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PREPARATION AND INVESTIGATION OF PHOSPHORS FOR EMISSIVE DISPLAYS

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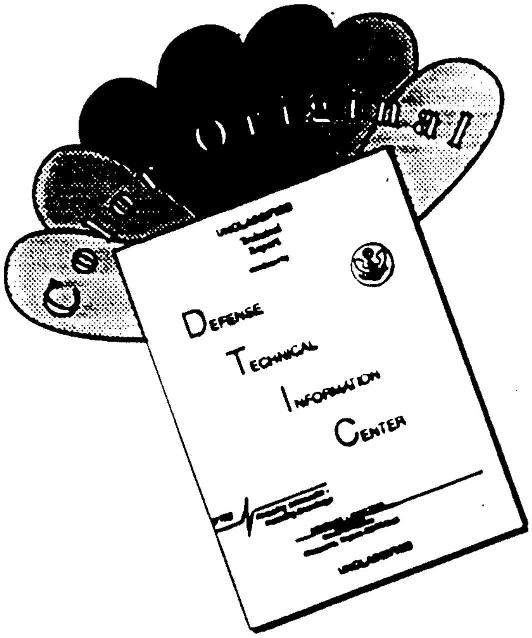

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New methods for the preparation of fine particle phosphors, based on novel microwave techniques and 'new' milling systems have been developed. Phosphors in the range of 1.7-3.2 μm have been made with efficiencies and brightnesses better than those available commercially, more especially, Y_2O_3:Eu and $Y_2(Al/Ga_5)O_{12}$:Tb.

Improved efficiency and stability has been achieved in ZnO:Zn by a range of novel surface modifications. Within the limits of our testing facility, it would appear that the maintenance of these phosphors would now make them commercially useful.

Of new lattices investigated, barium substituted ZnO:Zn, which produced a red shift, and lanthanide activated $YNbO_4$ were of most interest.

Aerosol spray pyrolysis methods previously developed have been refined and improved to yield the best ZnO:Zn and Y_2O_3:Eu films reported so far. The results from different thickness films in simple and composite thin film layers indicate a definite relationship between phosphor volume and efficiency.

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Introduction

This annual report describes the progress made in the work outlined in the ARPA contract number N68171-94-C-9110 and covers the first year from mid-August 1994 until the end of September 1995. The objective was to investigate methods of phosphor synthesis for both high and low voltage application in high resolution screens.

The literature over the last year has been surveyed and periodically updated. For refractory materials, microwave heating has been used for the synthesis of the precursors for fine grain red, green and blue (RGB) phosphors. Sol-gel synthesis has also been tried. A method was successfully developed using a McCrone mill for particle comminution. On low voltage phosphors, both etching and surface modification by the incorporation of foreign ions in ZnO:Zn were extensively researched and the effect of modifying this matrix by the partial substitution of Zn was also tried. Other new lattices, including $YNbO_4$ have also been investigated. The range of thin film phosphors was extended and a programme on multilayer structures was initiated.

On the measurement side, particle size distribution can now be characterised using a Coulter Counter. The measurement of low voltage phosphors has been facilitated by a number of measures including the incorporation of a Faraday cup. A high voltage measurement system is also being set up.

More detailed descriptions follow.

Table of Contents

1) Literature Survey

In our three interim reports we have outlined the more important developments in phosphor research. Whereas a few years ago the review of the important phosphor literature consisted of digesting about a dozen papers and publications, in the last half year or so, there has been an explosion of interest in light emitting materials. In this report, we will mostly confine our attention to two of the most recent conferences covering this area. Well over one hundred publications have to be reviewed. These were presented at:

1) The Electrochemical Society Meeting (ECS), held in Chicago, October 8-13, 1995, and
2) Asia Displays, held in Hamamatsu, October 16-18, 1995.

The main subjects covered can be summarised under the following headings:

A) Amorphous Silicon and Organic Electroluminescence

It is somewhat surprising that the search for better light emitting materials is far more dependent on known techniques than on genuine research. For example, the ECS International Symposium on Advanced Luminescent Materials consisted of no less than approximately 50 papers on amorphous silicon, none of which seem to have even the possibility of any practical results. The data presented does not seem to be very concerned with any maintenance problems, temperature stability or practical efficiency. Therefore, no details will be presented here but are available in the extended abstracts.

Renewed attention has also been focussed on organic electroluminescent systems. These have even been the subject of articles in the popular press, such as the Scientific American (1). Although such devices may prove useful eventually in fixed legend displays, they are still very far from practical IT devices. The team at Kodak, under the leadership of Tang, has claimed EL efficiency of 1-2% photons per injected charge and a maintenance of more than 10,000 hours half life of brightness at 100cdm^{-2} (2).

B) Phosphor Synthesis

I) Sol-gel

Renewed attention on new methods of synthesising more conventional phosphors have shown some progress in the use of sol-gel techniques (3) (4). Thus, sol-gels have been used for the preparation of tin oxide europium (SnO_2:Eu). However, results so far do not combine fine particle preparation with a commercially useful efficiency.

II) Special preparation

A new method for making spherical phosphor particles, for example, of Y_2O_3:Eu, has been developed by Toshiba (5) using a somewhat complicated thermal plasma method. This enables spherical particles to be prepared. Such particles are more easily settled on to the screen and improve the light scattering properties. It is claimed that a decrease of about 30% in the thickness of screening yields required results. Such screens may prove invaluable in projection television systems where the light transmittance is increased by 50%.

Ion implantation as a method of phosphor doping has been tried for many years. Futaba has used this technique for the preparation of manganese doped zinc gallates. It should be emphasised that an annealing process is still required after implantation. Limited improvements using such techniques are claimed (6).

III) Deposition techniques

Considerable attention is being devoted by the industry into deposition and screening techniques to improve display performance. The latest edition of the SID journal reviews the considerable progress that has been achieved by controlling the packing density of phosphor particles and minimising of voids in the preparation of screens (7).

IV) Coating techniques

It is quite clear that for the preparation of low voltage phosphors, novel surface treatments are being employed to improve both maintenance and low voltage characteristics. Such techniques are still proprietary but improved results have been claimed (8). Typical results are shown in Fig. 1 and Table 1. It will be interesting when details are made available to compare these methods with the ones we have developed under recent ARPA contracts.

TABLE 1

Characteristics of Low Voltage Phosphors

Phosphor	**Colour**	**Coordinates X Y**	**(L/W) at 500V**	**(L/W) at 1000V**
Y_2O_2S:Eu	Red	0.628 - 0.337	3.5	5.7
Y_2O_3:Eu	Red	0.638 - 0.350	2.2	5.3
ZnO:Zn	Green	0.251 - 0.421	10.7	13.5
$ZnGa_2O_4$:Mn	Green	0.082 - 0.694	2.1	3.0
Gd_2O_2S:Tb	Green	0.334 - 0.555	7.9	13.9
ZnCdS:Cu,Al	Green	0.321 - 0.613	4.8	8.5
ZnS:Ag	Blue	0.147 - 0.137	0.8	1.4
$ZnGa_2O_4$	Blue	0.153 - 0.086	0.2	0.3

C) New Phosphor Lattices

It is somewhat surprising how few new phosphor lattices have been reported despite the proliferation of publications. Perhaps the most significant result is the development of oxide long afterglow phosphors by Nemoto Company in Japan. They have demonstrated that doubly rare earth doped strontium aluminates produce extremely stable, long afterglow phosphors. They suggest Eu^{3+} and Dy^{3+} is giving best results. Such phosphors will have wide range industrial applications. It is not clear from another review (9) whether the results reported make use of coating treatments.

It is perhaps disappointing to note that over the last three years no new AC EL phosphor lattices have been reported. However, steady improvements have been obtained with rare earth doped sulphides and thiogallates.

D) Mechanistic Studies

Useful mechanistic studies are few and far between in recent phosphor publications. An effort to relate the particle size and surface recombination rate of low voltage phosphors has been reported (10). Unfortunately, although useful data on electron penetration with depth and carrier concentrations are presented, the relationship proposed between the brightness and particle size seems to be the opposite of what is actually found in practice, thus, according to these authors, large particle size phosphor should be inefficient; the converse, however, is true!

2) **Powder Phosphor Development**
- Small Particle RGB Materials

Good quality, fine particle standard CRT refractory phosphors of yttrium oxide:Eu (P56), yttrium silicate:Ce (P47) and yttrium gallium aluminium oxide:Tb (YAGAG:Tb, P53) were prepared in kg quantities, using conventional procedures, on 120g plus size batches. We tried to avoid the use of fluxes so as to minimise the concentration of foreign ions in the phosphor which may cause problems on ageing. The particle size was reduced in a McCrone mill which we found offers certain advantages compared with ball milling. An accurate estimate of the particle size distribution of the phosphors was obtained using a Coulter Counter.

2a) Conventional Synthesis

i) Yttrium oxide:Eu, Y_2O_3:Eu

Firing the mixed oxides of yttrium and europium is the simplest route but very high temperatures (>1650°C)are required if no flux is employed and particle size and aggregation tend to increase. An alternative oxalate co-precipitation method was therefore used, producing materials of superior luminance with a smaller, more uniform, particle size. Some comminution was required and this was carried out in a McCrone mill (see later, Section 2c). Yields greater than 90% of fine phosphor of 2.7-3.0 µm were obtained which was superior to the commercial product.

ii) Yttrium aluminium gallium oxide:Tb, $Y_3(Al/Ga)_5O_{12}$:Tb (YAGAG:Tb)

In contrast to Y_2O_3:Eu, the co-precipitation route was not successful, so a mixture of oxides was used. Al_2O_3 can be obtained in several different forms which materially affect the product. The low temperature form, γ-Al_2O_3, an ultra-fine grain powder, was the most successful. Again, the use of fluxes was avoided but high temperatures were required to make efficient phosphors and post-firing treatment in a McCrone mill was required. Again, the phosphor, of particle size 3-3.2µm, was more efficient than the commercial product as shown in the V/L plot of Fig. 2.

iii) Yttrium Silicate:Ce, Y_2SiO_3:Ce

This proved the most difficult of the refractory phosphors to make. The most efficient phosphor was produced by a mixed oxide/oxalate process, whereby colloidal silica is intimately mixed with a mixed Y/Ce oxalate during the precipitation stage along with a Gd co-activator. Again, no fluxes are employed but extended firing times at 1500°C (up to 24 hours) were necessary. Both elutriation and McCrone milling have been used to give a very fine product (1.8-2.7µm). This was more efficient than a sample of the commercial phosphor as indicated in Fig. 3.

2b) Particle Size Measurement

A Coulter Counter Multisizer II has been obtained to enable us to assess accurately the weight/size distribution data for most phosphors. This type of instrument is commonly used by both CRT and lamp phosphor manufacturers for the quality control of their phosphors.

In this technique, a dispersion of the phosphor is formed in an electrolyte containing a surfactant. This dispersion is drawn through a glass tube with a fine calibrated orifice near its tip. The resistance across the orifice is monitored and each particle, on passing through, gives rise to a pulse proportional to its volume and hence weight. In a typical analysis over 150,000 particles are counted over a 45 second period.

Analyses carried out on a fine-grain yttrium oxide:Eu are shown in Fig. 4 to demonstrate the difference in number and volume statistics. An SEM of the same sample is shown in Photograph 1.

We have found most phosphors to be stable in sodium chloride solution, the usual electrolyte for the system. The important exception is ZnO:Zn, which is slightly soluble. The fine particles, i.e. those with the greatest surface/volume ratio, will tend to dissolve first. In this instance, we find that successive Coulter measurements indicate a gradually increasing particle size, in accord with the dissolution theory. Alternative electrolyte systems are being examined.

