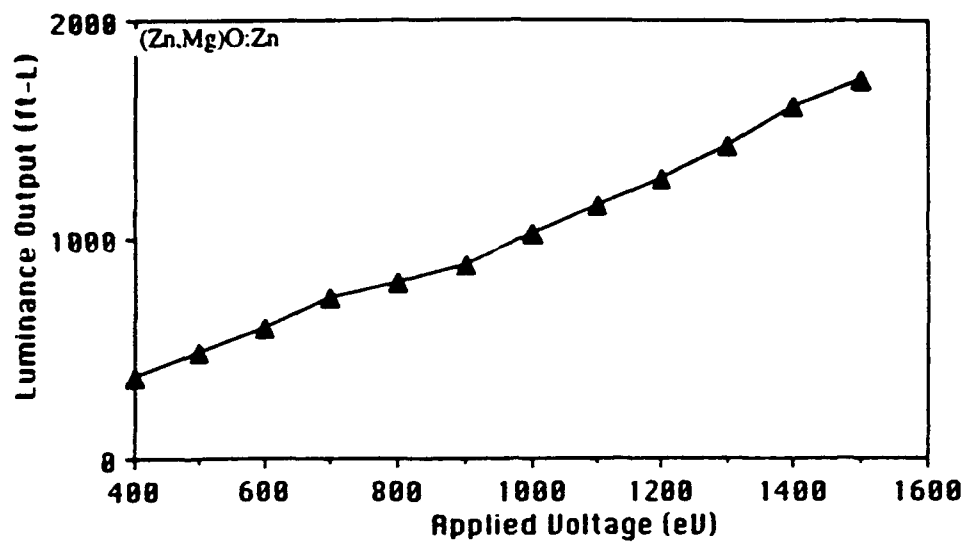


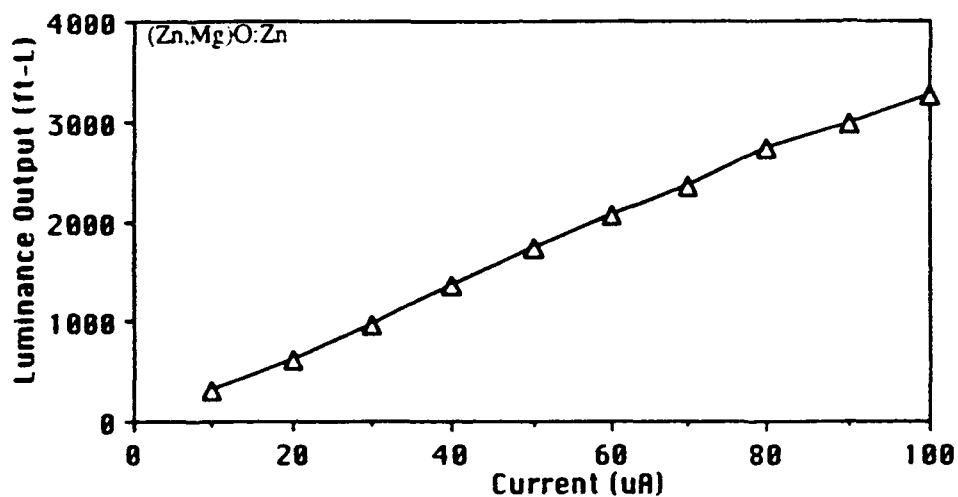
Fig. 10

Fig. 11 SEM micrograph of blue emitting (ZnMg)O:Zn phosphor

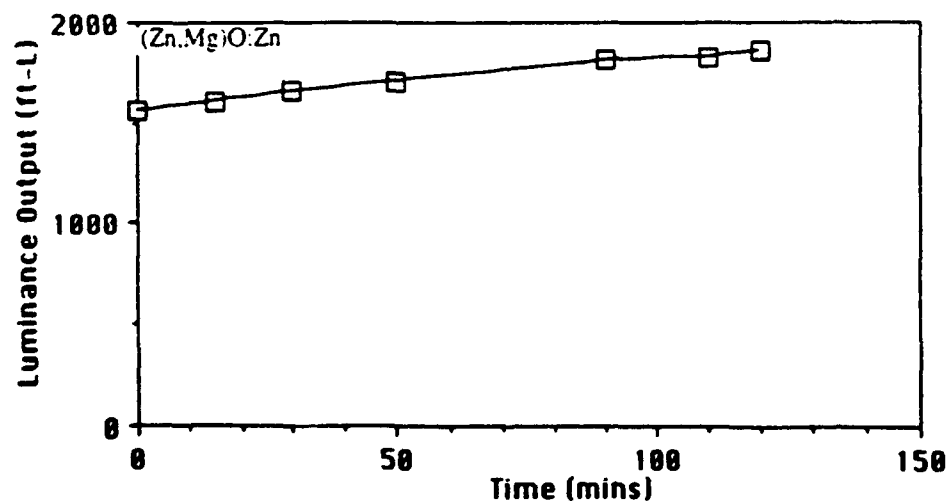




a)

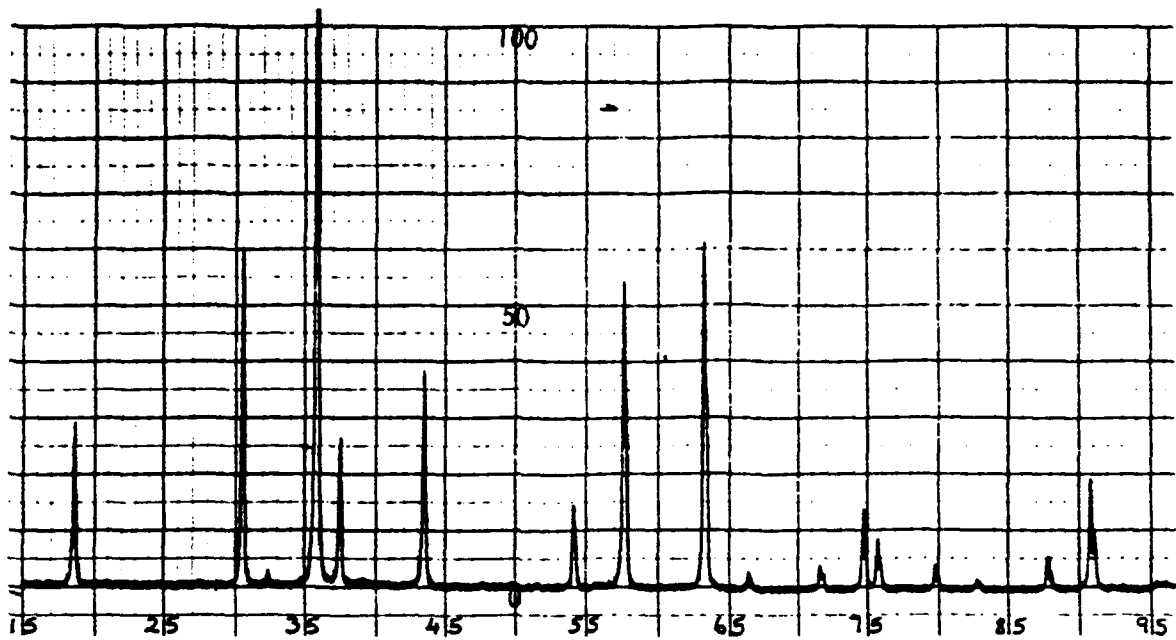


b)

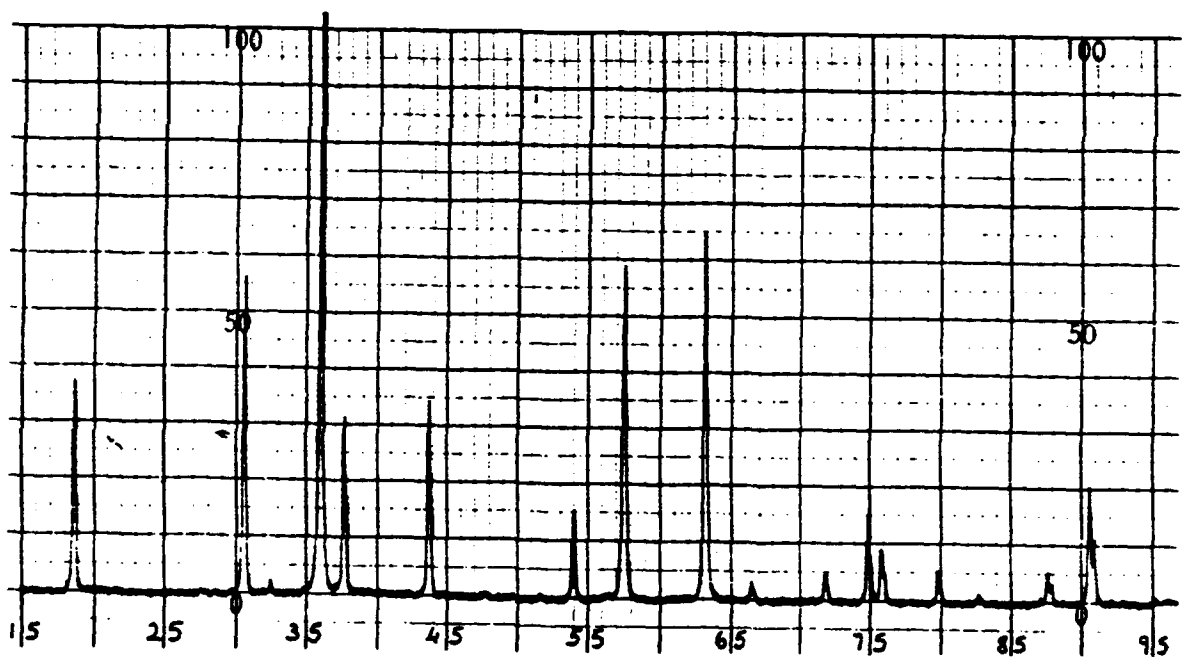


c)

Fig. 12 a) L/V b) L/I c) L/t
curves for (Zn,Mg)O:Zn



(a)



(b)

XRD of gallate phosphor showing Fig. 13) long persistence (a) and Fig. 14) short persistence (b)

Fig. 15 SEM micrograph of $\text{ZnGa}_2\text{O}_4\text{:Mn}$

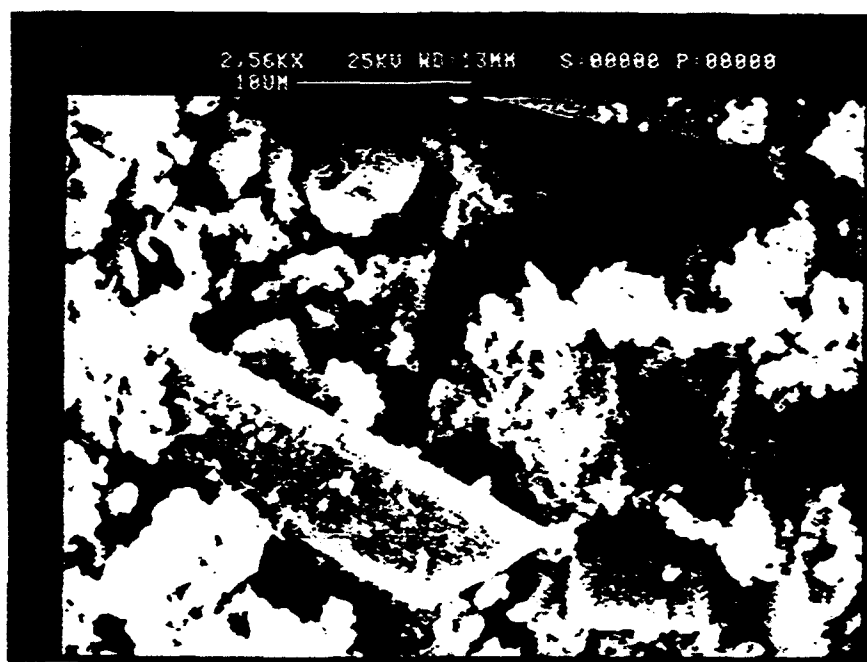
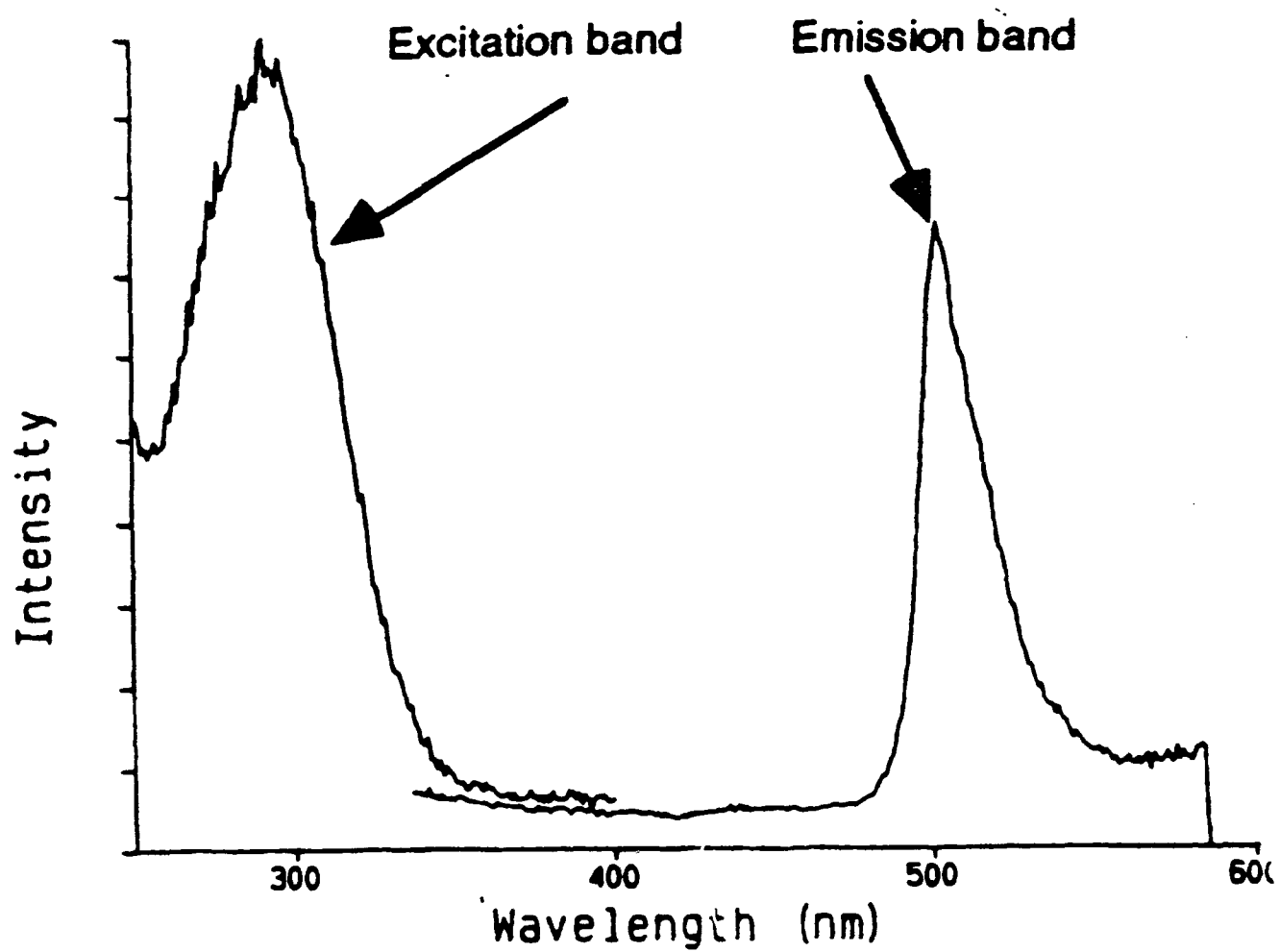