2c) Particle Comminution

Refractory phosphors, such as those described above, are resistant to many methods of particle reduction. The size can be reduced by extended ball milling, but usually less than 25% of the mass will be below 3μm diameter even after prolonged milling, and there will be a high proportion of very fine material. There is also significant contamination from the grinding elements. Planetary milling is faster but with either method, lengthy sedimentation procedures are required to extract the size fraction required.

As an alternative, a McCrone vibratory mill was employed. The grinding vessel is a 125ml capacity polypropylene jar packed with an array of 48 identical solid, cylindrical alumina or agate elements, stacked in six layers. A cross-section of the grinding jar is shown in Fig. 5, illustrating the movement of the elements when the pot is agitated under vibratory milling action. The powder is ground by both impact between the cylindrical surfaces and by shearing between the flat ends of the rows of elements.

All the refractory phosphors described above were ground satisfactorily using this method. Figs. 6 and 7 contrast the effects of ball and McCrone milling.

The advantages we have found for McCrone milling may be summarized as under:

1) Particle dimensions can be reduced to 3μm and below without recourse to sedimentation and elutriation.
2) The particle size spread is reduced indicating minimal creation of unwanted ultrafines.
3) There is no significant increase in contamination, at least when agate grinding elements are used.
4) High yields are obtained.

5) All three phosphors were superior to their commercial counterparts indicating that any structural damage to the crystal during milling is limited.

The main disadvantage of the method is one of scale. Batch sizes are 15-20g per pot. Discussions have taken place with the manufacturers and it is estimated that the cost of prototype equipment designed to accommodate a ten-fold increase would cost over $21,000.

2d) Yttrium Niobates

We have begun an investigation of the yttrium niobate system, initially on the 1:1 compound, i.e. $YNbO_4$. This is a refractory material. The phosphors were prepared by slurrying the oxides of yttrium and niobium with a number of rare earth oxide or nitrates, drying and then firing in stages to 1600°C in air.

It was found that the unactivated material had a fairly broad, deep blue band, peaking at 395 nm, as shown in Fig. 8, with the characteristic activator spectrum superimposed. This is exemplified by the emission spectrum of $YNbO_4$:Eu in Fig. 9. Europium gave the most efficient phosphor and the V/L plot is shown in Fig. 10. Of the rest, thulium and gadolinium, both blue, were of most interest. The investigation is continuing.

3) Powder Phosphor Development etc.
- Alternative Approaches

Although McCrone milling enables refractory phosphors to be satisfactorily ground to produce bright, fine-grain material, a better approach would be to produce fine particles directly from the firing stage, thus eliminating or reducing the necessity for milling. Such an approach should be favoured by the preparation of fine particle precursors, provided, of course, that agglomeration does not occur on firing. Sol-gel methods should satisfy this criterion but we also have evidence that such precursors can be produced by carrying out the precipitation at high temperatures in a microwave cavity.

3a) Microwave Synthesis

Initial experiments were concentrated on yttrium oxide:Eu, a relatively simple phosphor system with straightforward firing methods. The technique was then extended to a blue (Y_2SiO_5:Ce) and a green ($ZnGa_2O_4$:Mn) phosphor. The latter was chosen instead of the refractory YAGAG:Tb as it is a simpler system and would lend itself better for making a direct comparison with a non-microwave method.

The vessels used in the microwave cavity are sealed fluorocarbon bombs (shown in Fig. 11) which can operate at up to 200 psig, resulting in temperatures of 200°C. Oxalates were used as the precursors for all phosphors and were generated from either oxalic acid or, less commonly, from diethyl oxalate. In order to control the pH during precipitation and to simultaneously provide controllable constant pressure conditions, a buffer was added to the bombs at a critical point in the multi-stage process.

i) Y_2O_3:Eu

Experiments were designed around a Taguchi L12 orthogonal array to optimise the parameters influencing fine particle nucleation. The conditions were established to produce a phosphor of 2.5μm median size after a minimum of McCrone milling. Temperatures of only 1200°C were required, much lower than the 1500 °C for the conventional synthesis. The Coulter result in Fig. 12 clearly indicates the symmetry of the particle size distribution associated with the log normal type and is characteristic of well-formed, discrete particles, shown in the SEM (Photograph 2). This may be compared to the non-microwave phosphor in Photograph 3. The gain in efficiency produced by the microwave method is demonstrated in the V/L plot of Fig. 13, where it is compared with a commercial phosphor sample.

ii) Y_2SiO_5:Ce

The method used was to precipitate the mixed rare earth oxalates in a suspension of ultra-fine silicic acid or colloidal silica to give an intimate mixture of oxalate/oxide. Ethyl silicate was also used as an alternative source of silica in a combined sol-gel/microwave process. The variables studied in a series of experiments based on Taguchi principles included the source of silica, the cerium and buffer concentrations, the microwave pressure and the firing conditions. Small concentrations of gadolinium were also added as it has been reported that increased output can be obtained by energy transfer from gadolinium to cerium.

The target median size of particles (2-5μm) was comfortably achieved. Comminution in a McCrone mill was necessary but the times were at least a factor of 6 shorter than for the non-microwave materials. The particle size distributions for phosphors made from different sources are shown in Fig. 14 a, b and c. The phosphor made via the sol-gel process (Fig. 14b) is much closer to a mono disperse system. The 'as-fired' phosphor taken directly from the crucible is shown in the SEMs (Photographs 4a and 4b). The powder contains a wide range of particle sizes with an apparently very fine microstructure (Photograph 4b), which is easily broken down on milling. Some difficulties were encountered in screening some of the samples for testing, giving poor quality coatings. The V/L characteristis of the best sample is shown in Fig. 15. This is slightly less efficient than the commercial material, although there are indications that it may be better at lower voltages. At present, we cannot get accurate readings below 400V.

iii) $ZnGa_2O_4$:Mn

In a conventional method for the preparation of this phosphor which we developed previously, the starting material consisted of the oxides of zinc and gallium intimately mixed with fine manganese (II) carbonate. For the microwave work, and with the experience gained with Y_2O_3:Eu and Y_2SiO_5:Ce, we preferred to use co-precipitated zinc/gallium/manganese oxalate. Phosphors were therefore prepared:

Using oxalate/microwave precursors
Using oxalate/non-microwave precursors
Using mixed oxides(non-microwave) precursors

A common firing procedure was used for all of the samples.

The CL of the 'microwave'phosphor is approaching that of the 'standard' phosphor (Fig. 16) but is significantly better than the oxalate/non-microwave material. All the phosphors were simply sieved before testing with no intervening grinding or milling. The Coulter data in Fig. 17 demonstrates that a significant reduction in particle size was achieved, with a better size distribution for the microwave phosphor. One of the more interesting aspects of the SEMs (Photographs 5 and 6) is the fine sub-structure on the microwave material. This system is still under investigation.

3b) Sol-gel Methods

The basis of the sol-gel process, illustrated in Fig. 18, is the controlled hydrolysis-condensation reactions of molecular precursors giving successively dimers, oligomers, polymers, then a colloidal suspension of solid particles of 1000nm radius. These particles then coalesce to form a gel, a highly viscous network of metal oxide bonds containing trapped solvent molecules. The gel may then be heated to remove solvents and organic groups and to densify the structure.

Initially, work was carried out on the Y_2SiO_5:Eu and Y_2SiO_5:Ce systems using tetraethyl orthosilicate as the SiO_2 source. Inorganic yttrium and rare earth salts were used in an ethanol/water solvent. The reactants were refluxed with HCl to form the metal oxide precursors. The solution was then gelled by raising the pH via the hydrolysis of hexamine. Alternatively, precipitation in a number of non solvents was tried. These included acetone, pentane, water and tetrahydrofuran. The best results were obtained by precipitation in water, at pH10, when very fine particles were formed. However, on drying, the particles tended to stick together. No de-agglomeration was noted after firing at 1380°C and only weak luminescence was observed.

A variety of other techniques were unsuccessfully tried in order to isolate the finely suspended solid material from the aqueous solution without coagulation. These were:

Centrifuging
Filtration
Solvent exchange with mixed non solvents
Rapid evaporation
Freeze drying

One possible method we still intend to pursue is via super critical drying. In this, carbon dioxide is used to replace the water in the solution. This is then removed without going through the liquid phase to leave the material in its very fine original state.

4) **Powder Phosphor Development** - low voltage materials

4a) Substituted ZnO:Zn

The preparation of the bright blue (ZnMg)0:Zn on which we previously reported was further refined using Ar and 90% Ar/10%H_2 as the reductant. By rigorous control of the gas mixture, firing temperature and also the firing time, reproducible phosphor batches can be made. It was particularly noticeable with this phosphor that the photoluminescence is of little value in predicting the cathodoluminescence. The batch size is limited to a maximum of 80g by the size of the tube furnace available. The rotary reactor furnace as used for the standard ZnO:Zn cannot be used because of the corrosive effect of the effluent on the outlet flanges.

The effect of substituting a number of other main group and transition metals from Groups II, III and IV was investigated. All, except the alkaline earth metals, proved very harmful, killing the luminescence. Neither calcium or strontium had much effect on the peak wavelength, but calcium tended to weaken the luminescence. The most interesting substituent was barium where a shift in emission from 505nm to 535-550nm was found, depending on the degree of substitution. The spectral emission of two of these phosphors, compared with that of ZnO:Zn and (ZnMg)O:Zn is shown in Fig. 19. The red shift is obtained at the expense of loss of brightness, as demonstrated in the V/L characteristics (Fig. 20). In Table 2 the characteristics of ZnO:Zn and (ZnMg)O:Zn are compared with two (ZnBa)O:Zn phosphors. An increase in brightness of about 5X would be necessary for it to be compatible with ZnO:Zn.

TABLE 2

Substituted ZnO:Zn Phosphors

Phosphor	**Luminance ftL (at 1500V, 5μA, 1.41mm dia. spot)**	**CL peak nm**
ZnO:Zn	290	504
(ZnMg)O:Zn	136	475
(ZnBa)O:Zn - low Ba	65	535
(ZnBa)O:Zn - high Ba	30	550

4b) Surface Modified Phosphor

In a low voltage phosphor like ZnO:Zn, because of the shallow penetration of electrons, the surface properties are of paramount importance in determining the efficiency of the luminescence process. As has previously been noted in a literature search, the Russians (Dmitrienko et al (12,13)) have been active in this field. They claim that the efficiency and stability of ZnO:Zn can be improved by the inclusion of surface modifiers such as a tungsten. We have examined the effect of this and other surface modifiers and also etchants on ZnO:Zn. As distinct from the lattice substituents described in the previous sections, we believe these modifiers are restricted to the surface layers and have no effect on the spectral emission. We have examined the effect of tungsten, molybdenum, barium, indium and germanium. ZnO:Zn phosphor from various sources was slurried with 0.1%-0.6% of a suitable salt of the metal (a nitrate or ammonium salt). The mixture was dried then heated to 600°C in air for a short period. Improved performance was shown after treatment with tungsten and barium. These were the heaviest of the metals tested. This improvement was not always apparent before ageing. The ageing characteristics for the samples of commercial ZnO:Zn treated with tungsten and barium is shown in Figs. 21 and 22 respectively. It can be seen that there is at least a 50% improvement in the treated samples compared with the control after 30 minutes ageing.

Previously, we had tried etching and found that hydrogen peroxide gave positive results. The procedure was modified and scaled up so that now it is probably our best and most repeatable surface treatment. Initially, there is little difference between etched and unetched samples, but again, the improvement in ageing is obvious, as shown in Fig. 23, for an in-house batch of ZnO:Zn. It was feared that this treatment was simply dissolving the fine particles but there is no evidence of this from the SEMs of etched and unetched phosphor, shown in Photographs 7 and 8.

4c) Zinc Gallate Systems

i) $ZnGa_2O_4$:Mn

The procedure for preparing this phosphor was refined in order to maximise the yield because of the high cost of the gallium oxide raw material. This comprises 70% w/w of the phosphor. Reduction with Ar/H_2 was found to give more consistent results than activated charcoal reduction and it was also found possible to recover sub-standard material by re-oxidation than re-reduction so that over 80% of the Ga_2O_3 can now be utilised.

ii) $ZnGa_2O_4$

The blue self-activated phosphor was also investigated. The CL intensity is at a much lower level than Zn:Ga_2O_4:Mn. It peaks at 430nm but with a much broader emission than the Mn activated phosphor (Fig. 24).

iii) Rare earth activated $ZnGa_2O_4$

A series of rare earths at around the 1% level were introduced into the $ZnGa_2O_4$ lattice. In the oxidized state, only Eu showed any significant CL emission but this was at a much lower level than for known Eu^{III} activated phosphors. Only Gd gave any noticeable CL emission on reduction but the intensity was no greater than the self-activated phosphor.

4d) Tin oxide:europium

As there still seemed some demand from industry for this phosphor, it was briefly re-investigated. The fluxed mixed oxide route was used in which the oxides are intimately mixed with alkaline earth chlorides by milling in 2-propanol. High firing temperatures of 1500°C and above were essential to obtain significant luminescence. The product is acid washed to remove flux and then McCrone milled to reduce the particles to 3-4μm diameter. It was found that much of the luminescence lost on milling could be regained by a short high temperature annealing with little increase in particle size. The final material is still inefficient as can be seen in the V/L data in Fig. 25, although it should respond to further experimentation.

5) Thin Film Phosphor Systems

5a) Simple Layers

Significant progress has been made in producing bright, luminescent thin films from organometallic precursors dissolved in organic solvents. The system, as shown in Fig. 26 was used but it proved very difficult to produce even films over an area greater than about 8mm^2. This system was therefore modified. The use of a peristaltic pump ensured better control of the liquid flow to the nebuliser in order to produce a fine mist spray over the substrates. The mist reservoir and reaction chamber were abandoned and, instead, the spray mist was passed directly over the substrates, which are heated to a temperature between 430°C and 470°C. This method provided for an increased growth rate from 10nm/min to 100nm/min but, more importantly, gave even films.

The preparation of bright, luminescent thin films not only relies on the precursors and the spraying method used, but relies heavily on the annealing conditions. The annealing procedure determines, to a great extent, the type of substrate employed. For films of ZnO:Zn, (Zn,Mg)O:Zn and $ZnGa_2O_4$:Mn, quartz substrates are sufficient, while for Y_2O_3:Eu, SnO_2:Eu, YAG and YAGAG films, which require higher annealing temperatures, sapphire substrates are needed.

ZnO:Zn

A range of films was prepared varying in thickness between 150nm and 2µm. The thickness of these, as with other phosphor films, was calculated from the internodal separation of a UV/VIS scan combined with examination of SEM photographs. The opacity of these films increases rapidly over 1µm, and from 1-2µm a double layer structure is present. The thicker layers tend to be powdery showing poor adhesion, the top layer can be separated from the layer that adheres to the substrate. This is clearly evident from Photograph 9. It has been established that this remaining layer still shows CL. The V/L plot over the range of thicknesses is shown in Fig. 27and this result demonstrates that even the thinnest films made produce CL. With thicker 2µm films of high current densities, luminance values exceeding 1000 ftL have been recorded (Fig. 28).

YAG:Tb and YAGAG:Tb

Thin films of both $Y_3Al_5O_{12}$:Tb (YAG) and $Y_3(Al/Ga)_5O_{12}$:Tb (YAGAG) were produced from mixed solutions of acetonyl acetate precursors. The colour and intensity of the emission depended both upon the Tb concentration and the Al/Ga ratio, similar to the observations reported by Ohno and Abe (14). For low Tb levels, the emission is distinctly blue (Fig. 29). As the Tb concentration is increased, it can be seen that the colour changes to green/yellow. There is also some rearrangement of the spectral power distribution when some Al is replaced by Ga (Fig. 30). Although the intensity of the CL is stronger at high Tb levels, it is unstable, showing distinct hysterisis during measurement of CL characteristics. After prolonged ageing at 1500V and 5µA, some stability was achieved and the V/L characterstics from YAGAG are shown in Fig. 31.

Y_2O_3:Eu

The quality of these films was improved by using very dilute solutions of the acetonyl acetate precursors which resulted in a much finer mist. A programmed annealing procedure was also introduced to ensure good adhesion to the sapphire substrate. As a result, we achieved our best results to date, demonstrated by the I/L characteristics in Fig. 32.

5b) Multilayer Structures

The effect of various interlayers between the substrate and a thin ZnO:Zn film is being examined. Internal controls were provided by masking half the substrate during the initial oxide deposition to give a multilayer structure like that shown in Fig. 33. All the layers, both phosphor and the intermediate layers, were deposited by aerosol spray pyrolysis. Most of the results so far have been obtained using a tin oxide interlayer. The V/L characteristics for a range of thicknesses of ZnO:Zn up to 0.45μm on a SnO_2 film about 0.5μm thick are shown in Fig. 34. In each case, the CL is improved compared with a simple layer, but interestingly the PL was reduced. Similar results were found with thinner SnO_2 interlayers (Fig. 35). We cannot be too definite about the mechanism of the process but it would appear that for CL to occur, only a very thin film is required, but that a greater volume is necessary for multiplication processes that increase efficiency. Experiments using Y_2O_3 and Al_2O_3 are still in an early stage.

6) Cathodoluminescence Measurements

Low Voltage System

Earlier this year, CL data on the same ZnO:Zn and Y_2O_3:Eu thin films was exchanged between the ARL at Fort Monmouth and the University of Greenwich. There was good agreement when the uncorrected beam current measurements were compared, as illustrated in Fig. 36 for the Y_2O_3:Eu film. As expected, the true current readings obtained via a Faraday cup were around an order of magnitude lower.

Modifications to our low voltage system were required in order to accommodate, firstly, a Faraday cup and, secondly, a multiple sample holder. A manipulator has been installed along with a multisample holder built to our own design. This holder enables up to six samples and a Faraday cup to be accommodated in the vacuum chamber. This new design has considerably accelerated the throughput of samples for measurement. The sample holder at present is made from PTFE. Some problems have been encountered with suitable earthing and a design has been submitted for the manufacture of an aluminium sample holder.

High Voltage System

The high vacuum system has been installed but the teething troubles with the rotary pumps have yet to be overcome. This is a much larger system than the low voltage one, with access flanges of 200 and 150mm compared with 70mm. It is also more versatile, provided with more manipulative facilities for the samples. Conversely, because of its size and the use of diffusion pumps (not turbo pumps), it takes longer to evacuate, with a higher probability of leaks.

The vacuum system consists of a stainless steel body separated into two independently pumped compartments by a manual gate valve. The smaller compartment serves as an antechamber for loading workpieces into the system. At present it is fitted with a horizontal motorised manipulator arm. Each compartment has its own diffusion/rotary pump provision and the main vacuum chamber has an added titanium sublimation pump. In normal operation, the system is capable of reaching 10^{-9} torr but with the sublimation pump back up, it can reach 10^{-10} torr. There is a gate valve system which allows the main chamber to remain under vacuum during sample changes. There are several view ports on the system, all at strategic locations, to allow full observation and also an additional vertically mounted x-y-z manipulator. An electron gun, with a capability of 20keV and incorporating a raster provision, has been purchased from Kimball Physics and is awaiting installation.

7) Collaborative Programmes with other ARPA Contractors

We have supplied appreciable quantities of phosphors to Micron, SIDT, as well as Sandia and Motorola. We have begun interchange of information with PTCOE, the University of Floriday, the University of Colorado, Sandia and MCNC, as well as our long-standing collaboration with the ARL at Fort Monmouth.

8) Conclusions

In the first year of the ARPA contract number N68171-94-C-9110, considerable progress has been made towards the main objectives outlined in the introduction. Methods of synthesising fine powder phosphors (1.7-3.2μm diameter) were developed. This was applied particularly to the refractory RGB systems of Y_2O_3:Eu, $Y_3(Al/Ga)_5O_{12}$:Tb and Y_2SiO_3:Ce respectively. It involved the use of a McCrone vibratory mill for comminution and gave high yields of phosphors which were more efficient than the commercial equivalents.

We also used synthetic methods involving microwave heating for producing fine grain precursors. The different morphology of the microwave phosphor appeared to favour shorter milling times with less consequential damage to the phosphor lattice. The results are very promising but further investigation is necessary. At present, we can produce improved Y_2O_3:Eu, whileY_2SiO_3:Ce and the saturated green $ZnGa_2O_4$:Mn are approaching our best. Sol-gel methods have also been investigated but, at present, cannot translate the small particles from the gel into discrete phosphor powder particles.

On low voltage materials, we have found that by modifying the surface of ZnO:Zn further by the introduction of foreign ions, or by an etching routine, we can improve the performance. These modifications have a marked effect on the maintenance of the phosphors. On new phosphor lattices we have modified the ZnO:Zn by substituting some of the zinc with alkaline earth metals. Barium was of particular interest, producing a shift of up to 30nm towards the red but with loss of efficiency. We have started to investigate yttrium niobate systems activated by rare earths.

Considerable improvement in the control of the deposition conditions for thin films has been achieved. We have prepared films of ZnO with a range of thicknesses from 0.15-2μm and have achieved the best ZnO results reported so far, yielding a brightness of over 1000 ftL. Similarly, we have obtained up to 250 ftL with Y_2O_3:Eu. A study of the preparation of multilayered systems is making considerable progress. It would appear that the results obtained so far point to the nature of the light emitting process taking place, as well as yielding improved performance. The possibility of two colour systems has been demonstrated and we hope to extend this work although this was not specified in our initial programme of work.

We have modified our low voltage measurement system to enable more accurate measurements to be taken with a faster throughput and have also acquired a high voltage system which, at present, is being assembled.

9) Future Work

We believe that much emphasis should be be placed on the surface treatment of phosphor systems in general to improve their maintenance and efficiency, more especially, low voltage. The study on niobates and related phosphors must be extended to other new systems. The increased scale modifications on both McCrone milling and microwave synthesis must be pursued. The thin film programme will be extended to a range of other phosphors, both in simple and composite structures. Our initial results indicate that the role of thicknesses and structure were previously underestimated and may well guide us to a true understanding of the processes taking place.

10) References

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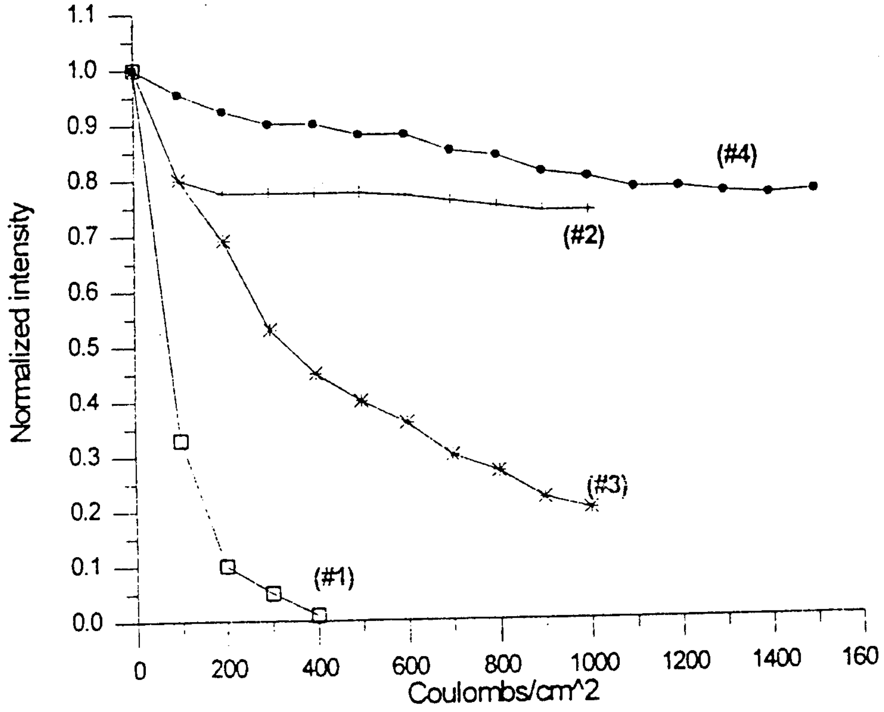


(#1) - ZnS:Cu,Al standard, (#2) - ZnS:Cu,Al - SIDT doped
(#2) - Y2O2S:Eu standard, (#4) - Y2O2S:Eu - SIDT doped

Fig. 1 - Phosphor coulombic aging at 700 V and 10 mA/cm^2.