Fig. 16 Excitation/emission of $\text{ZnGa}_2\text{O}_4\text{:Mn}$



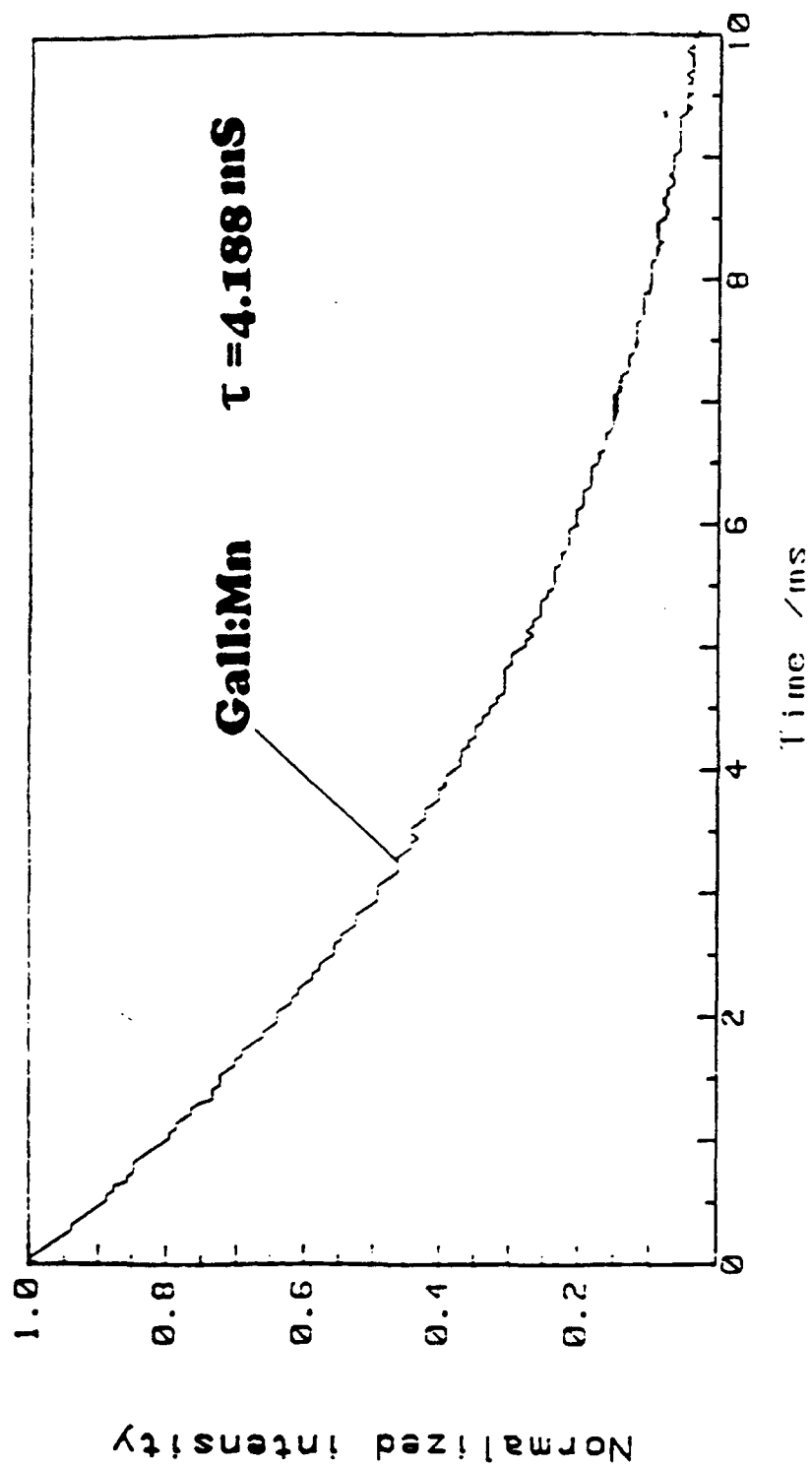
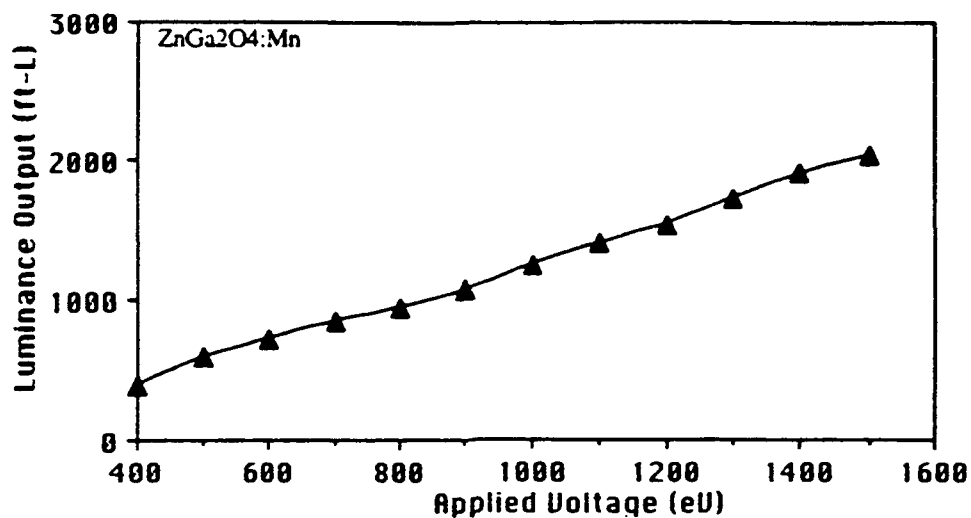
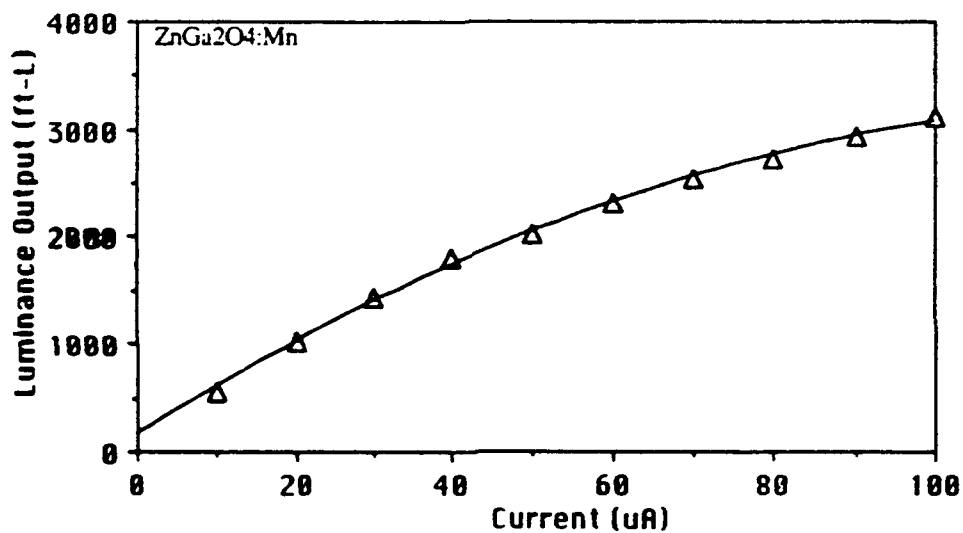


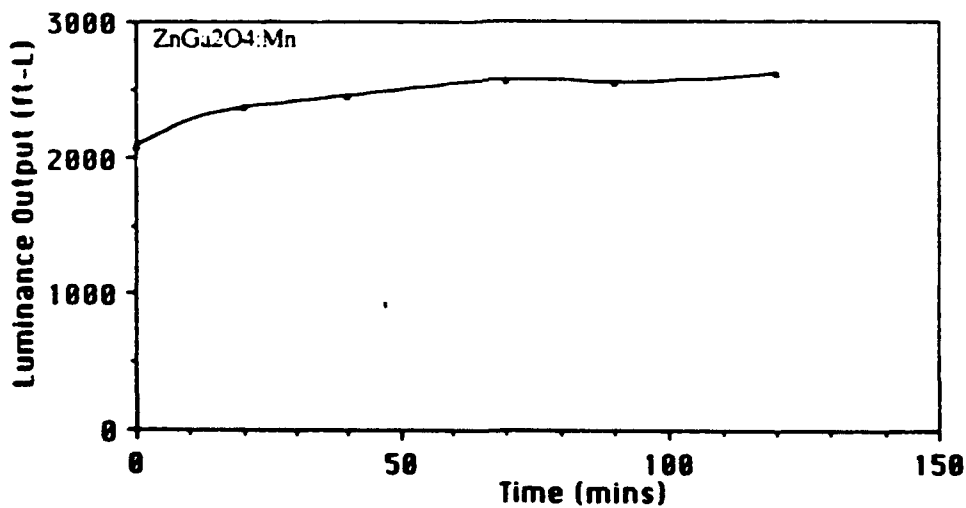
Fig. 17 PL decay profile of Gall:Mn



a)



b)



c)

Fig. 18 a) L/V b) L/I c) L/t
curves for ZnGa₂O₄:Mn

Fig. 19 XRD plot of titanate phosphor

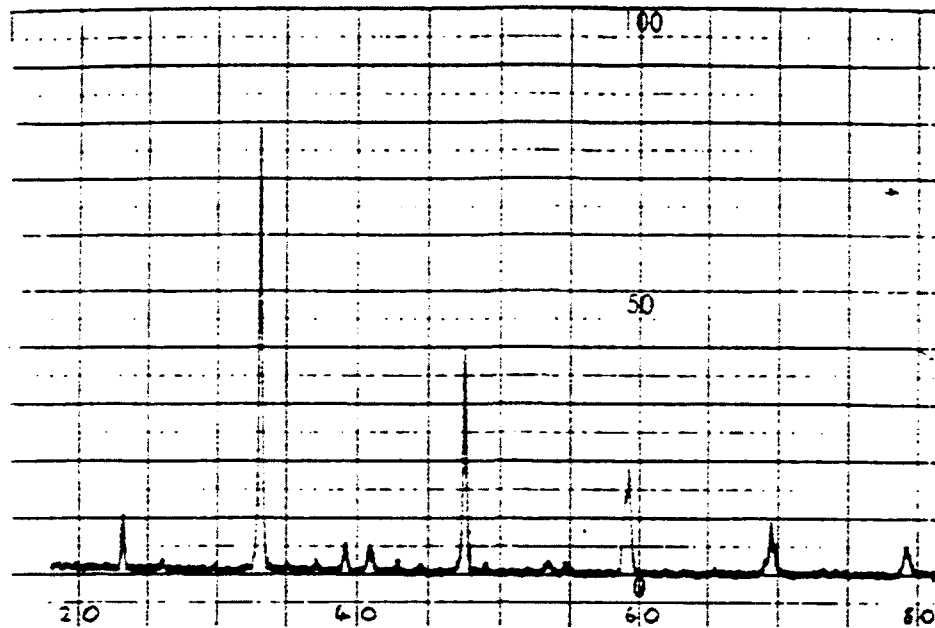


Fig. 20 SEM micrograph of titanate phosphor

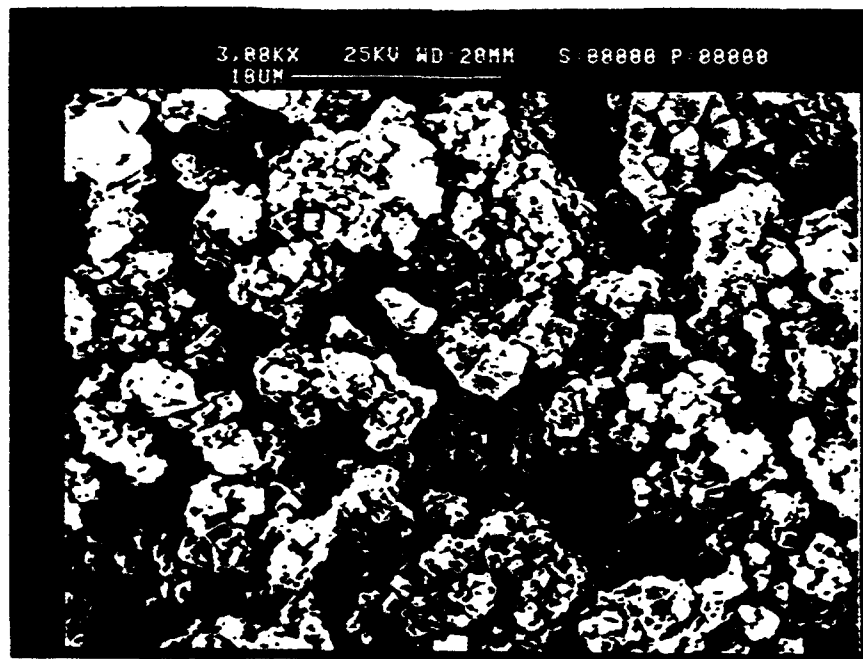
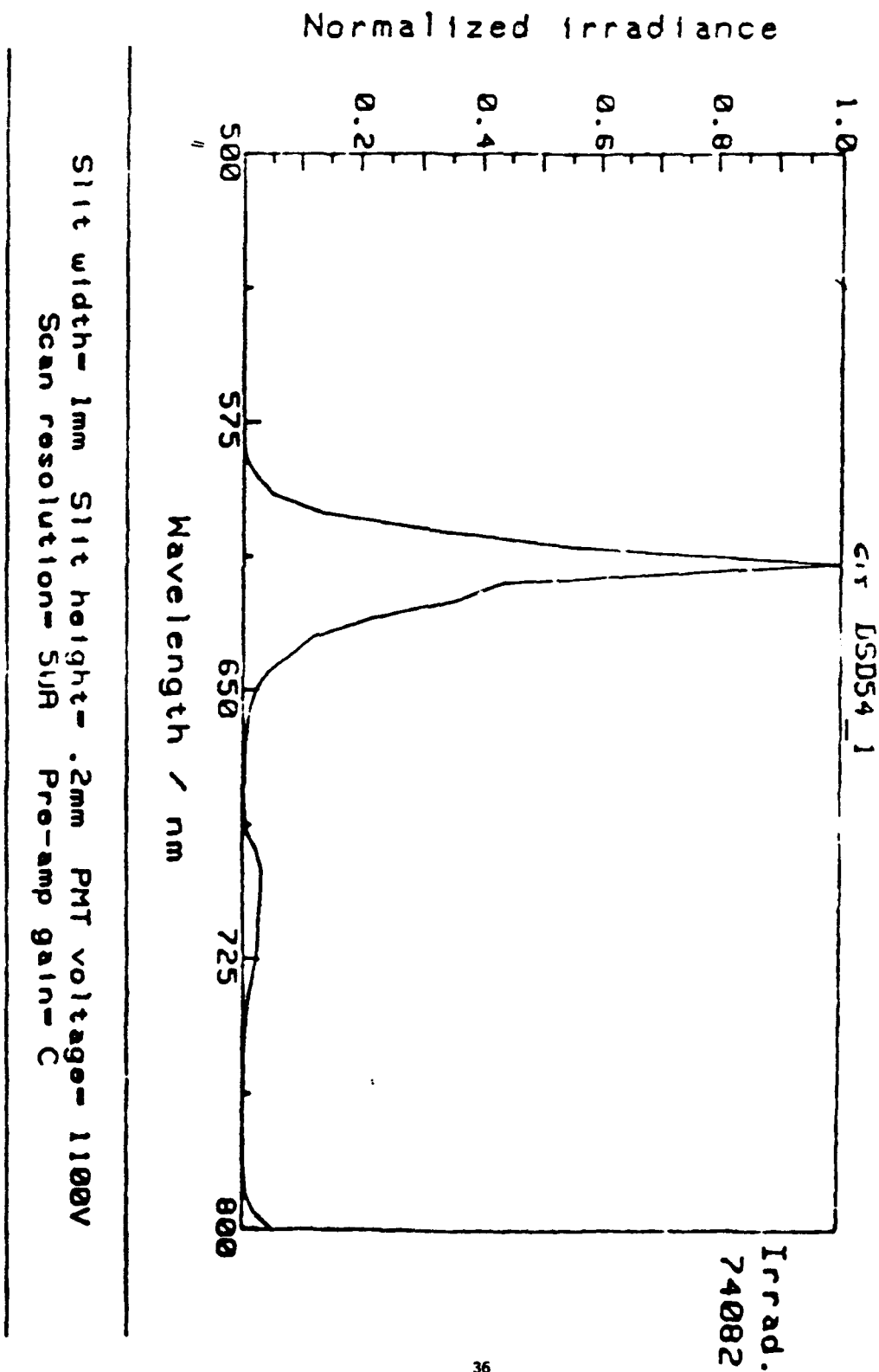
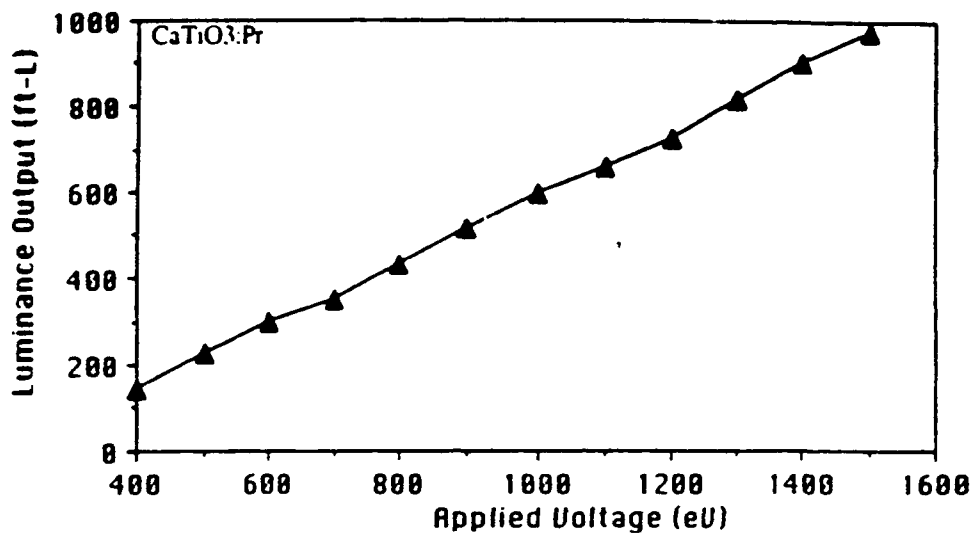
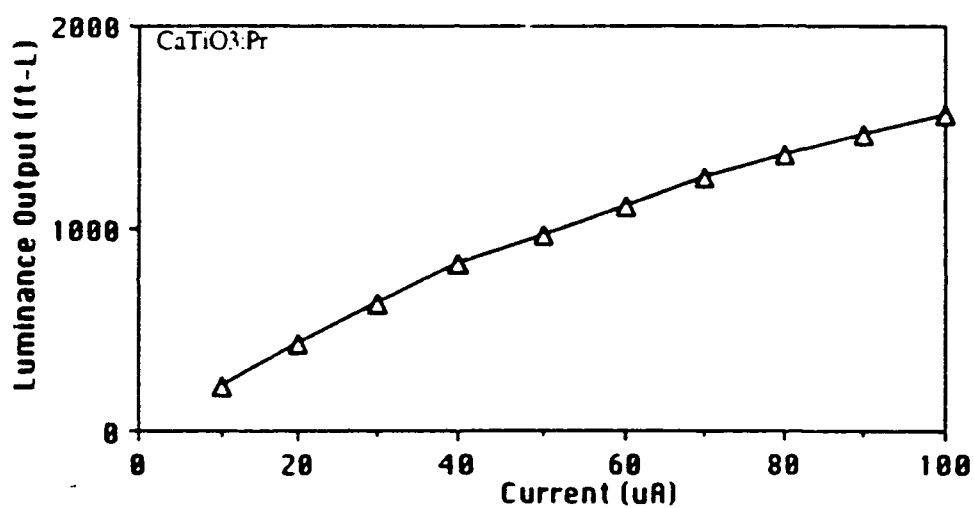


Fig. 21 Emission spectra of calcium titanate:Pr phosphor under laser excitation

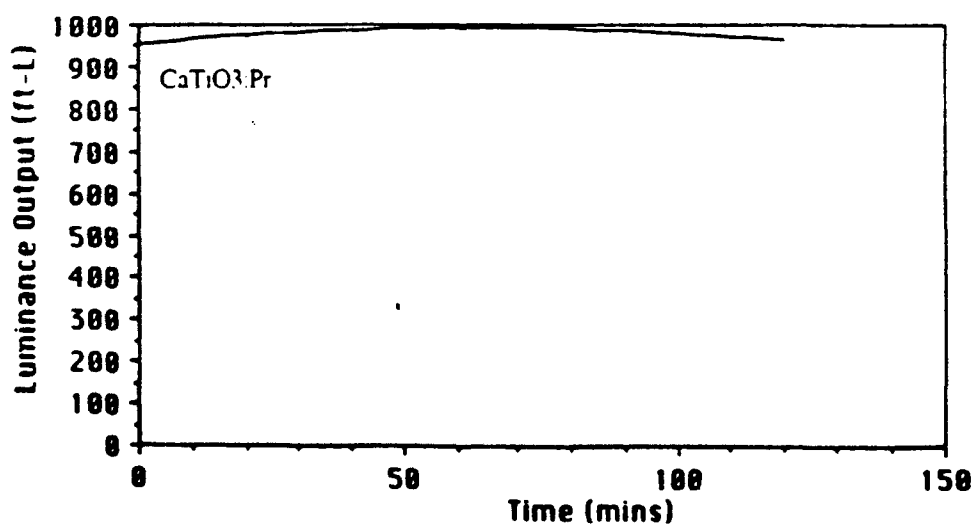




a)



b)



c)

Fig. 22 a) L/V b) L/I c) L/t
curves for $\text{CaTiO}_3:\text{Pr}$

Fig. 23 XRD of $\text{SnO}_2\text{:Eu}$

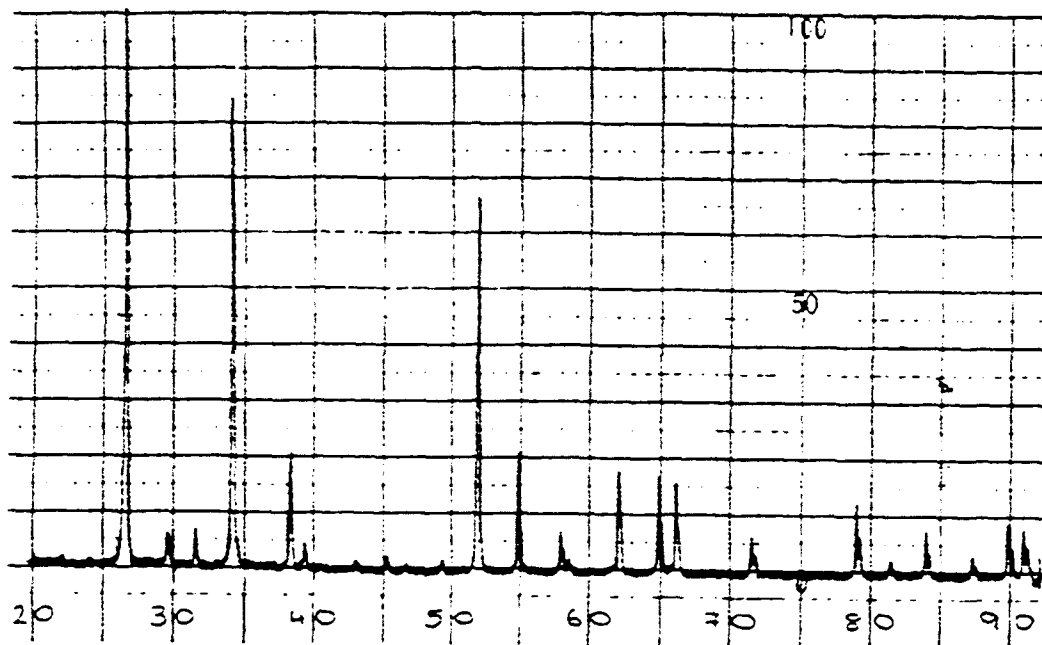


Fig. 24 SEM micrograph of $\text{SnO}_2\text{:Mn}$

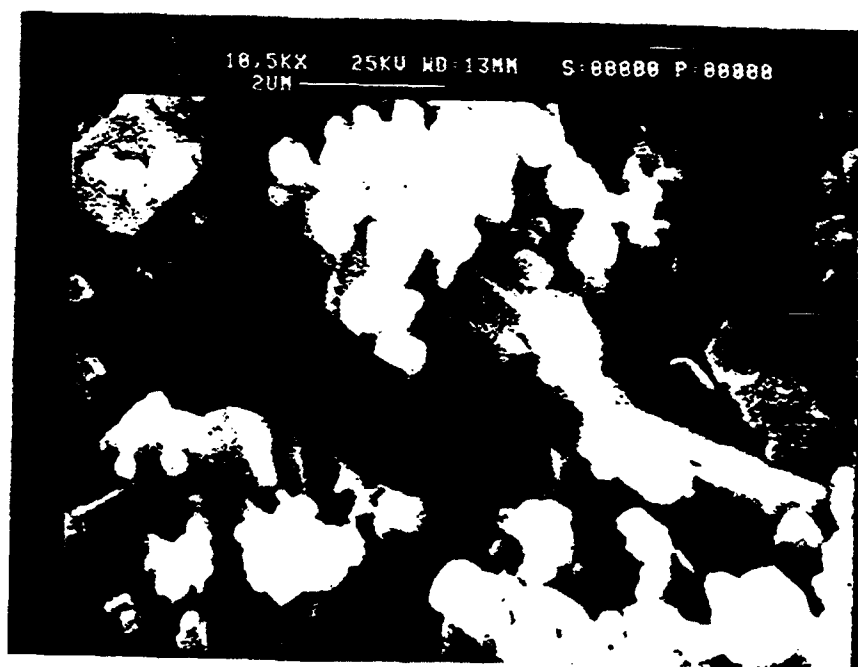


Fig. 25 a) L/V b) L/I c) L/t
curves for $\text{SnO}_2:\text{Eu}$

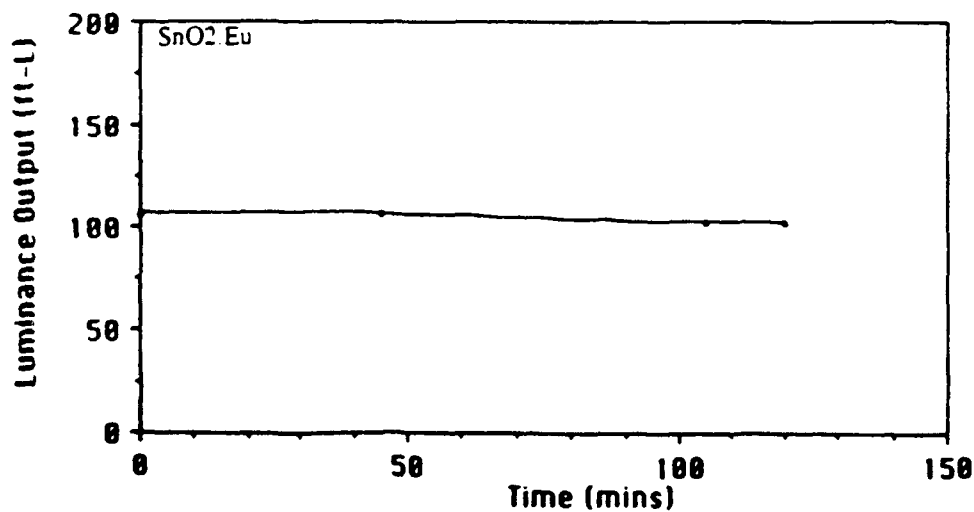
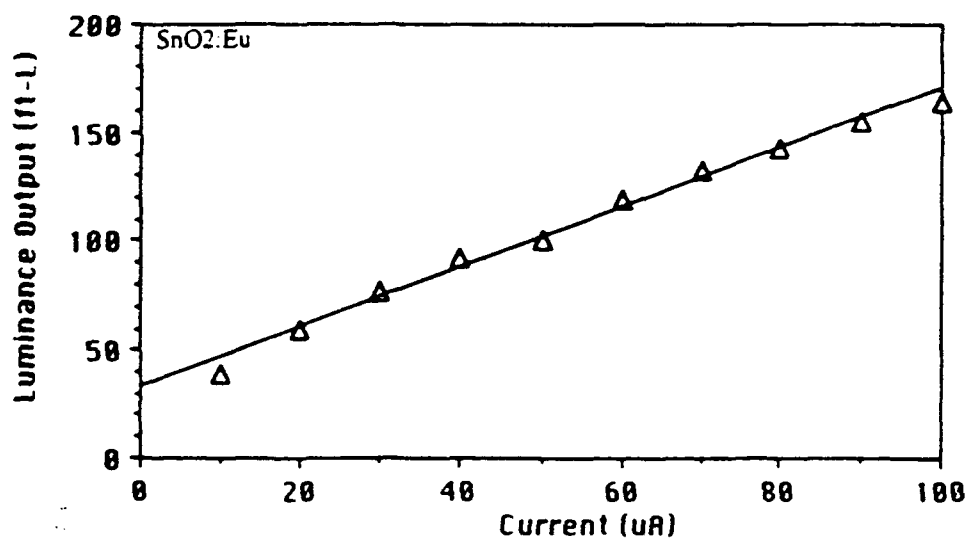
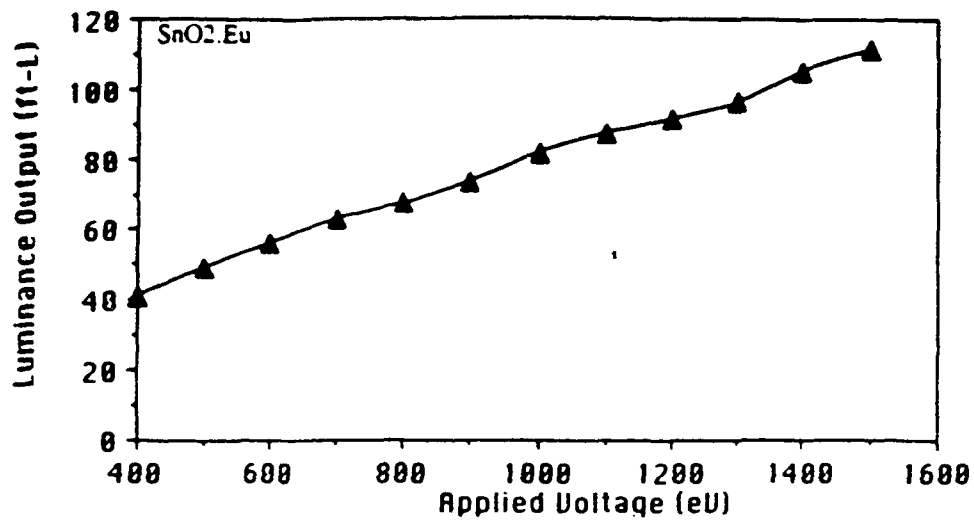