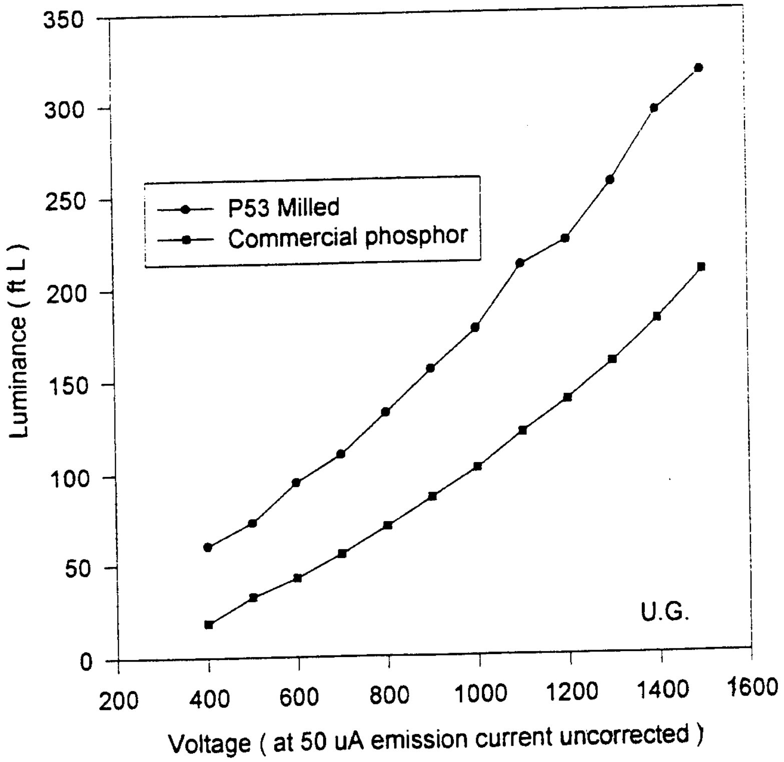


Fig 2 V/L Characteristics for P53

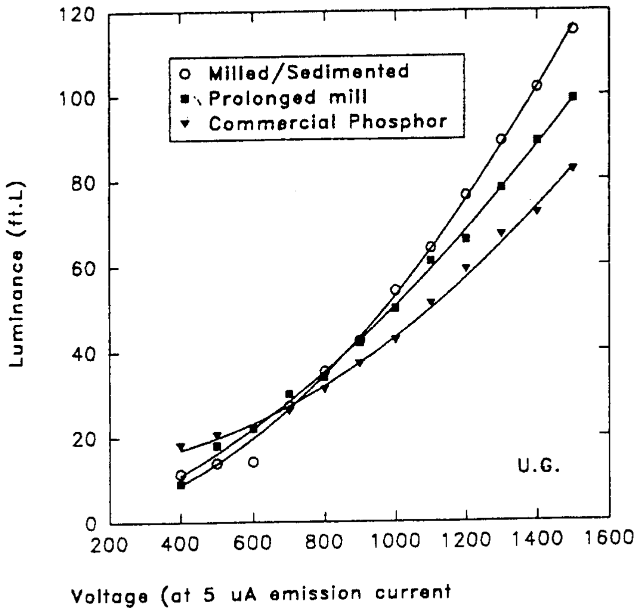
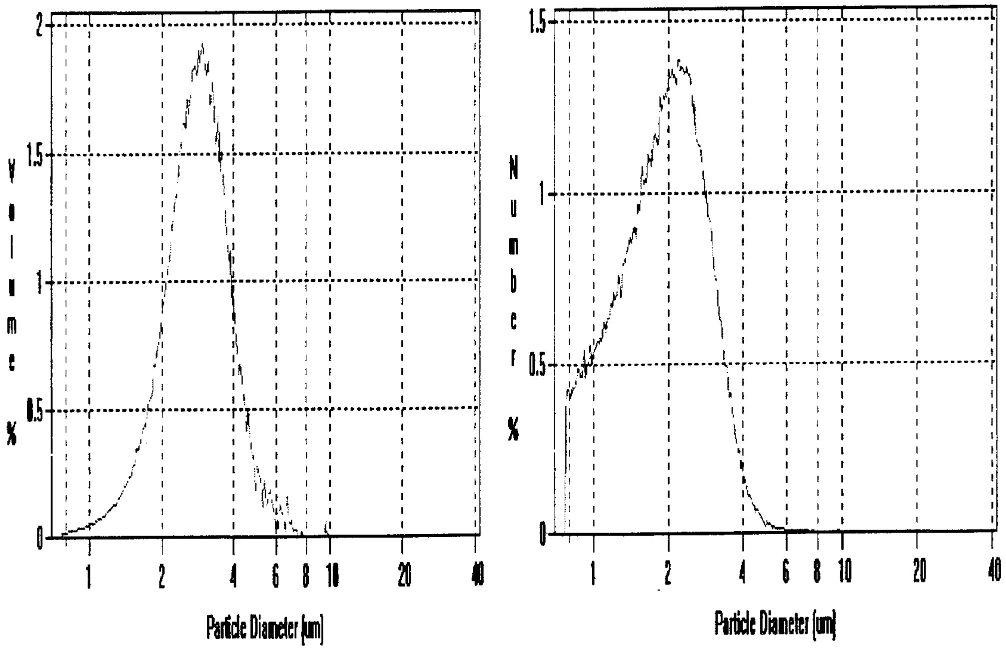


Fig 3 V/L Characterisitics for P47



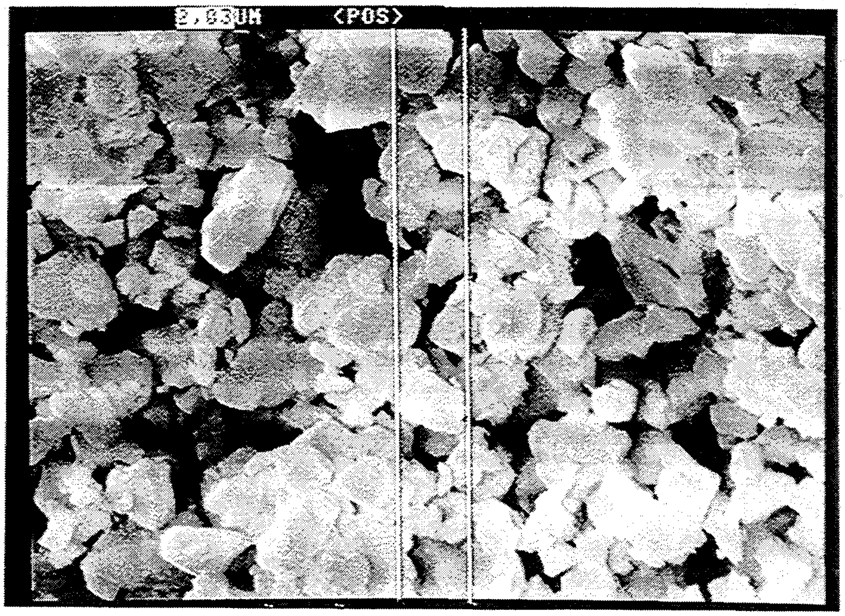
(median 2.84μm)

Fig. 4a. Volume statistics

(median 1.95μm)