Fig. 26 SEM micrograph of Zn_2SnO_4



Fig. 27 XRD of Zn_2SnO_4

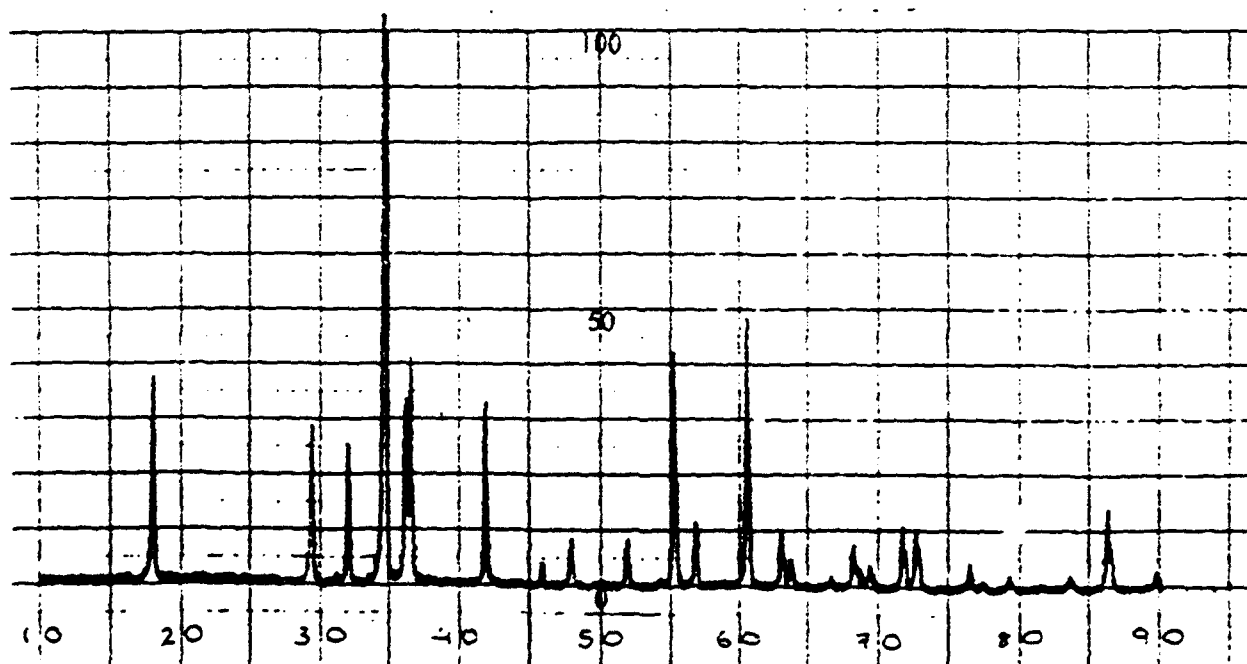


Fig. 28 Simplified sketch of apparatus used for ASP

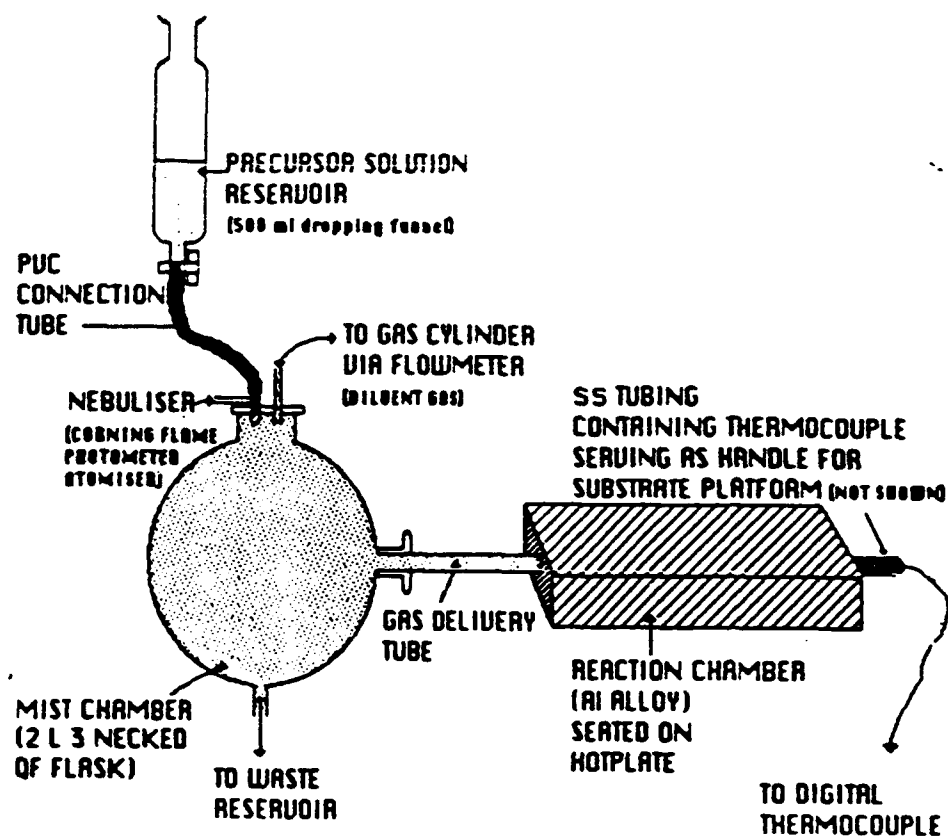


Fig. 29 UV/Vis spectrum of a zinc oxide film on sapphire (used for determining the thickness of the zinc oxide thin films)