Fig. 4b. Number statistics

Fig 4 Coulter results for P56



Photograph 1 SEM of P56

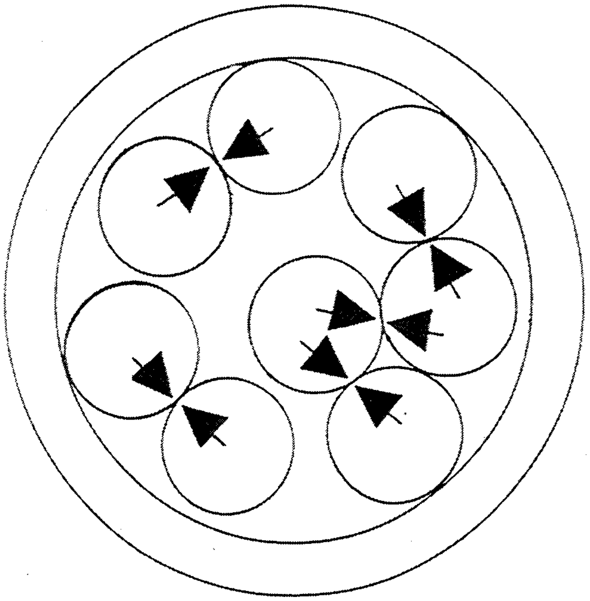


Fig. 5 Cross section of a McCrone grinding jar

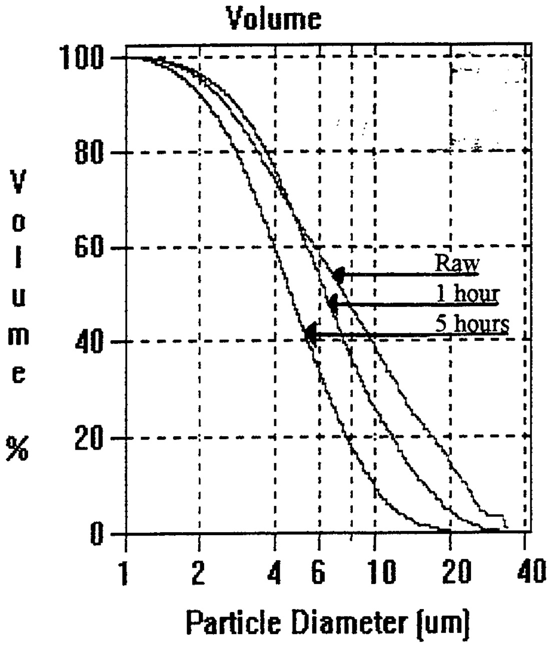


Fig. 6 P56 Particle size reduction on ball milling

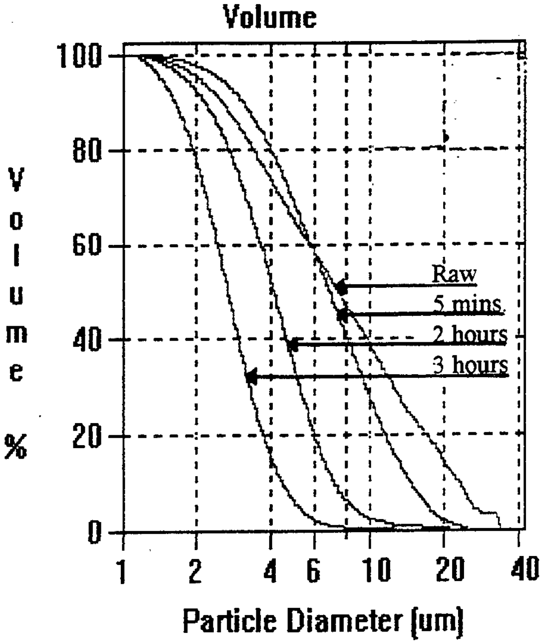


Fig. 7 P56 Particle size reduction on McCrone milling

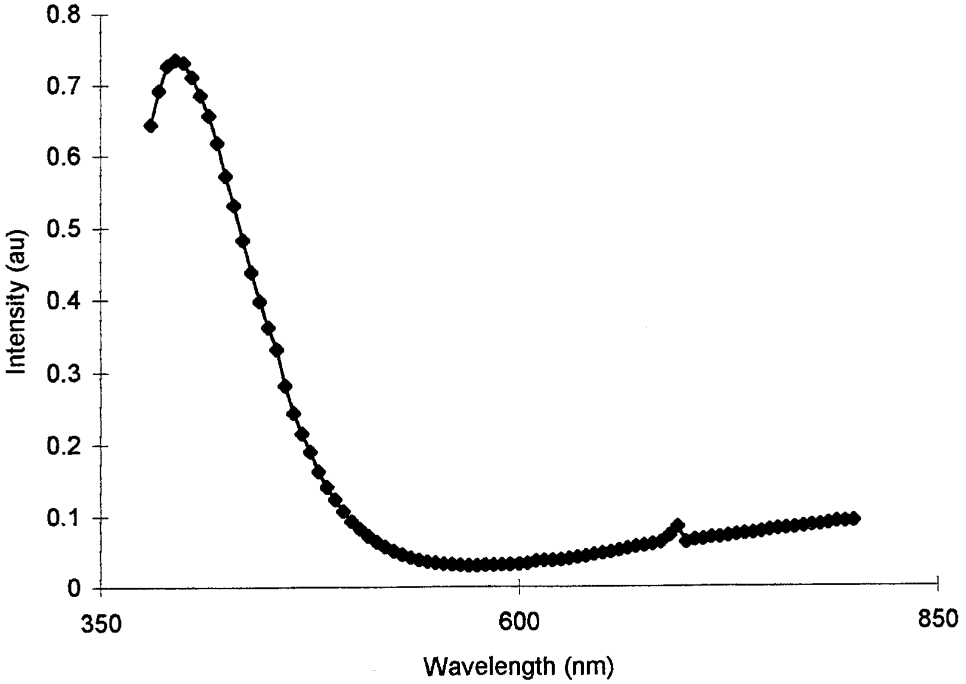


Fig. 8 CL spectral emission of YNbO4

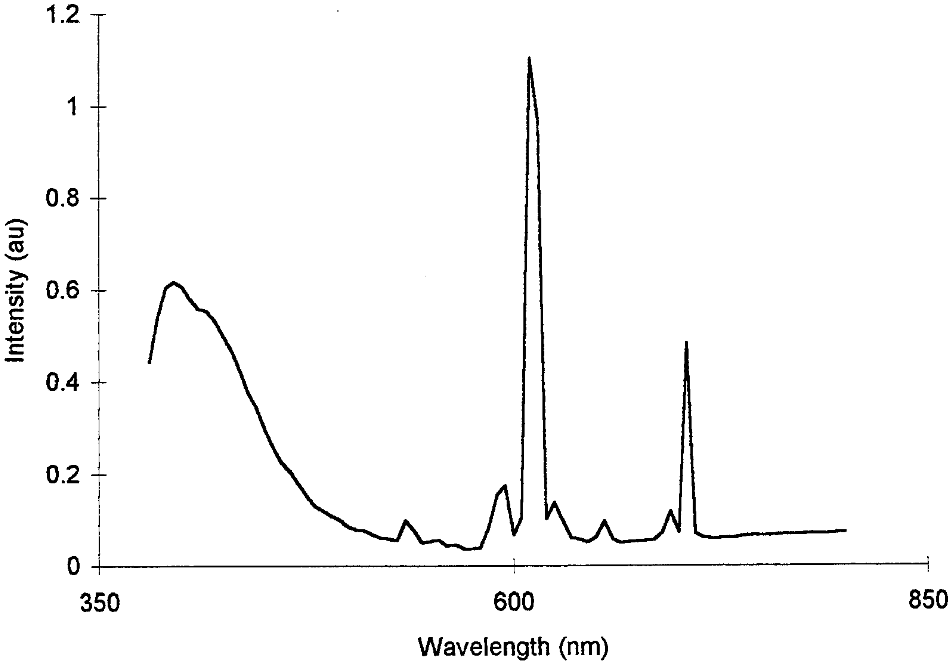


Fig. 9 CL spectral emission of YNbO4:Eu

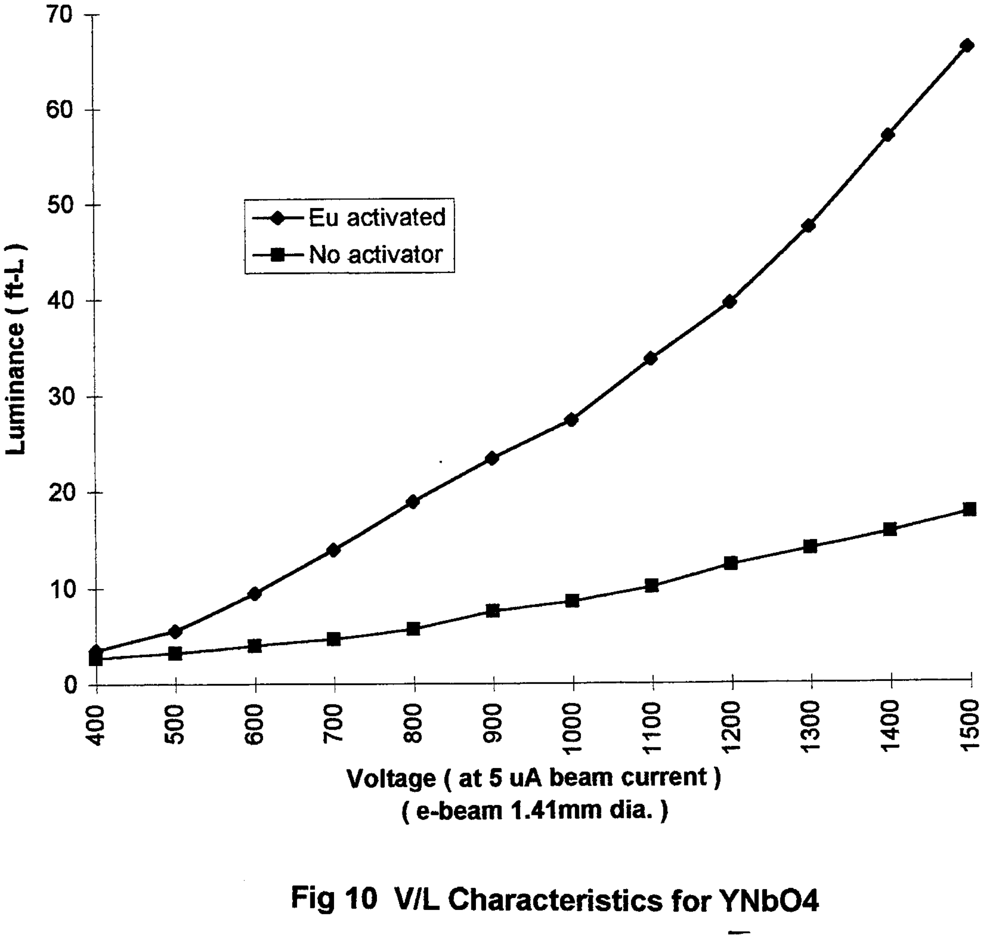


Fig 10 V/L Characteristics for YNbO4

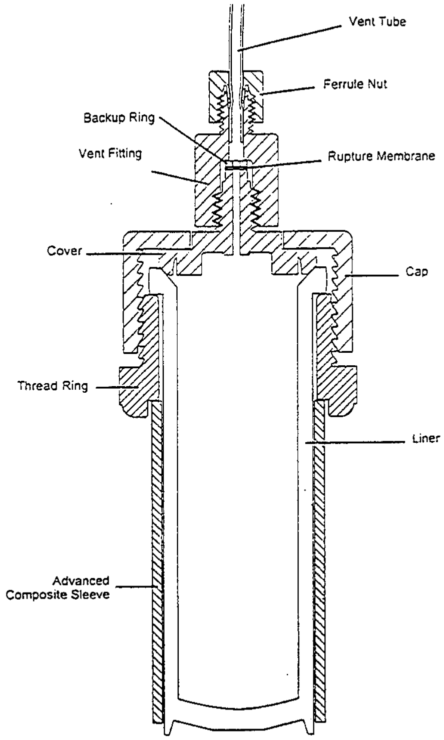


Fig 11 Microwave digestion vessel

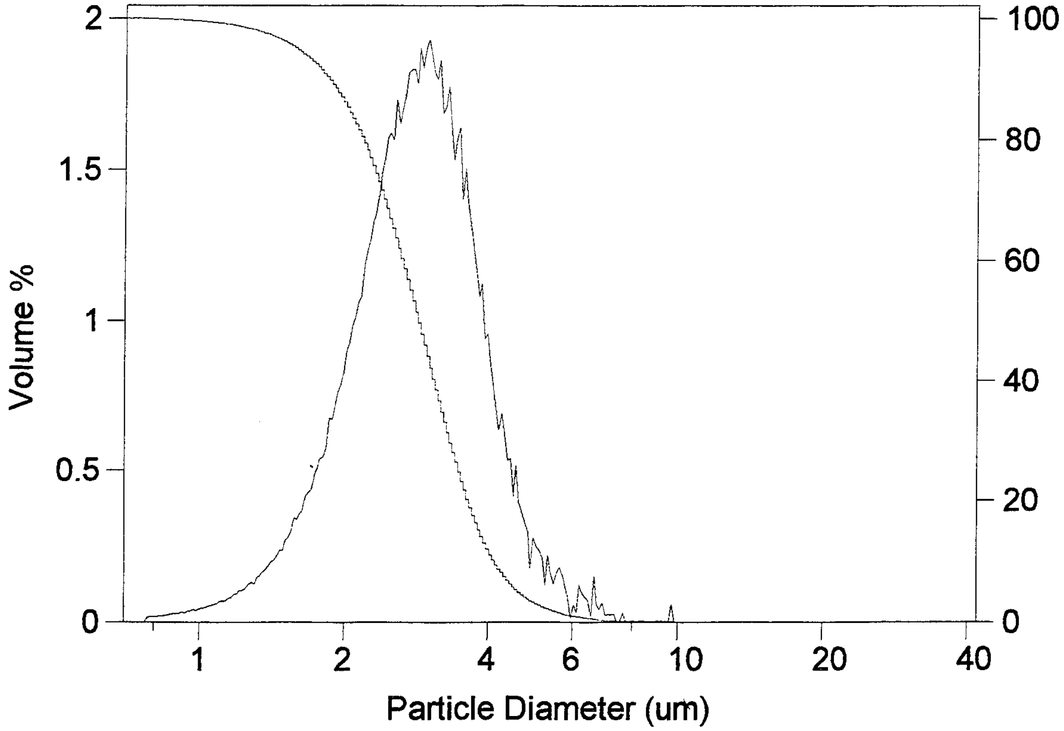
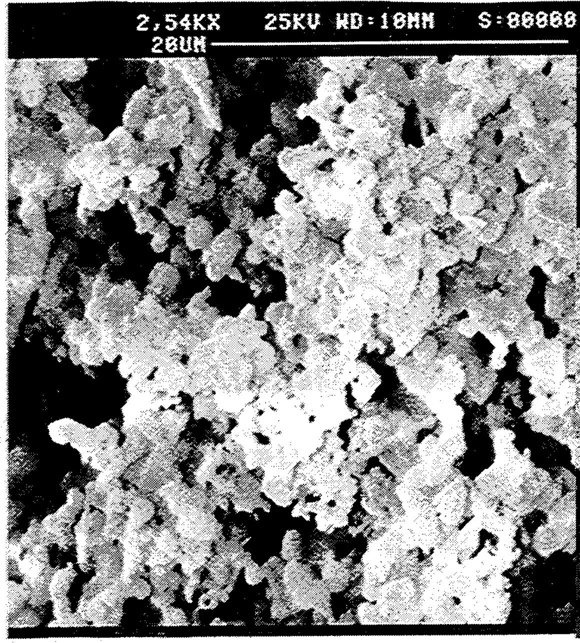
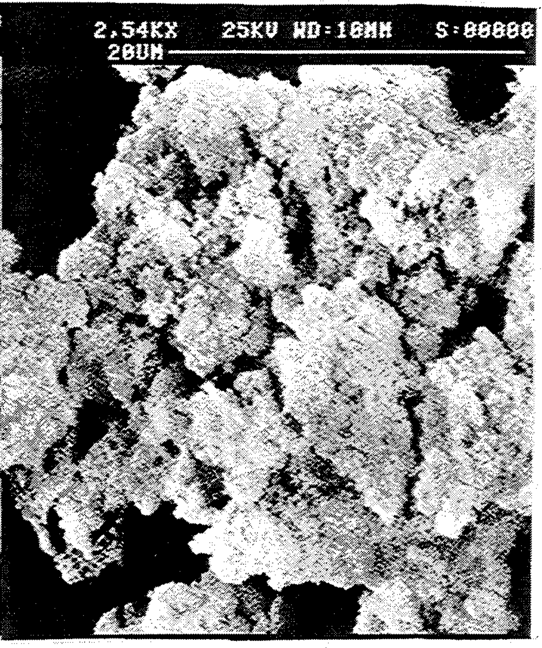