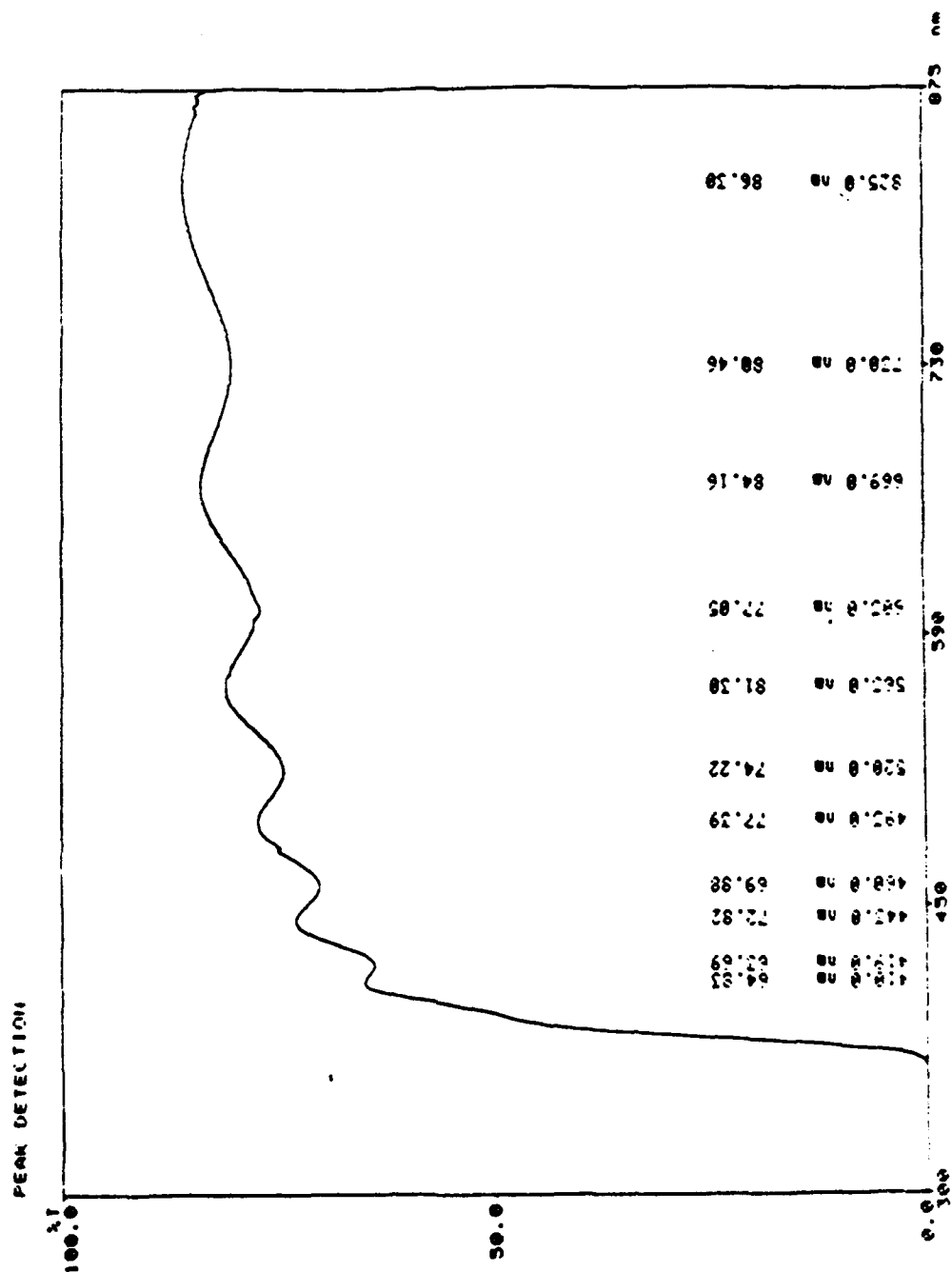


Fig. 30 SEM micrograph of unannealed ZnO on glass

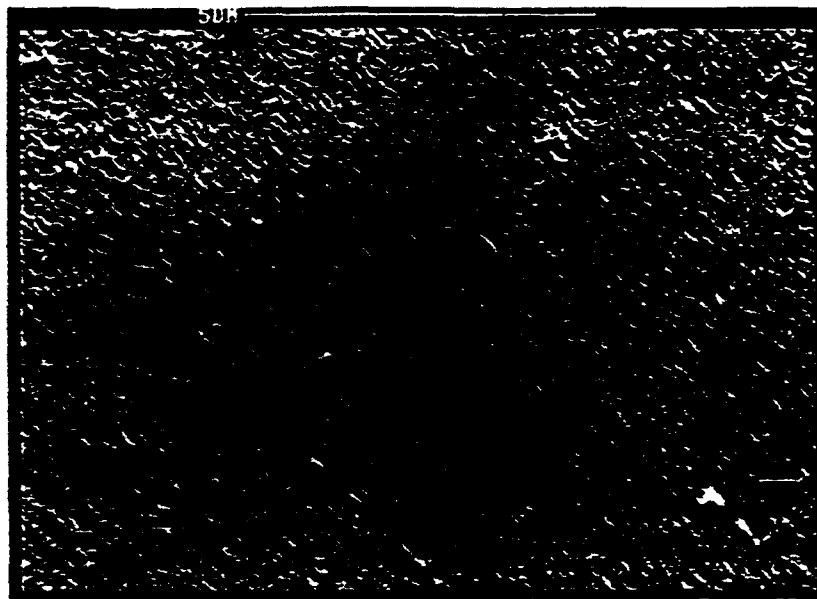


Fig. 31 XRD spectrum of annealed ZnO:Zn film on sapphire

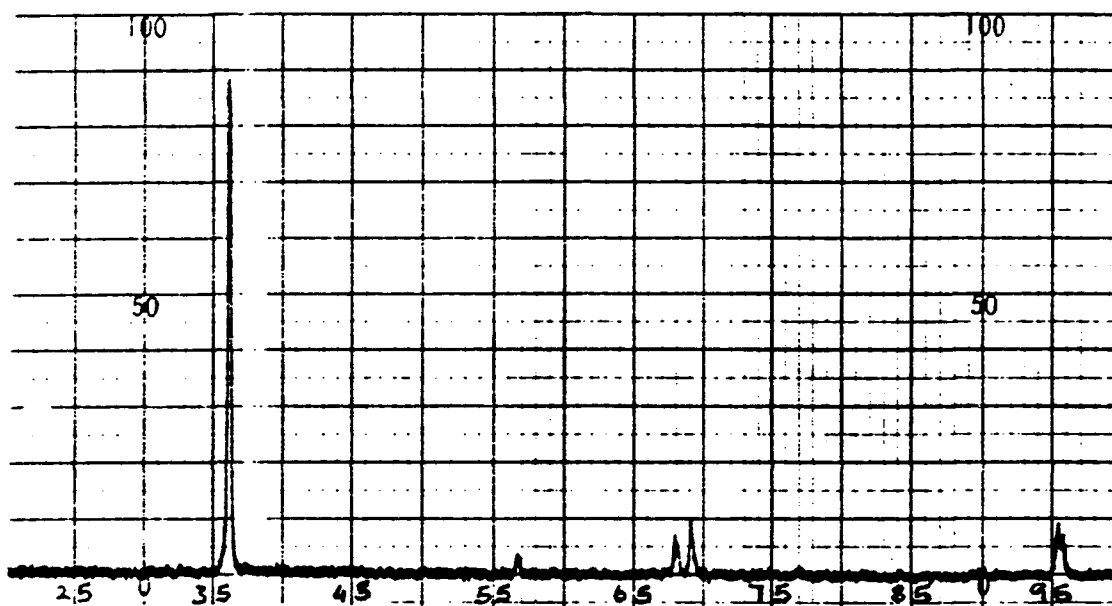


Fig. 32 SIMS analysis of ZnO:Zn thin film on silicon

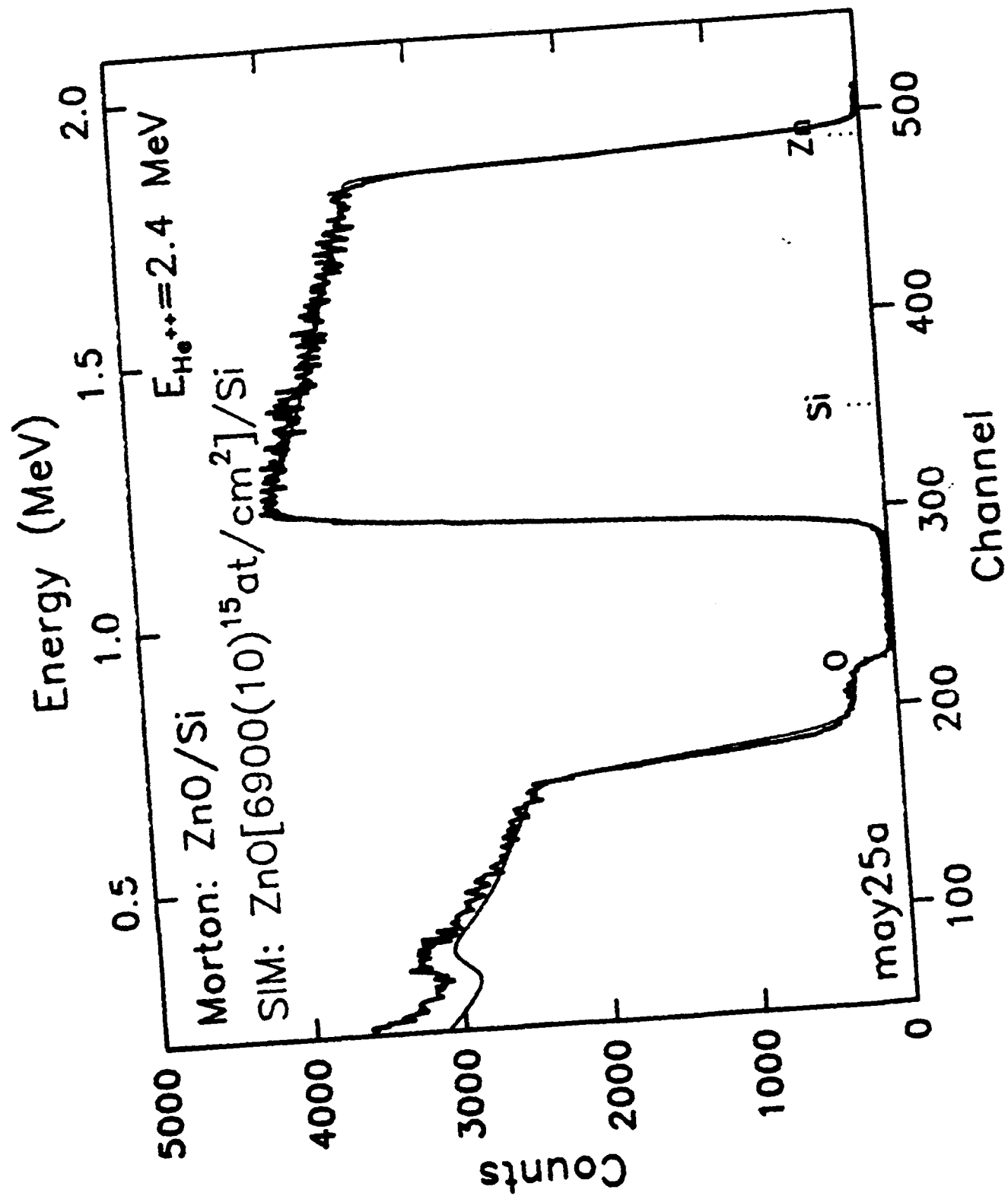


Fig. 33 UV/VIS spectrum of zinc gallate thin film

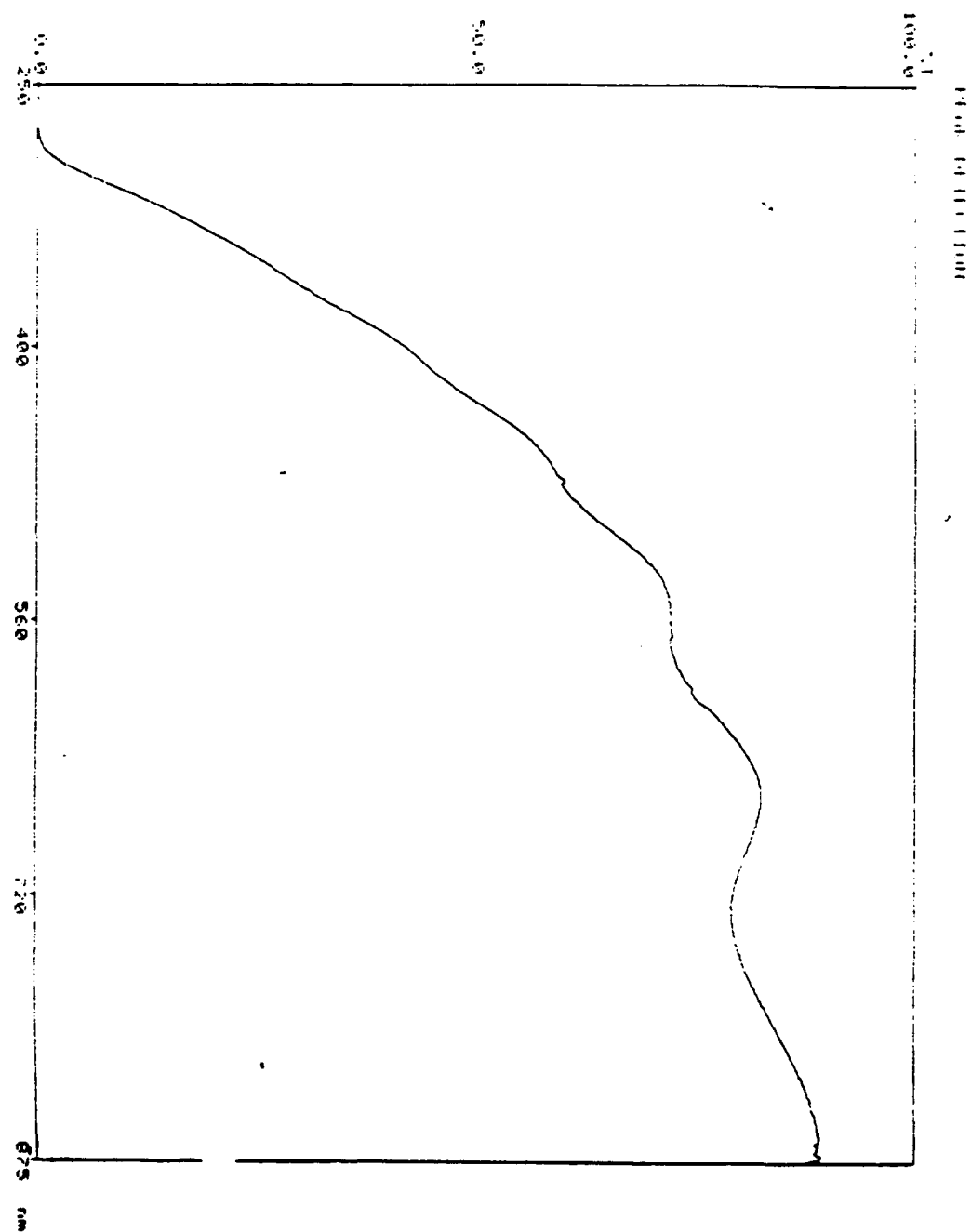


Fig. 34 XRD of $\text{ZnGa}_2\text{O}_4\text{:Mn}$ thin film

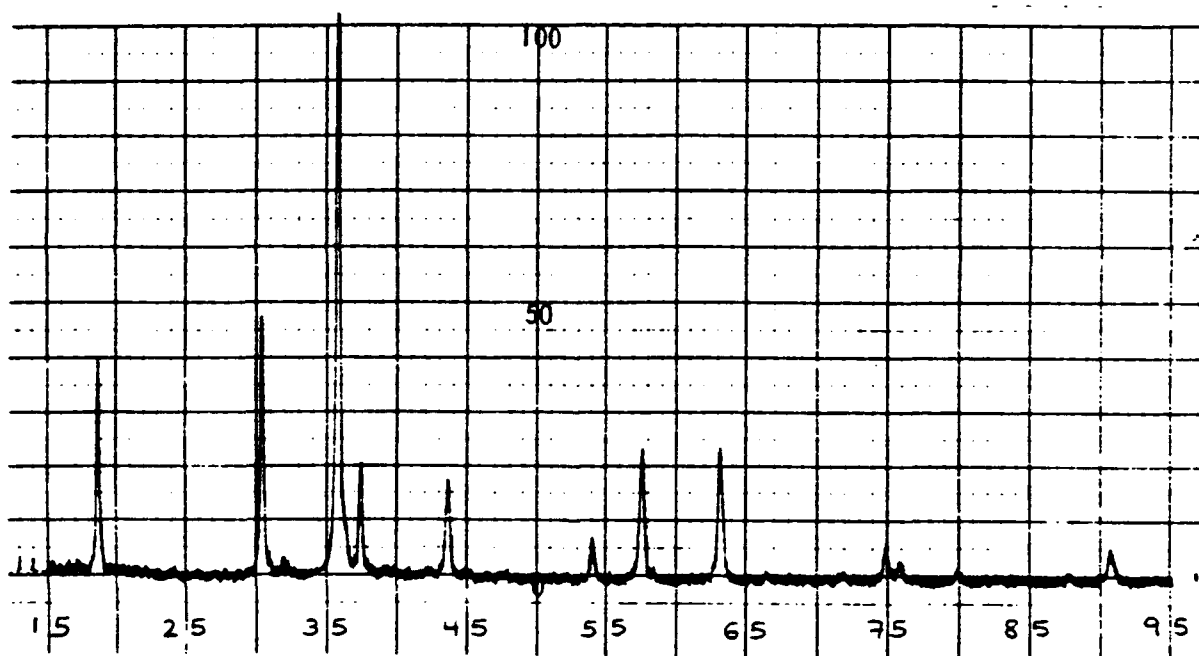


Fig. 35 SIMS analysis of $\text{ZnGa}_2\text{O}_4\text{:Mn}$ thin film on sapphire

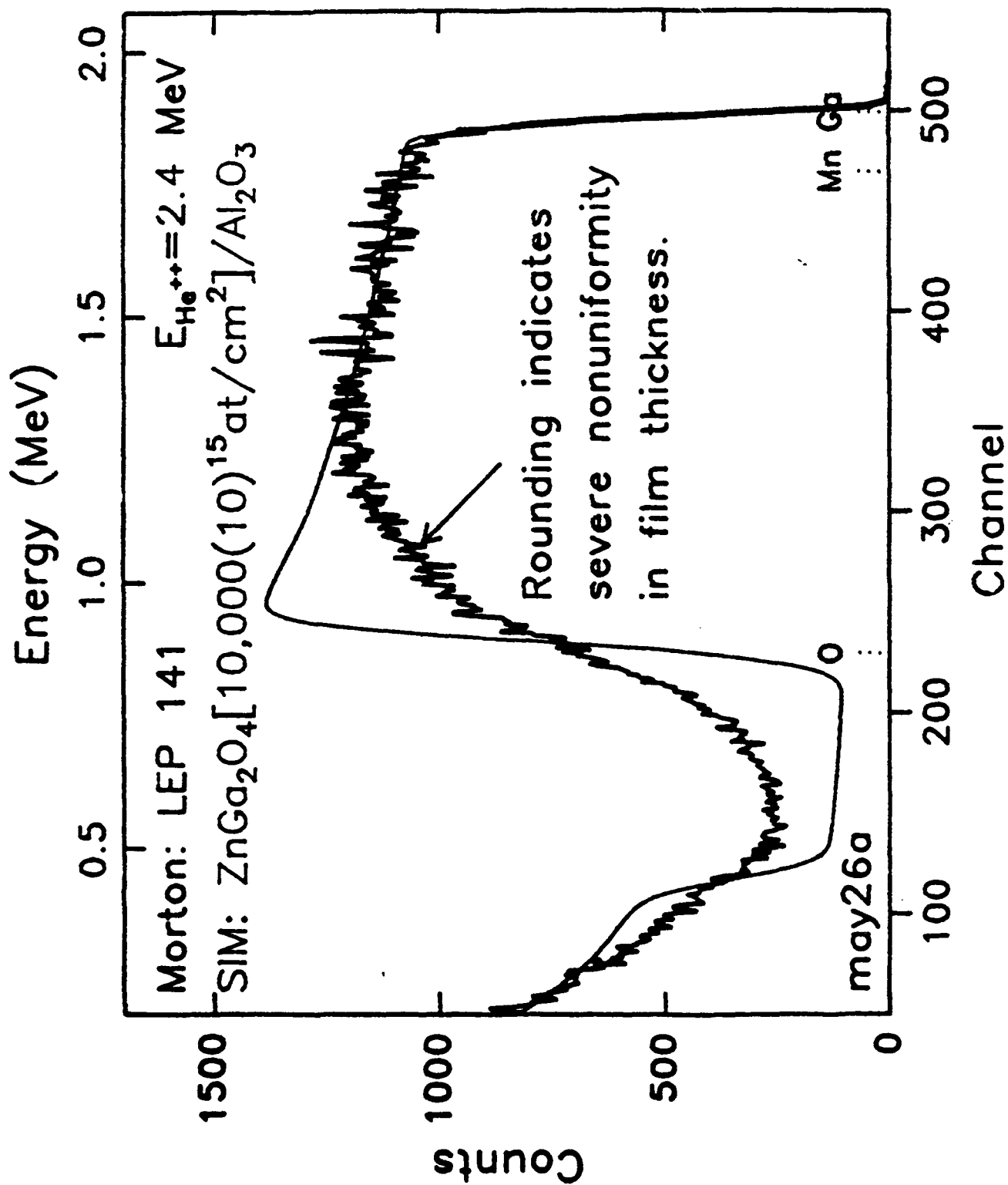
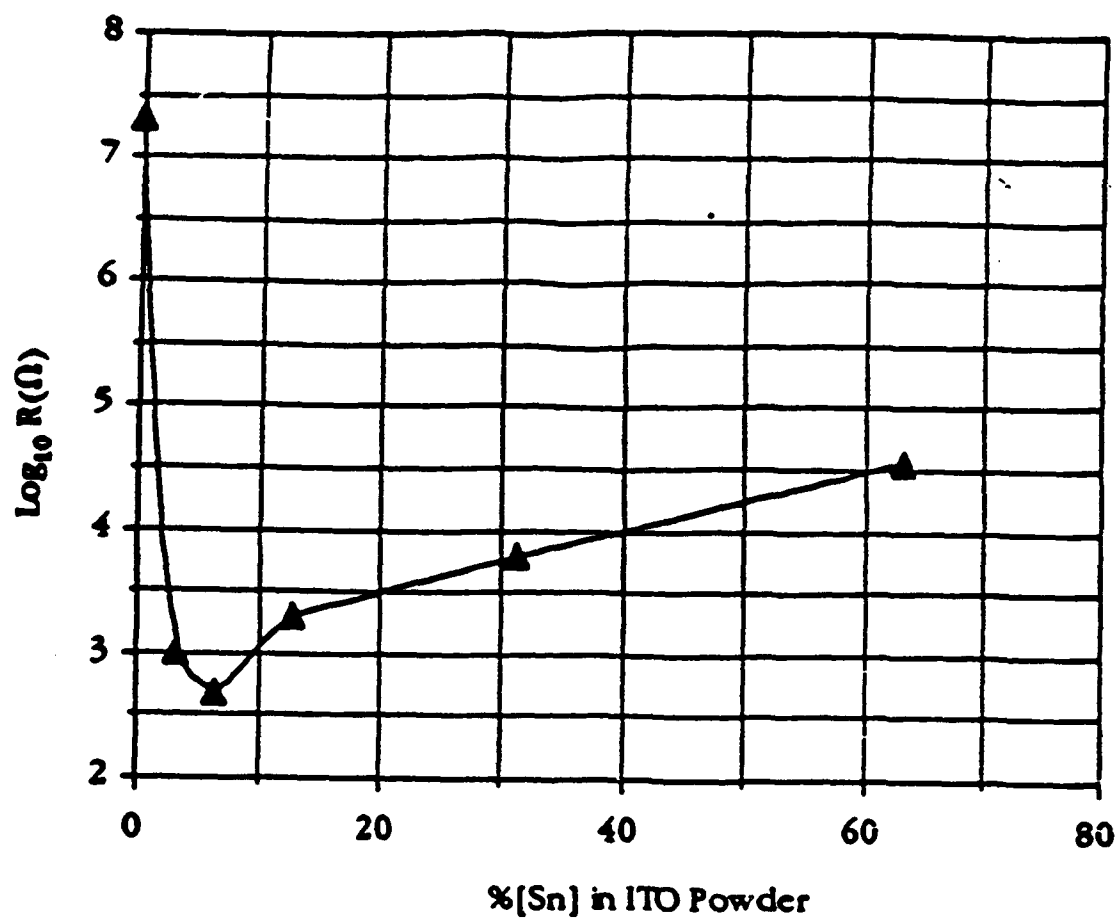


Fig. 36 Tin concentration in ITO powder



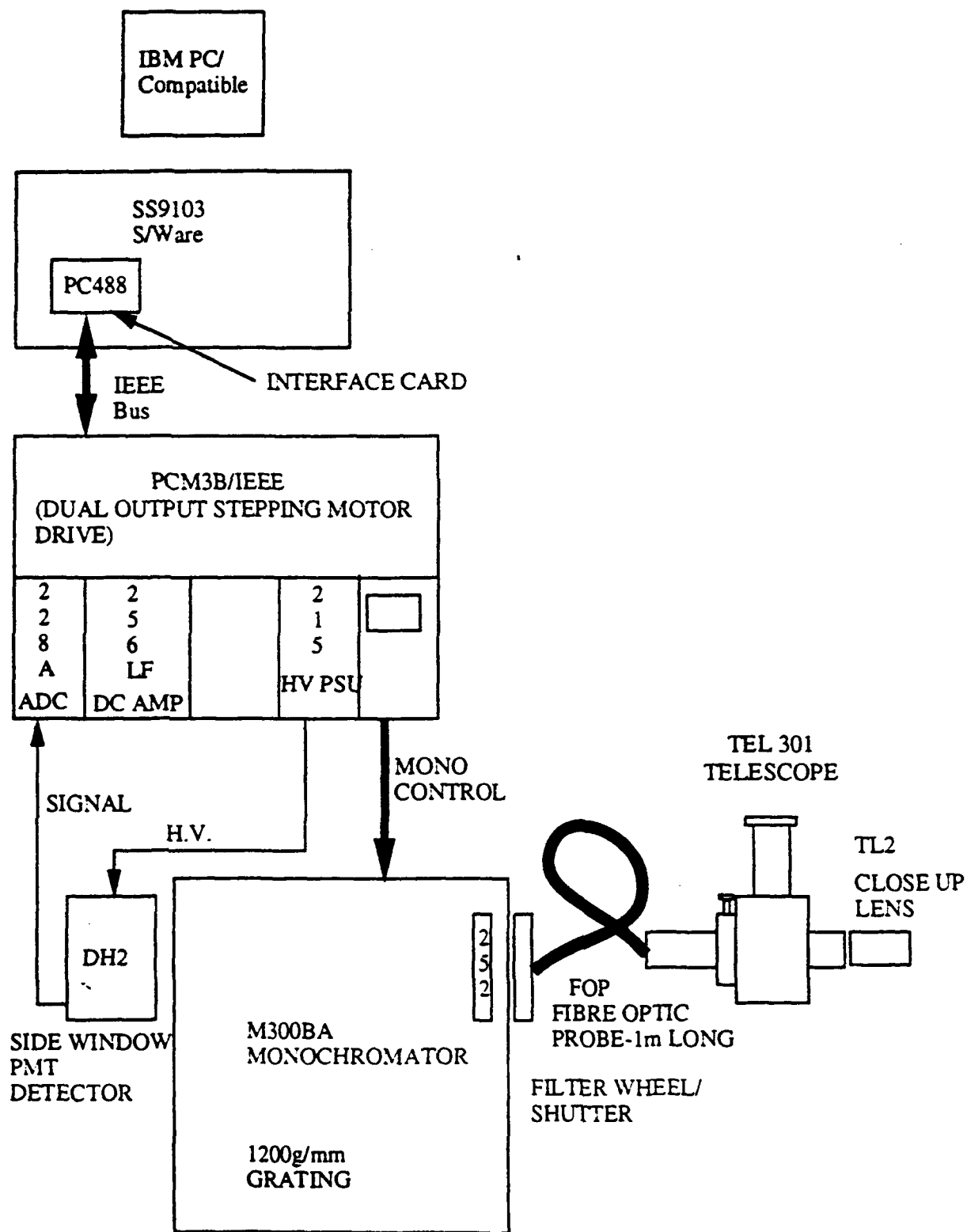


Fig. 37 Diagrammatic representation of the Monochromator system

Fig. 37a The new Bentham Monochromator System

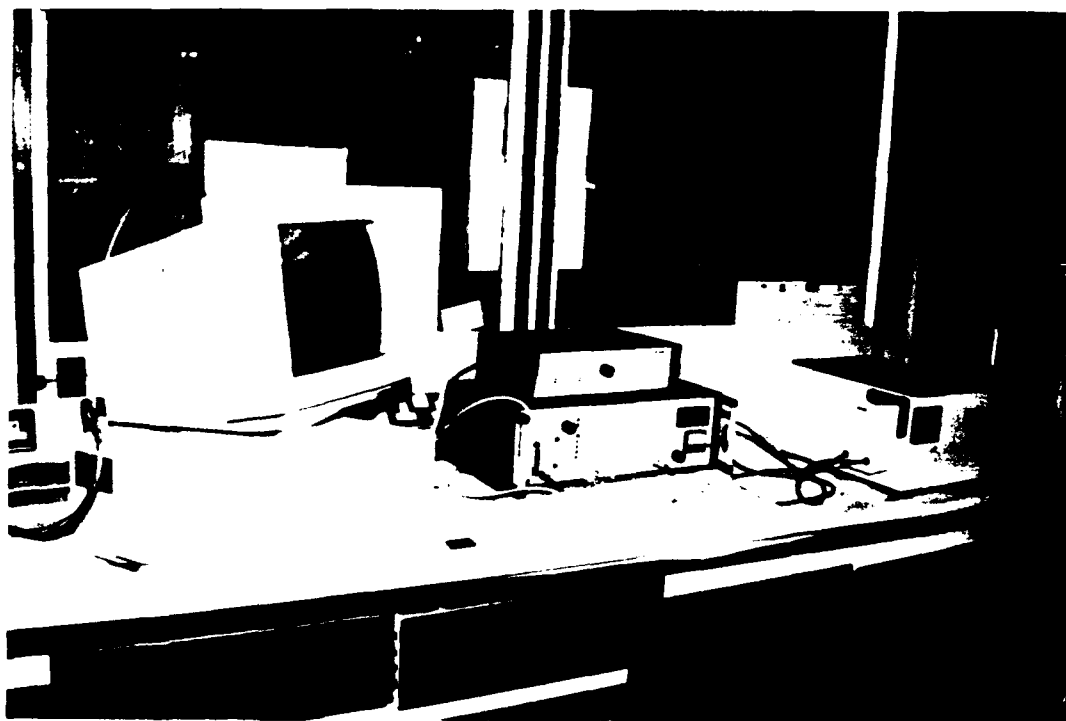


Fig. 38 Low voltage demountable cathode ray apparatus

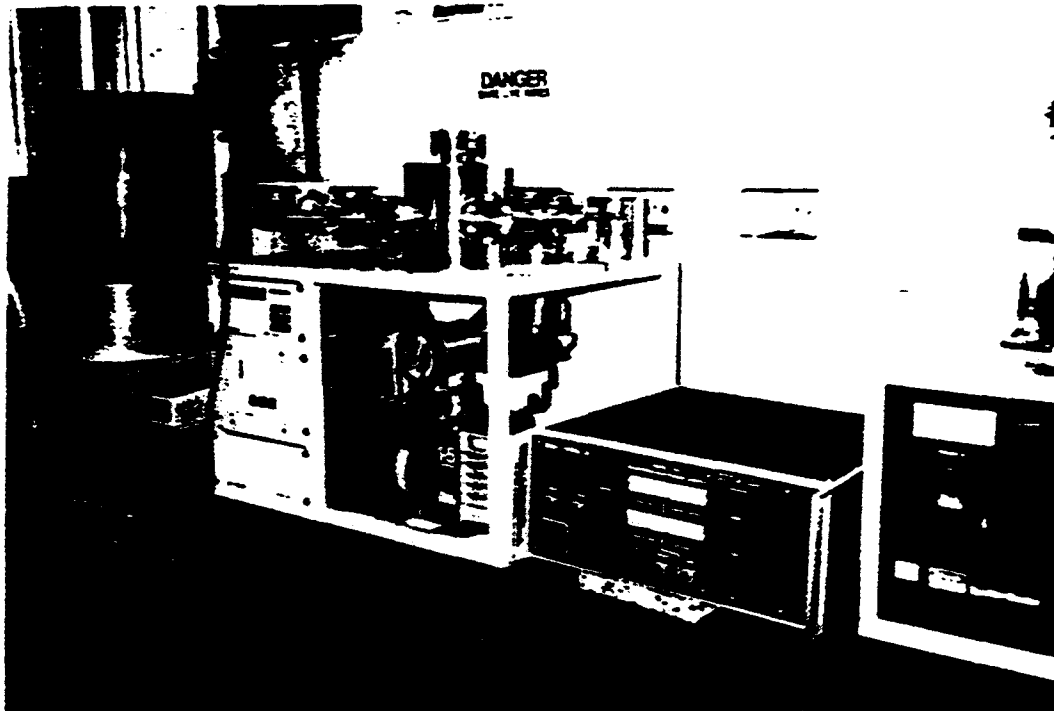
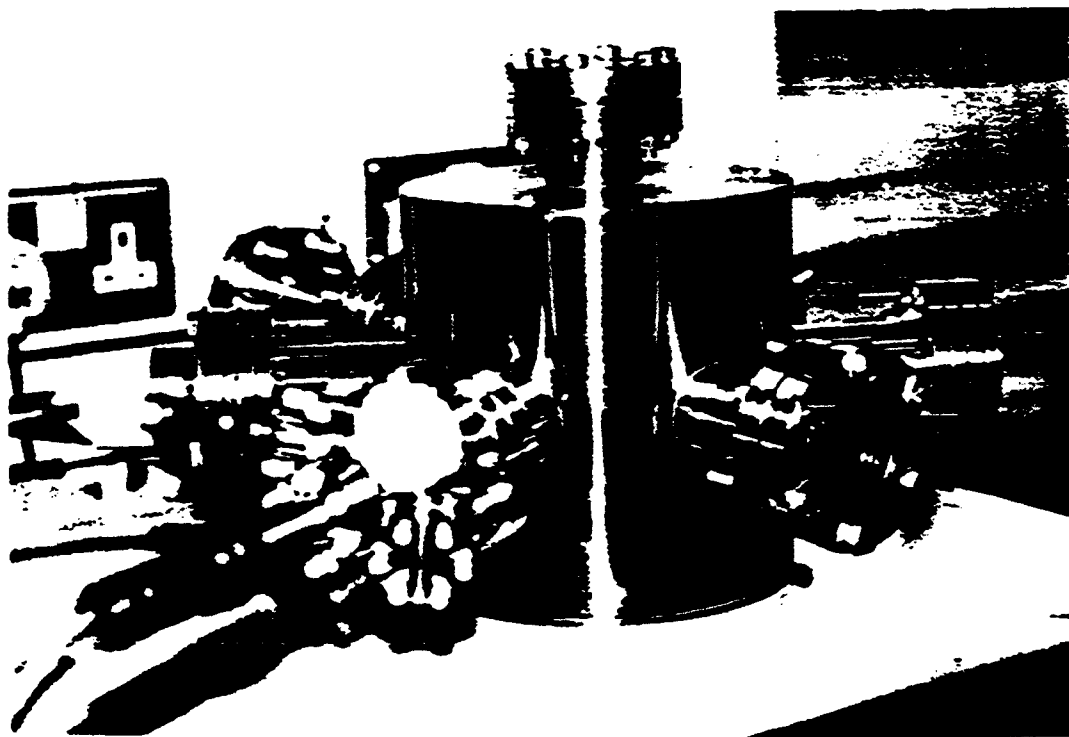
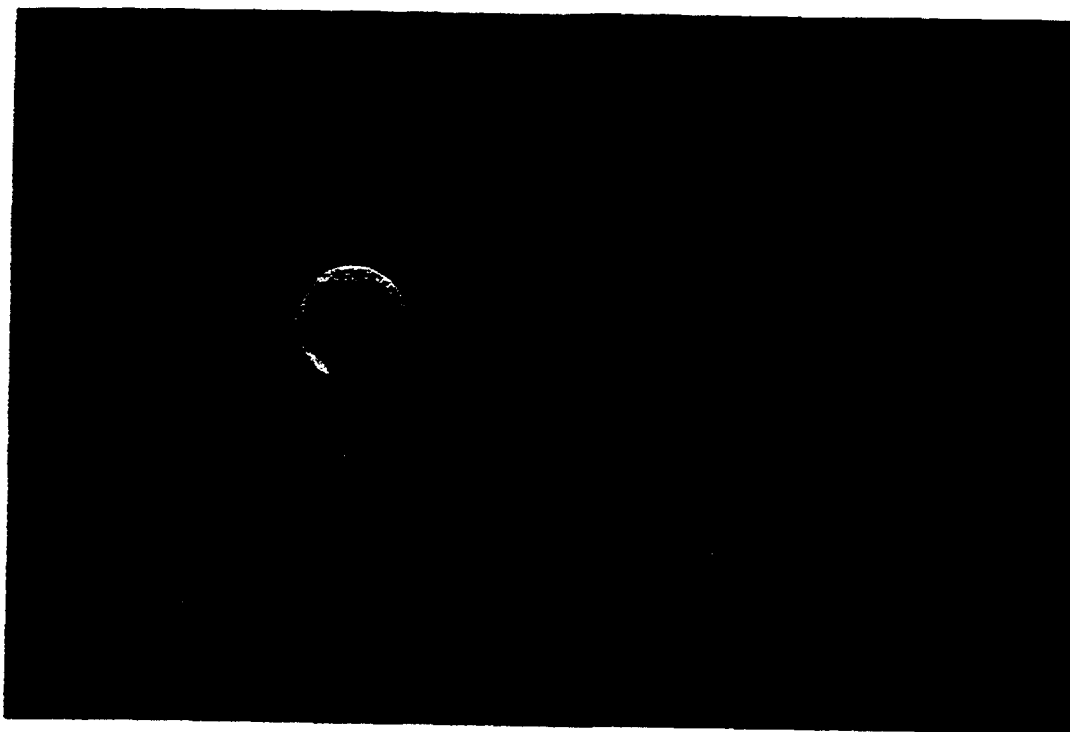


Fig. 39 Close-up of electron gun



Photograph 1 PL emission from $\text{ZnGa}_2\text{O}_4\text{:Mn}$,
 $\text{SnO}_2\text{:Eu}$ and ZnO:Zn thin films



APPENDIX C

Publications: 1) SID 2) IVMC

6.3: New and Improved Phosphors for Low-Voltage Applications

S. S. Chadha, D. W. Smith, A. Vecht, C. S. Gibbons
University of Greenwich, London, U.K.

Abstract Various phosphors have been investigated to achieve full colour from field emission displays. As a result, phosphors have been prepared which emit green (ZnO:Zn, ZnGa₂O₄:Mn), blue ((Zn,Mg)O:Zn) and red (CaTiO₃:Pr, SnO₂:Eu). For the first time thin films of ZnO:Zn, ZnGa₂O₄:Mn and SnO₂:Eu showing low voltage luminescence are reported.