Fig 12 Coulter results for P56



Photograph 2 SEM of microwave P56



Photograph 3 SEM of non-microwave P56

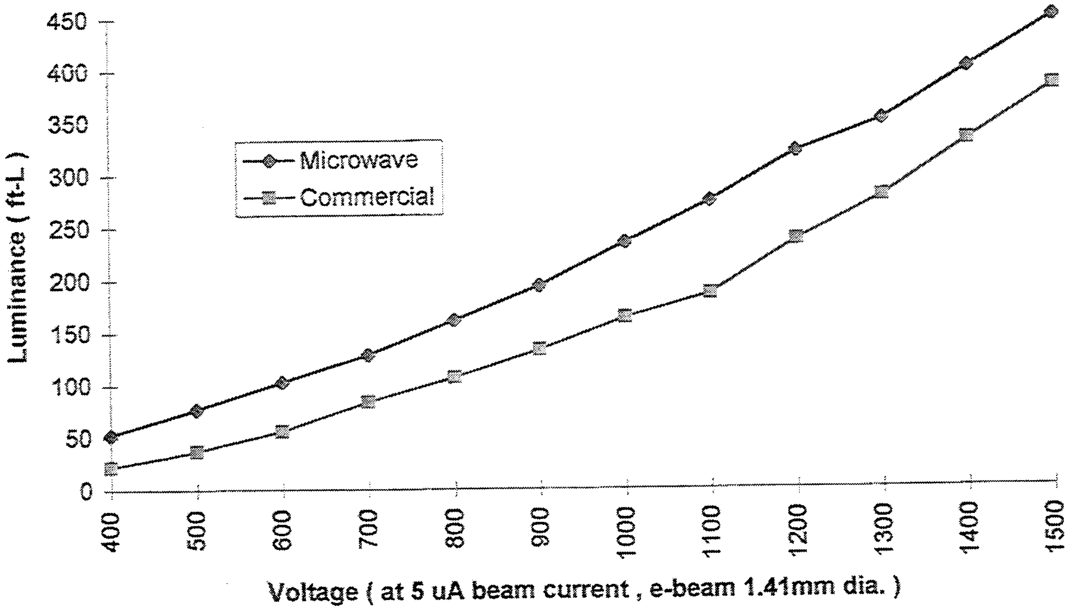


Fig. 13 V/L Characteristics of Y_2O_3:Eu Phosphors

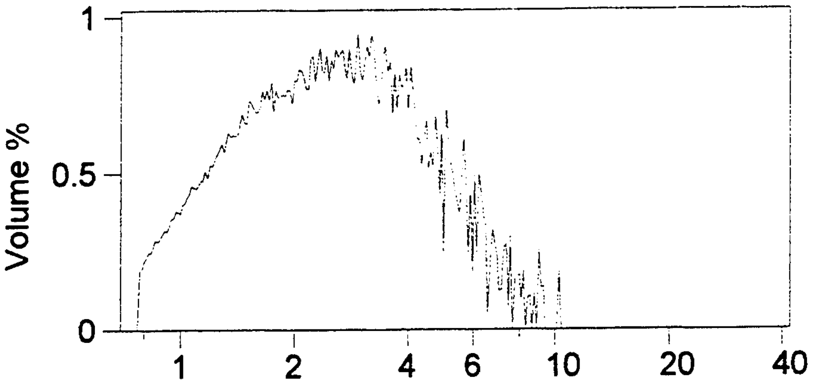


Fig. 14a. Microwave - Colloidal SiO_2

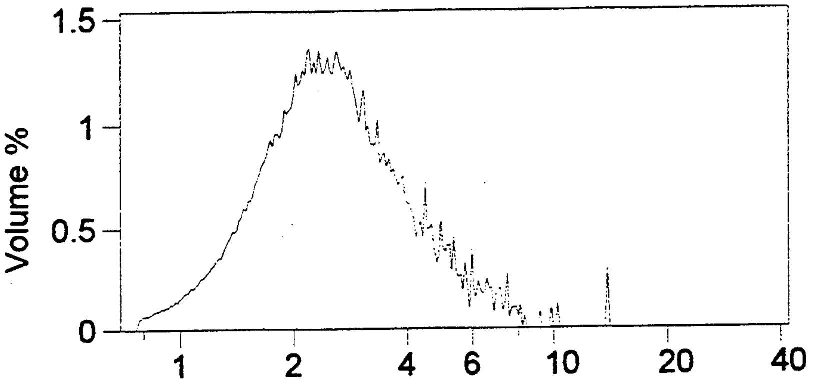


Fig. 14b. Microwave -Sol Gel , using ethylsilicate

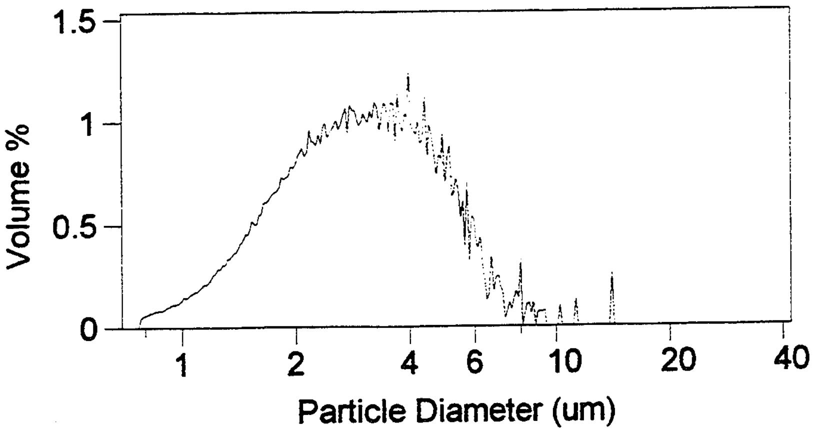
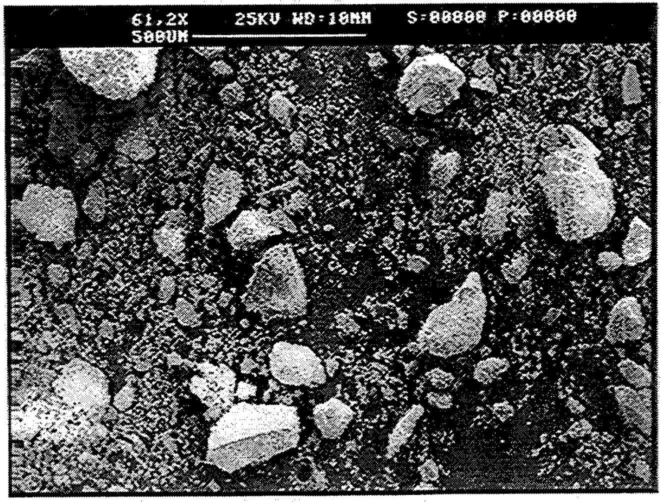
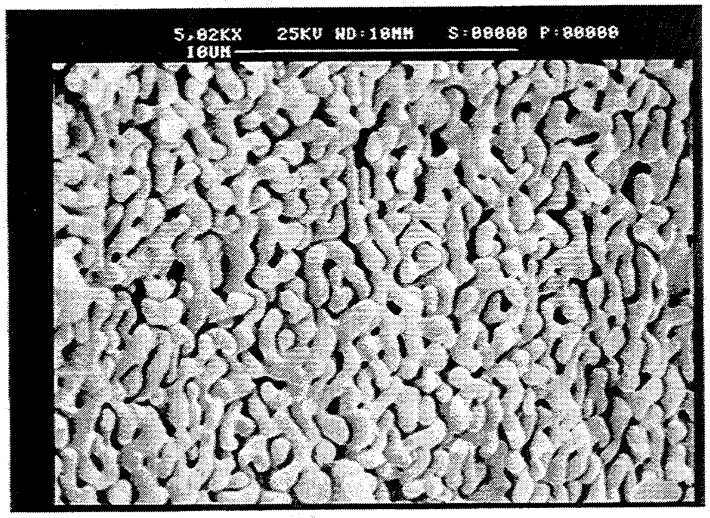


Fig. 14c. Non Microwave

Fig. 14 Coulter results for P47



a) Showing large range of particle sizes



b) Demonstrates fine structure

Photograph 4 Fine structure of Y_2SiO_5:Ce

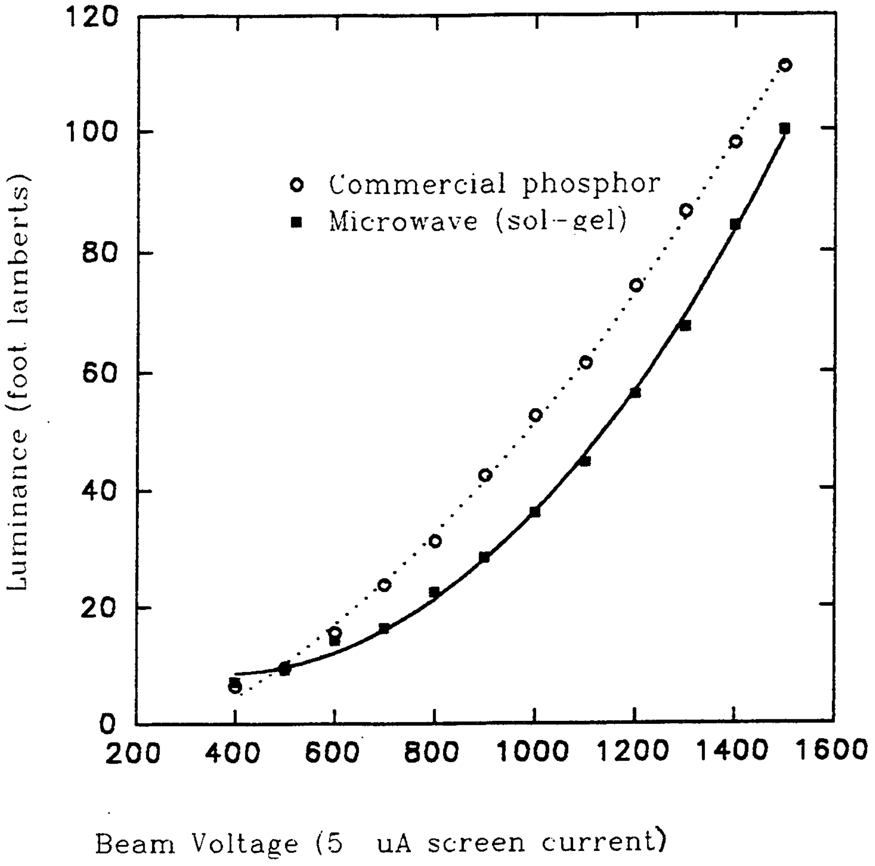


Fig 15 V/L characteristics for P47

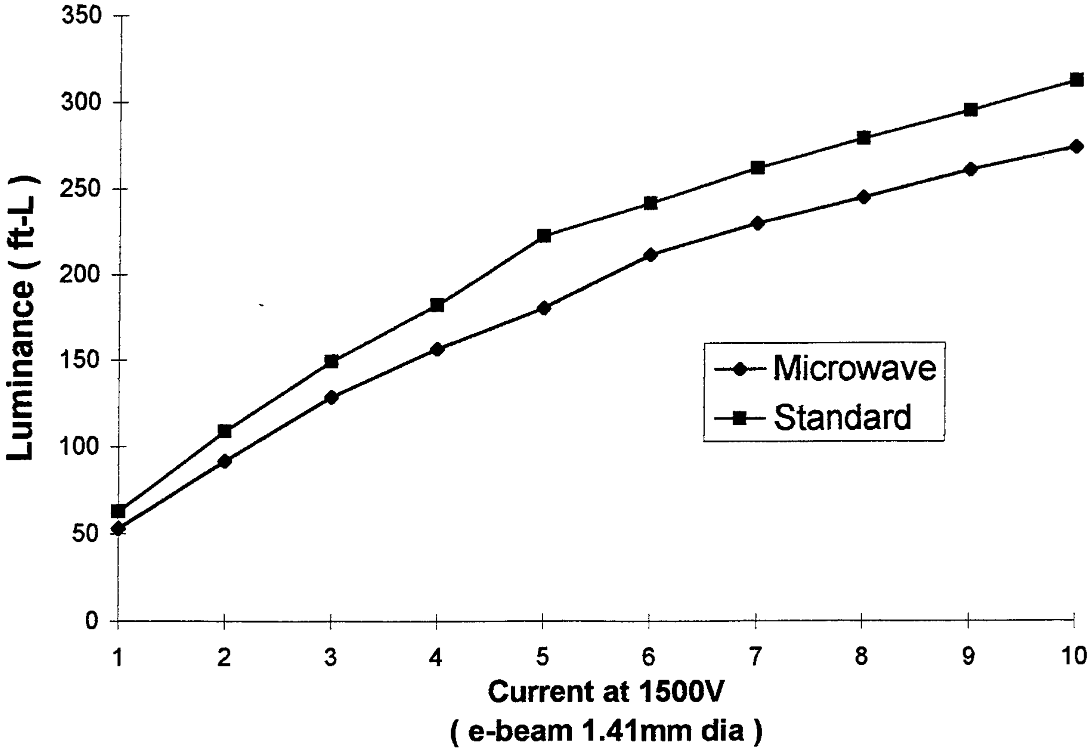


Fig 16 I/L characteristics for ZnGa2O4:Mn

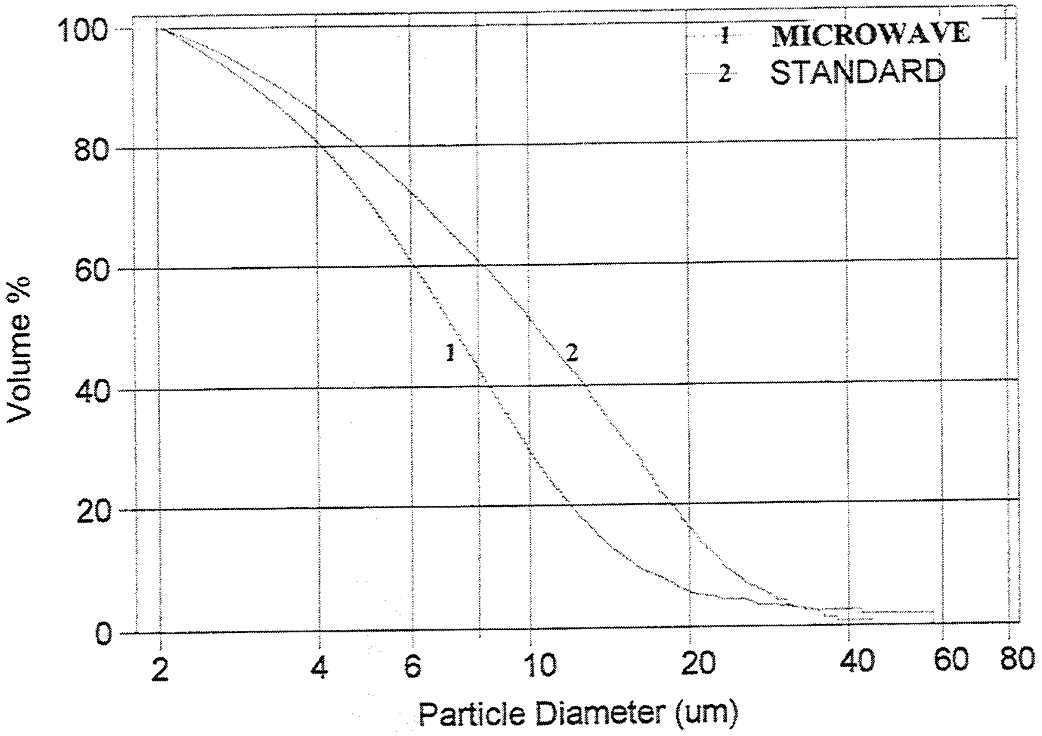
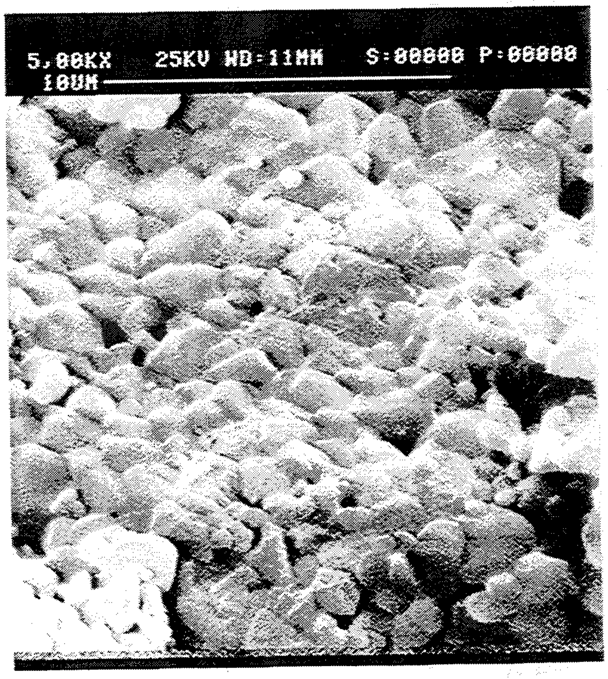
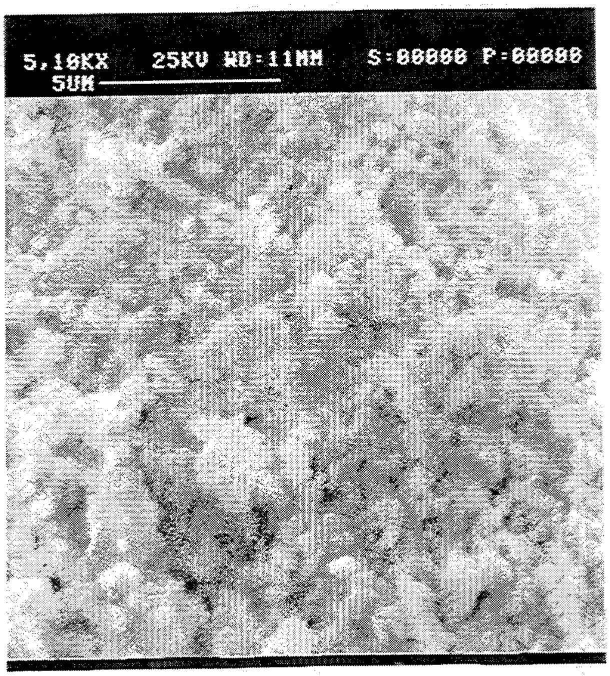


Fig 17 Coulter results for ZnGa2O4:Mn



Photograph 5 SEM of standard $ZnGa_2O_4$:Mn



Photograph 6 SEM of microwave $ZnGa_2O_4$:Mn

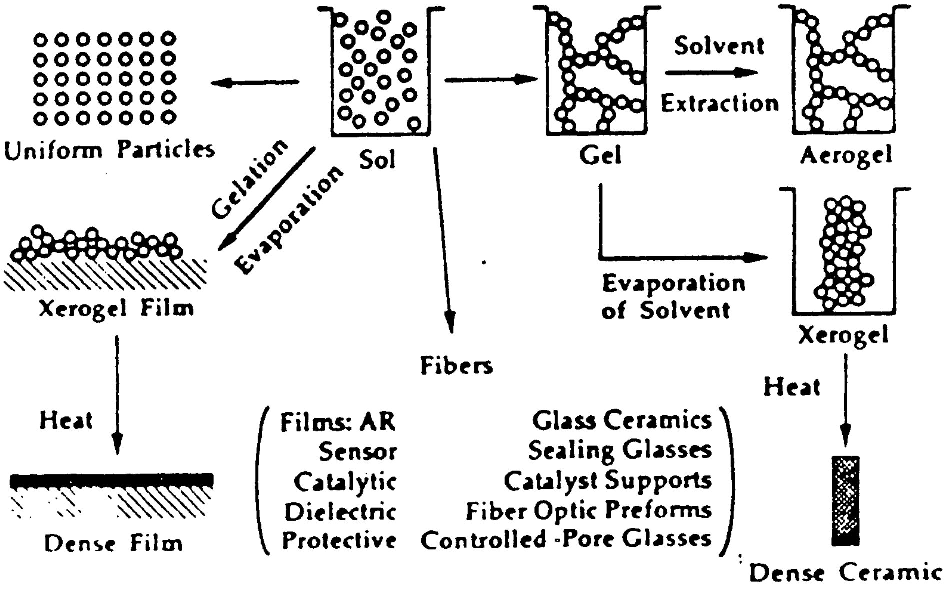


Fig. 18 Overview of sol-gel process.