INTRODUCTION

Monochrome vacuum fluorescent displays (VFDs), utilizing the well-known low electron energy green-emitting phosphor zinc oxide:zinc, have been in use for many years (1). More recently, LETI has introduced the field emission display (FED) based on cold electron emission from microtips (2).

The early versions of these FEDs were again monochrome, utilizing the highly efficient ZnO:Zn phosphor. However, for commercial development in the 1990's, only full colour displays are acceptable. Though some advances have been made in obtaining multi- and full colour displays, the efficiency of most phosphors is an order of magnitude lower than ZnO:Zn. Furthermore, ZnO:Zn is a wide band emitter. Narrow band emitters are preferred for greater colour saturation and possibly for improving the contrast by appropriate filtering.

At the University of Greenwich we have developed a range of phosphors with red, green and blue emission in both powder and thin film forms. This work is supported by ARPA funding.

EXPERIMENTAL AND RESULTS

The results of our investigation are summarised below for various red, green and blue emitting

phosphors. Some work on thin film phosphors is also presented.

GREEN PHOSPHORS

Our initial approach was to improve the ZnO:Zn phosphor which has a bluish-green broad band emission centred around 505 nm (Fig. 1). This was achieved with both the photoluminescence (PL) and cathodoluminescence (CL) exceeding that of the commercially available phosphor. Table 1 shows the results obtained under low voltage CL for ZnO:Zn and other phosphors reported in this paper. The maintenance curve for various ZnO:Zn phosphors (1500 V and 50 μ A) is shown in Fig. 2.

Various techniques were explored for the preparation of high brightness ZnO:Zn phosphors. Starting materials included commercially available pure ZnO, oxides prepared from the pure precipitated oxy-salts, such as the oxalate, and the oxy-salts themselves. Reduction of the oxide at 900-1050 °C using either carbon monoxide derived from activated charcoal or H₂/Ar and carried out in crucibles or closed tubes, led to bright ZnO:Zn phosphor. However, a novel firing technique resulted in both higher brightness and better maintenance. Moreover, there was little batch to batch variation.

ZnO:Zn has a broad band peak centred around 505 nm with a decay time of less than 1 μ s. Its low voltage properties have been well documented (3) due to its extensive use in VFDs. However, whilst ZnO:Zn is highly suitable in VFDs, full colour FEDs would benefit from bright narrow band emitting phosphors. Our previous work in this area led us to reinvestigate ZnGa₂O₄:Mn phosphor (4), a system with the spinel structure of the type AB₂O₄.

The phosphor was prepared by firing Ga_2O_3 , ZnO and MnCO_3 using a multi-stage firing sequence in the temperature range $900-1300^\circ\text{C}$. The final firing was always in a reducing atmosphere to ensure conversion to the Mn^{II} state. The emission peak of gallate (Fig. 3) is also centred at 505 nm (cf. $\text{ZnO}:\text{Zn}$) with a decay

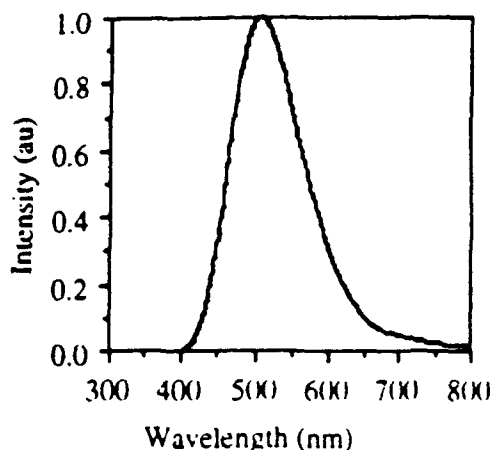


Fig. 1 Emission spectrum of $\text{ZnO}:\text{Zn}$

time of around 4 ms. As can be seen, the peak width is significantly narrower than $\text{ZnO}:\text{Zn}$ and this results in improved colour purity in the green.

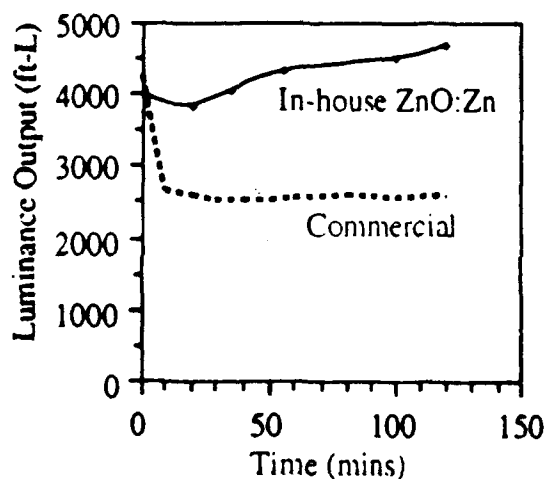


Fig. 2 Maintenance curves for commercial and in-house $\text{ZnO}:\text{Zn}$ phosphors

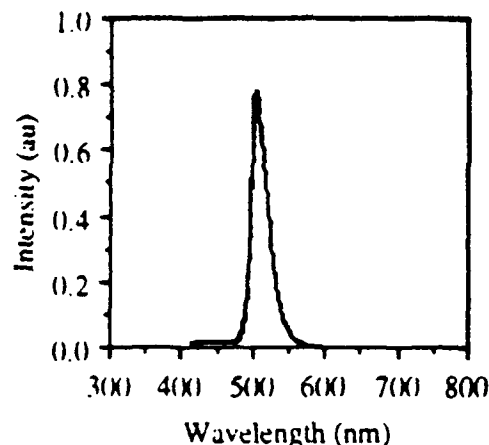


Fig. 3 Emission spectrum of $\text{ZnGa}_2\text{O}_4:\text{Mn}$

RED PHOSPHORS

We have investigated both $\text{SnO}_2:\text{Eu}$ and $\text{CaTiO}_3:\text{Pr}$ phosphors. Preparation of $\text{SnO}_2:\text{Eu}$ involved firing pure SnO_2 powder with EuCl_3 and fluxes within the temperature range of $1450^\circ\text{C} - 1600^\circ\text{C}$. Bright phosphors were made with an Eu concentration around 0.2 a/o. The dominant peak for $\text{SnO}_2:\text{Eu}$ was found at 595 nm with a decay time of nearly 6 ms (Fig. 4).

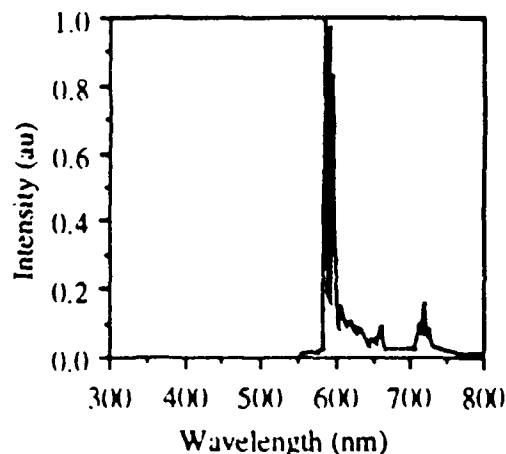


Fig. 4 Emission spectrum of $\text{SnO}_2:\text{Eu}$

$\text{CaTiO}_3:\text{Pr}$ phosphors were prepared using CaCO_3 , TiO_2 , PrCl_3 and suitable fluxes. Firing was within the range $1000 - 1150^\circ\text{C}$. The optimum Pr concentration was 0.1-0.2 a/o. The CaTiO_3 was found to be intrinsically conducting and, hence, useful for low voltage

operation. The dominant peak for $\text{CaTiO}_3\text{:Pr}$ was around 615 nm as shown in Fig. 5, with a decay time of 4 ms.

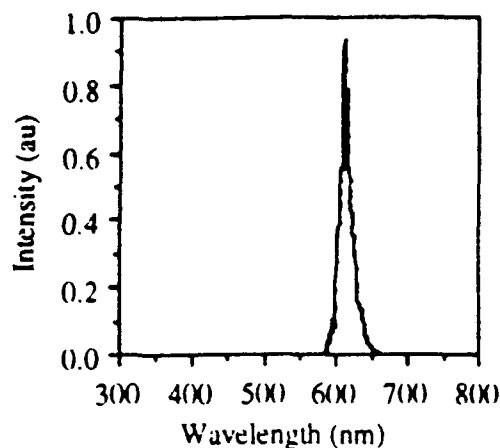


Fig. 5 Emission spectrum of $\text{CaTiO}_3\text{:Pr}$

BLUE PHOSPHORS

Though a reasonable blue emission can be obtained by filtering the broad band emission of ZnO:Zn , it is obviously desirable to have a blue emitting phosphor. During experiments to dope ZnO with various activators, it was found that a colour shift was perceptible with the addition of Mg . MgO appears to form a solid state solution with ZnO and a shift of nearly 30 nm towards the blue was observed with 15 % MgO addition. As shown in Fig. 6, the shape of the emission band is narrower and more symmetrical than that of ZnO:Zn .

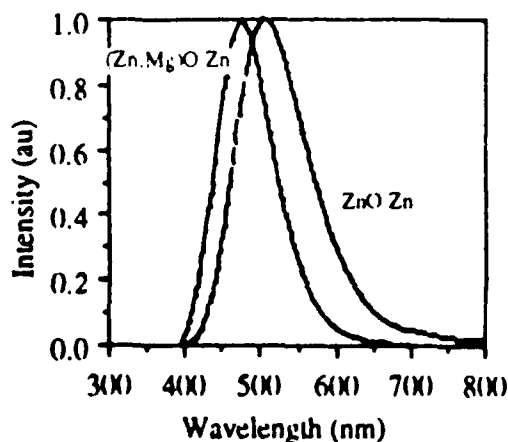


Fig. 6 Emission spectrum of $(\text{Zn,Mg})\text{O:Zn}$ compared with that of ZnO:Zn

THIN FILM PHOSPHORS

For ultimate resolution, thin film phosphors are preferred and we have started research into such structures. The thin film were produced by chemical vapour deposition (CVD) using aerosol spray pyrolysis (ASP) described previously (5,6,7.). The aerosol was formed by spraying a solution of the organo-metallic precursors into a large reservoir. The fine mist was led to the reaction chamber held at $450^\circ - 470^\circ \text{C}$ where it decomposed at the substrate surface. Films up to $2.5 \mu\text{m}$ were built up on sapphire or quartz substrates. These were subsequently annealed in controlled atmospheres at temperatures up to 1200°C , depending on the phosphor. Bright films of ZnO:Zn , $\text{ZnGa}_2\text{O}_4\text{:Mn}$ and $\text{SnO}_2\text{:Eu}$ were prepared. These are shown in Photograph 1 under UV excitation.

CONCLUSIONS

New and improved phosphors are vital for full exploitation of FEDs. In this paper we have reported on a tri-colour system of bright, low voltage phosphors. The ZnO:Zn phosphor made in our laboratories compares favourably with the commercially available material. Also reported, for the first time, are our preliminary findings on thin films.

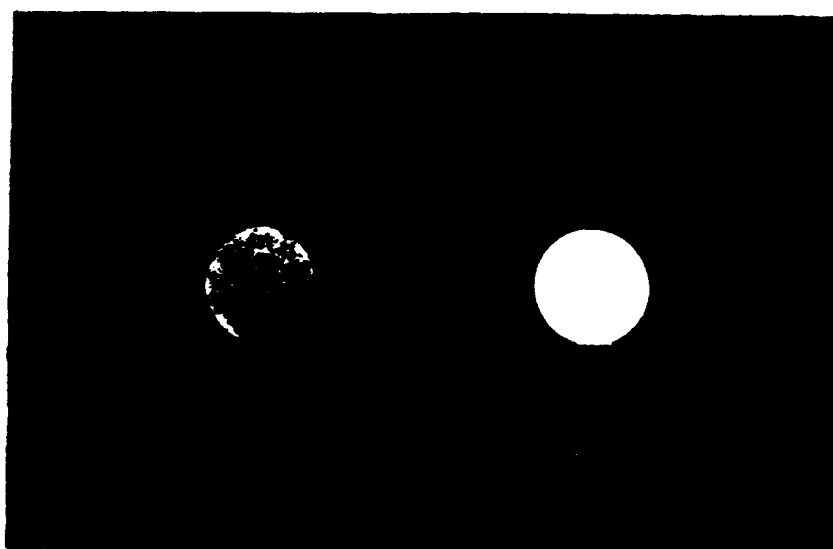
However, though we have made considerable progress in achieving a system of RGB phosphors, further investigations are necessary for newer narrow band emitters with even higher efficiencies and colour purity.

ACKNOWLEDGEMENTS

The research reported in this document has been made through the support and sponsorship of the US Government through its European Research Office of the US Army under an ARPA contract number DAJA-45-92-C-(XX)7. This is gratefully acknowledged. We express our sincere thanks to Mr M R Miller, Dr D Morton, Mr J Koh and Mr C Wadding of Fort Monmouth for some of results and useful discussions over the last two years.

Table 1. Some typical results of the low voltage phosphors (powders and thin films)

Phosphor	Colour	Peak (nm)	Luminance (fL) (1500 V, 50 μ A) after 2 hours	CIE	
				x	y
ZnO:Zn	blue-green	505	4650	0.227	0.443
ZnO:Zn (Commercial)	"	"	2600	"	"
(Zn,Mg)O:Zn	blue	476	2150	0.171	0.2843
ZnGa ₂ O ₄ :Mn	green	505	2610	0.109	0.757
CaTiO ₃ :Pr	red	610	1450	0.680	0.311
SnO ₂ :Eu	Orange-red	595	102	0.587	0.383
ZnO:Zn (thin film)	blue-green	505	380	0.227	0.443



Photograph 1. PL emission from thin films of ZnGa₂O₄:Mn, SnO₂:Eu and ZnO:Zn

This figure is reproduced in color on page 989.

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New electron excited light emitting materials*

A. Vecht, D. W. Smith, S. S. Chadha, and C. S. Gibbons

School of Biological and Chemical Sciences, University of Greenwich, Wellington Street, London SE18 6PF, England

James Koh and David Morton

Display Devices Team, US Army Electronics Command, Fort Monmouth, New Jersey 07703-5601

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A range of bright, multicolor phosphor systems for field emission displays is reported. These include the standard ZnO:Zn and newer, narrow band emitting systems based on green ZnGa₂O₄:Mn and red CaTiO₃:Pr. A modified, blue emitting ZnO:(Zn/Mg) and thin films of ZnGa₂O₄:Mn have also been prepared.

I. INTRODUCTION

The cathode ray tube, after a century of development, is still the major display component used in information technology. The extension of its usefulness, from oscilloscope to monochrome and then full color television, has always been accompanied by improvements in the phosphors used. For example, the advent of the present color television systems depended on the development of efficient, narrow band red phosphors.¹ Similarly, the recent progress made in field emission/microtip technology² will not be exploited to its full potential until the red, green, and blue (RGB) phosphors operating at the required conditions have been synthesized.

Although cathode ray phosphors have been optimized to work at high voltages (over 10 keV), and relatively low current densities (a few microamps per cm²), the requirements for field emission displays (FEDs) are totally different. The voltages of operation range from 10 to 1500 eV, but high current densities are needed. Because of the relatively low operating voltages, aluminizing of the phosphor layer to avoid space charge is not possible. To date, the only phosphor systems used with any success are the ZnO systems.

In this paper, we report some of the initial results on low voltage phosphors for FED application. It should be emphasized that although we are dealing with FEDs in a general way, there are many proposed FED systems and each may require a phosphor system designed for it. Every application has specific *I-V* conditions of operation, resolution, and maintenance. These, in turn, will be governed by the size of the display required and the method of address used.

II. BACKGROUND

It is usually assumed that the high efficiencies obtained in cathode ray phosphors are partly due to the high voltage excitation processes that are used. Thus, the light emitting process is considered to be the result of a multistage high energy collision and deceleration process. Efficiencies of about 15%–20% can only be obtained at above 10 keV. Some of the most efficient phosphors are copper or silver doped zinc sulfides, where efficiencies of ~22% have been reported. Only the ZnO:Zn system shows reasonable efficiencies (1%–5%) at low voltage (10–50 eV). The reason

for the anomalous behavior, never fully explained, is attributed to high surface conductivity. Zinc oxide has a much higher conductivity ($\sim 10^{-3} \Omega \text{ cm}^{-1}$) than typical CRT phosphors such as ZnS or Y₂O₂S ($\sim 10^{-11} \Omega \text{ cm}^{-1}$). Some insulating phosphors can also show limited low voltage light emission when mixed or coated with conductive compounds, e.g., ZnS and Zn(Cd)S. The main application of conducting zinc oxide phosphors has been in the familiar "vacuum fluorescent" display, which emit in the blue-green part of the spectrum. They have also been used in prototype microtip devices. A significant recent development is the production of a range of field emitters in the form of "metallic" (e.g., Mo or diamond) cones on a silicon substrate forming an extended cathode for a multielement flat panel display.

Recently, colors other than bluish-green have been demonstrated by adding conducting powders, usually indium oxide, to conventional phosphors [Table I, (Ref. 3)]. The efficiencies of the red and blue emitting systems are about an order of magnitude lower than ZnOP:Zn. Furthermore, none of the phosphors listed are narrow band emitters.

There was therefore an urgent need for a systematic investigation of FED phosphors. As far as is known, no thin film FED phosphors other than ZnO have been reported. Such phosphor films would be essential for very high resolution displays.

A. Excitation at low voltage of insulating phosphors

When an electron strikes the phosphor lattice, some secondary electrons may be emitted, as well as photons of visible light. The ratio of secondary electrons emitted to primary electrons striking the lattice is termed δ and varies with the energy of the primary electrons. Figure 1 shows the typical variation of δ in relation to primary electron energies. At low energies of the primary electrons, secondary emission is small, leading to the build-up of a surface space charge in an insulating phosphor. Furthermore, low energy primary electrons are unable to overcome the electrostatic barrier, resulting in low light output. As the energy of the primary electrons increases, the ratio δ approaches one. At this voltage, and above, no build-up of negative space charge occurs. Secondary emission increases up to a value of E maximum and then drops off monotonically until the second crossover is reached, as shown. This is generally when the voltage

*Published without author corrections.

TABLE I. State of the art of vacuum fluorescent phosphors and phosphor color characteristics (Ref. 3)

Ingredients of phosphors	Emission color	Peak wavelength (nm)	Color coordinate		Emission efficiency (lm W ⁻¹)
			X	Y	
ZnO:Zn	Bluish-green	505	0.25	0.44	5-7
(ZnCd)S:Ag+In ₂ O ₃	Red	665	0.67	0.33	0.5-1
ZnS:AuAl-In ₂ O ₃	Lemon	555	0.39	0.65	1-1.5
ZnS:Mn-In ₂ O ₃	Yellow	585	0.52	0.47	0.3-0.6
ZnS:Ag-In ₂ O ₃	Blue	450	0.16	0.12	0.1-0.3
ZnS:CuAl-In ₂ O ₃	Green	520	0.25	0.59	1-1.5

reaches 1000 eV or more. Above this point the energies of the primary electrons are sufficiently great to overcome any space charge barrier.

B. Surface treatments

In most publications, very little reference is made to the surface treatment of FED phosphors. However, Petersen reported⁴ that most phosphors prepared for high voltage operation require some type of surface cleaning to yield maximum low voltage efficiency. He found that acid etching improved the brightness, as well as the efficiency, of oxysulfides and oxybromides, by almost a factor of 2, when such phosphors were operated at 300 V. This etching probably removes dead layers (nonluminescent) from the surface of the phosphor.

III. EXPERIMENT

A. ZnO:Zn

As ZnO:Zn is an established low voltage phosphor, it was used as the reference material against which results from the new phosphors were assessed.

Detailed evaluation of zinc oxide phosphors will be reported elsewhere.⁵ We can summarize our results on ZnO to date as follows.

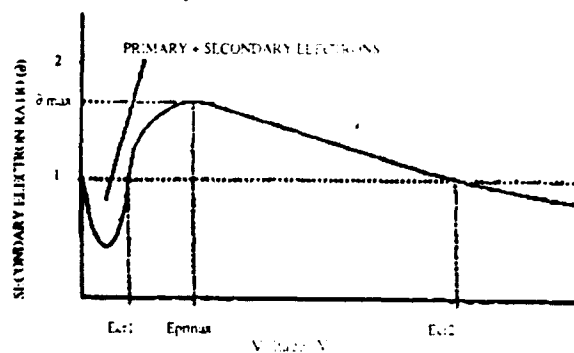


FIG. 1. The secondary emission ratio (δ) as function of the accelerating voltage (V).

TABLE II. Chemical analysis of zinc oxide phosphors and raw materials

Phosphor sample	Elements (ppm)						
	Cd	Ni	Ca	Cu	Fe	Pb	Mn
Commercial ZnO:Zn	0.965	0.760	0.082	0.028	0.138	4.67	0.054
BDH-ZnO	0.944	0.752	0.102	0.074	0.012	5.11	0.052
Rose chemical-ZnO	1.4	0.761	0.074	0.039	0.074	5.66	0.053
ZnSO ₄ -Zn oxalate-ZnO	0.906	1.19	0.433	0.203	0.326	4.18	0.065
Zinc acetate-Zn oxalate-ZnO	0.932	0.751	0.496	0.171	0.153	4.35	0.074

1. Synthesis

Although numerous methods of preparing zinc oxides are known, relatively little literature on the synthesis of ZnO phosphors exist. We have concentrated on two methods:

(a) Salt decomposition, e.g., the preparation of precursors such as oxalates from zinc sulfate, zinc nitrate, zinc acetate, and the controlled firing/decomposition of the precursor to give the zinc oxide phosphor.

(b) The firing of zinc oxide from a range of commercial suppliers.

The performance of ZnO:Zn under photoluminescence (PL) and cathodoluminescence (CL) were considerably improved when the reducing firing conditions were controlled for temperature, time, heating, and cooling rates.

2. Surface treatment

Etching treatments were carried out on both starting material (ZnO) and phosphor (ZnO:Zn) using a range of acids and oxidizing and reducing agents. Oxidizing agents proved to be the most effective in increasing the photoluminescent intensity. We did not confirm results indicating general improvements with acid etching as suggested previously.⁴

3. Analytical

The impurity levels detected in commercially available ZnO phosphors and those made from purchased raw material, as well as those synthesized in-house, seemed comparable. Typical results are illustrated in Table II.

It can be seen that the composition of the materials are very similar, and minor differences in Ca, Cu and, in one case, Fe, are observed. It is quite clear that impurities do not play a direct role in the luminescent process. This confirmed the accepted view that ZnO is self-activated and, contrary to previous claims,⁶ Cu plays no role in activation.

4. Particle size and x-ray data

The particle size of the ZnO:Zn phosphor was similar (1-2 μ m), regardless of the source material. Similarly, XRD analysis showed no discernible difference between ZnO:Zn phosphors made using various techniques and starting materials.

5. Photoluminescence and cathodoluminescence

The photoluminescence under laser excitation of phosphors prepared in-house approached and, more often, ex-

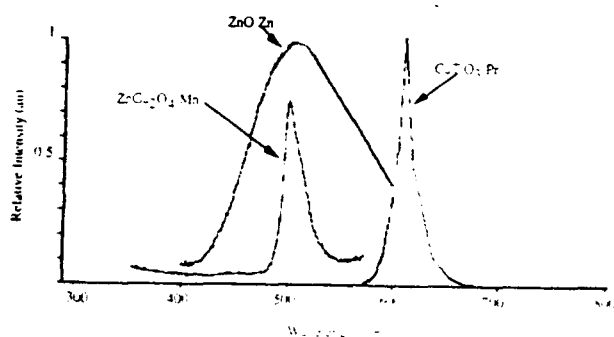


FIG. 2. Emission spectra of ZnO:Zn (blue-green), ZnGa₂O₄:Mn (green), and CaTiO₃:Pr (red) phosphors.

ceeded that of the commercial material. Under CL excitation ZnO:Zn emitted an intense whitish-green luminescence. The emission spectrum is shown in Fig. 2. The broad emission peak of ZnO:Zn is centered at around 505 nm with a short decay time, approximately 0.3 μ s to 1/e.

The CL output under flood excitation conditions vs voltage is shown in Fig. 3. The brightness-voltage characteristics of commercially available and in-house materials are indicated.

From our experiments so far, we can deduce that the brightness and efficiency of ZnO powder (once sufficient purity control has been established) is strongly dependent on the controlled firing ambient during synthesis, as well as the pre-firing and post-firing treatments of the phosphor surface.

6. Blue ZnO

We have recently shown that the emission of ZnO phosphors can be moved towards the blue end of the spectrum by the addition of magnesium. We believe that the shift of approximately 25 nm is primarily due to a change in the band gap of the ZnO as a result of Mg substitution.

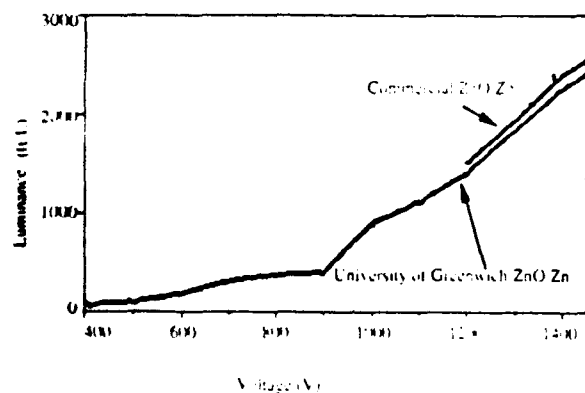


FIG. 3. Brightness-voltage characteristics for ZnO:Zn commercial phosphors.

TABLE III. Luminance of some low voltage phosphors.

Phosphor	Luminance (ft-L) at 50 μ A	
	500 V	1500 V
ZnO:Zn (UG ^a average)	100	2600
ZnO:Zn (Comm)	100	2700
ZnO:Zn (blue)	30	40
ZnGa ₂ O ₄ :Mn	30	350

^aUG=University of Greenwich.

B. Zinc gallate:Mn

1. Powder

The broad emission spectrum of zinc oxide is not ideal for an RGB system. The emission spectrum of zinc gallate also peaking at 505 nm (Fig. 2) is considerably narrower and yields a more saturated green. The decay time of this phosphor is approximately 4 ms to 1/e. Although this system has not been optimized, we have so far obtained 350 ft L at about 1500 V. The brightness-voltage characteristics are indicated in Fig. 4. Preliminary measurements indicate good stability under CL excitation, better than that shown by conventional ZnO materials.

2. Thin films

Thin films of ZnGa₂O₄:Mn were deposited by organometallic chemical vapor deposition using aerosol spray pyrolysis described previously.⁸ Details of the synthesis will be reported elsewhere.⁹ Such films show emission characteristics similar to those of the powder system described above. The efficiency and brightness of the films are not yet comparable to those obtained in powder systems, the luminance of the thin film being about 1/50th of that of the powder. However, the feasibility of thin films of ZnGa₂O₄:Mn for FED application has been demonstrated for the first time.

C. Calcium titanate:Pr

We investigated a range of possible low voltage phosphor systems emitting over a narrow band in the red part of the

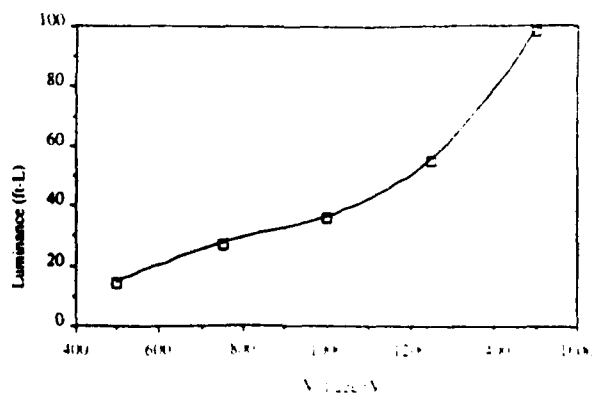


FIG. 4. Brightness-voltage characteristics for ZnGa₂O₄:Mn phosphors.

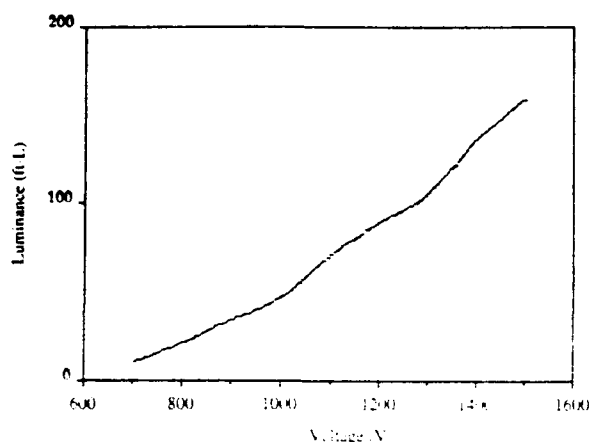


FIG. 5. Brightness-voltage curve for $\text{CaTiO}_3:\text{Pr}$.

spectrum. Certain titanates showed considerable promise with a good red emission at relatively low voltages. The emission spectrum and brightness/voltage characteristics for $\text{CaTiO}_3:\text{Pr}$ are shown in Figs. 2 and 5. We also found the phosphor to be intrinsically conducting, which should aid low voltage performance. The properties of this phosphor system can be varied by the partial replacement of calcium in the host lattice with strontium.

IV. CONCLUSIONS

Although considerable progress has been made recently in microtip technology and related structures, little progress on the development of suitable phosphors for displays, based on

these systems, has been reported. In this paper we have summarized our initial results of a concerted attempt to develop RGB phosphors, under ARPA auspices, for FEDs.

Methods have been developed for the preparation of "standard" $\text{ZnO}:\text{Zn}$ phosphors comparable to the best commercially available. Bright, narrow band, green emitting zinc gallate:Mn and red emitting calcium titanate:Pr powder phosphors, have been developed for low voltage application. Early results point to the potential of thin film phosphors based on zinc gallate and zinc oxide. Furthermore, the emission spectrum of zinc oxide has been moved towards the blue end of the spectrum with a peak at 480 nm. These promising results point to the possibility of achieving full color, flat panel FE displays.

Before commercial devices can be manufactured, detailed investigations are required on the stability of low voltage phosphors running at high current densities. The decay characteristics and saturation effects will also have to be evaluated.

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