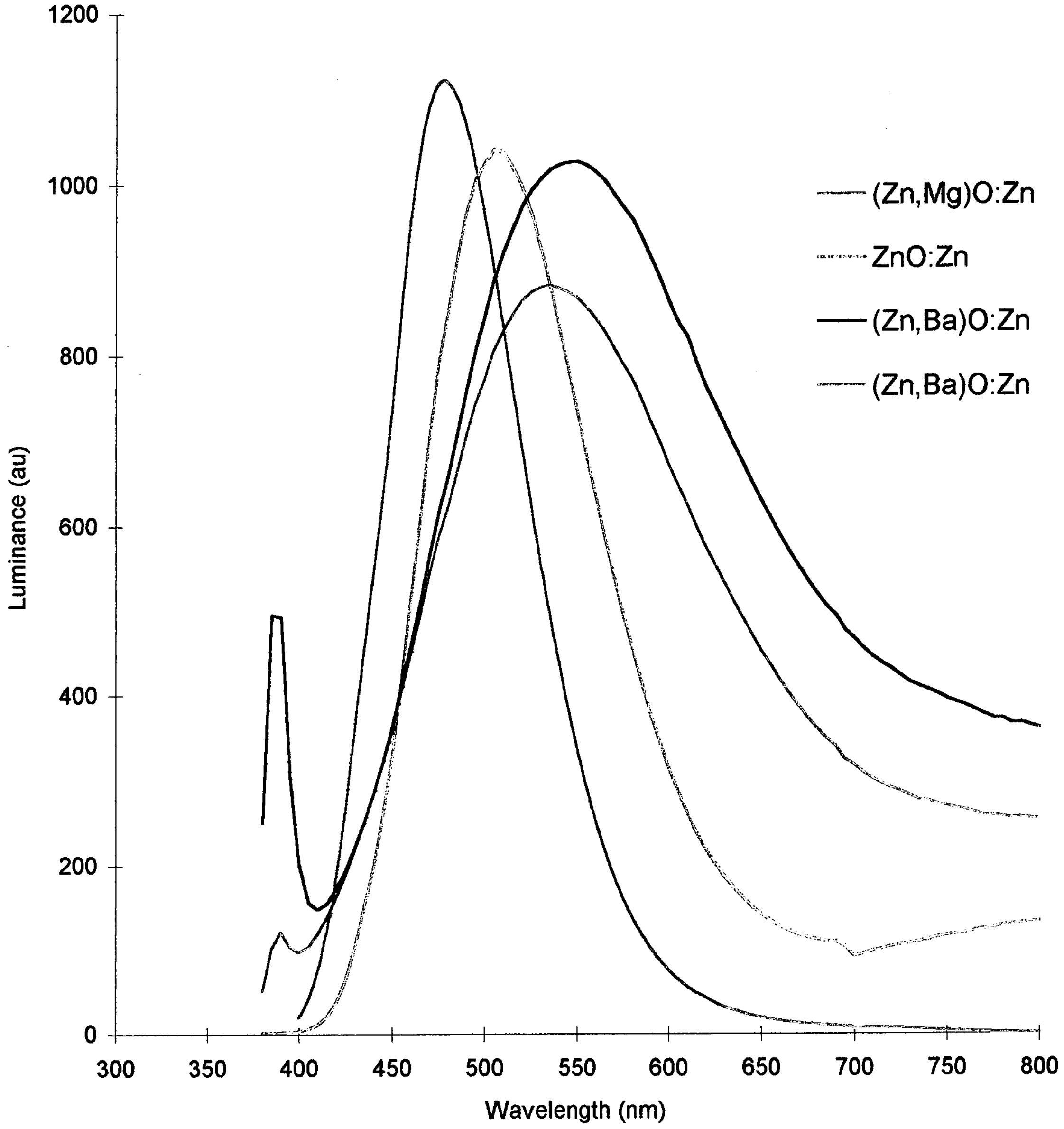


Fig. 19 Spectral emission of substituted ZnO:Zn phosphors

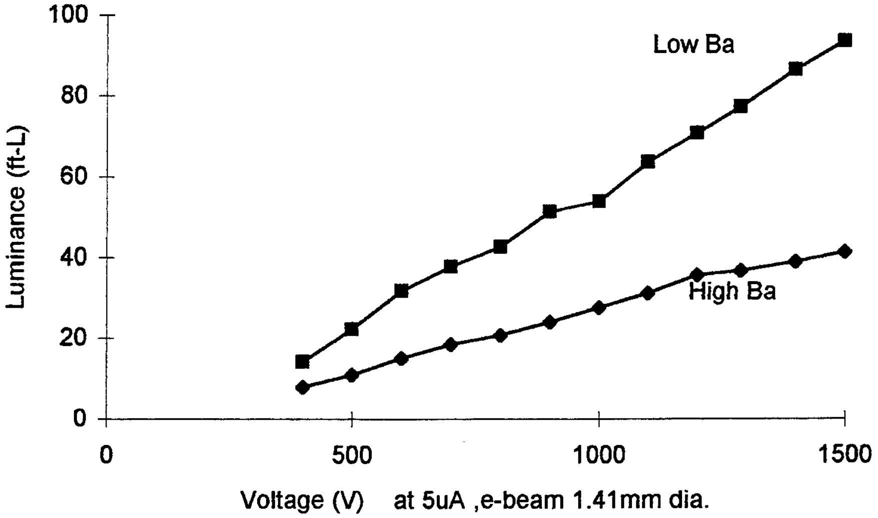


Fig. 20 V/L characteristics of (Zn,Ba)O:Zn

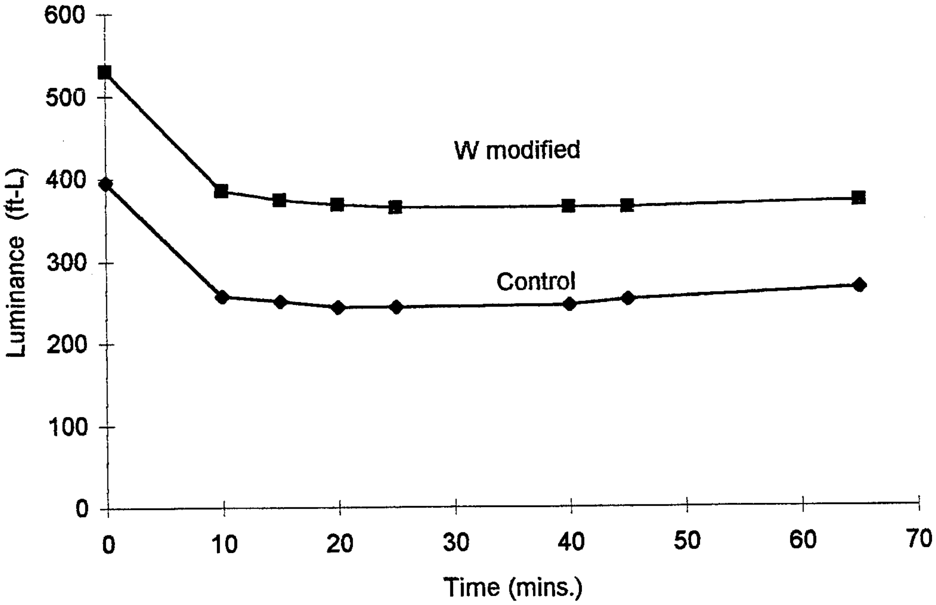


Fig. 21 Ageing characteristics of best ZnO:Zn commerical phosphor, tungsten modified

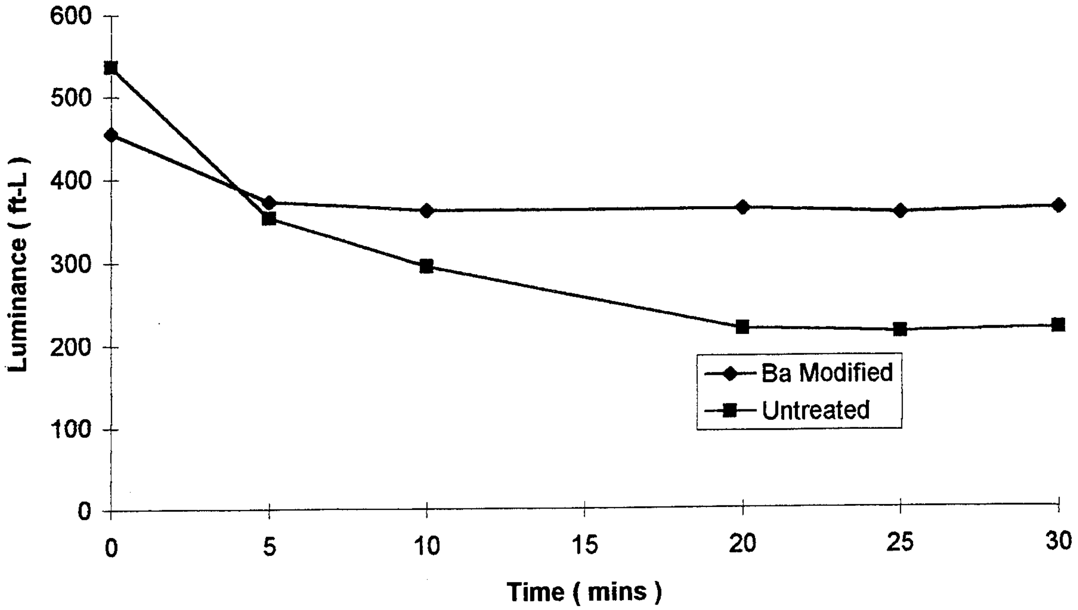


Fig. 22 **Maintenance of treated commercial ZnO:Zn (1500V, 5 uA current, e-beam 1.41mm dia).**

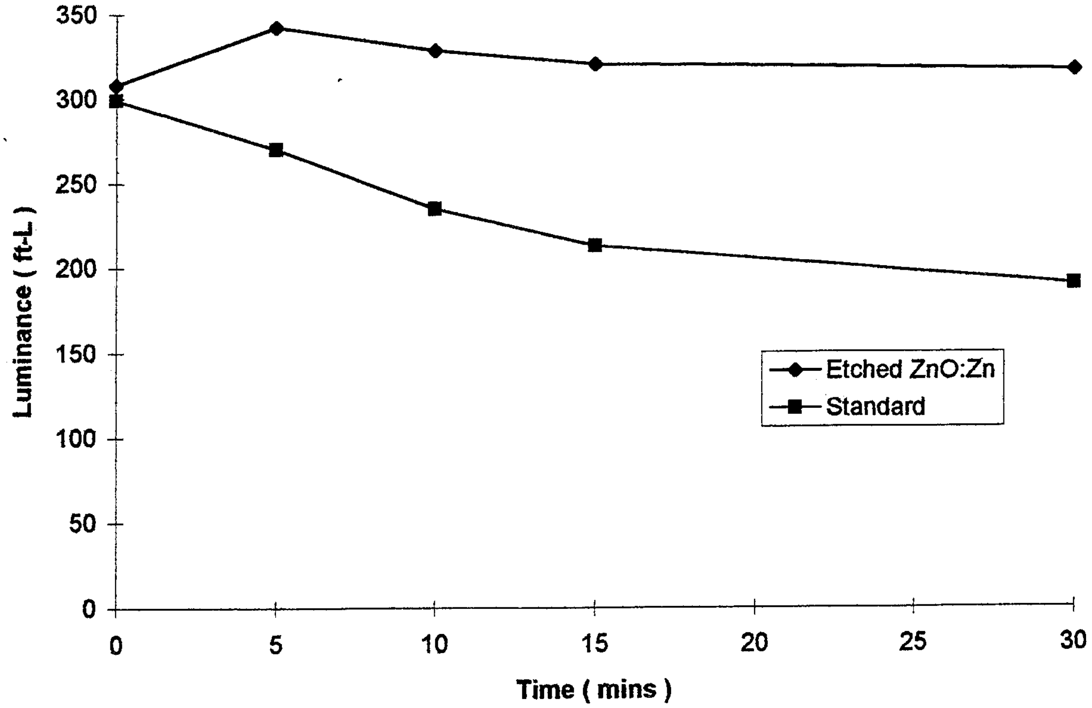
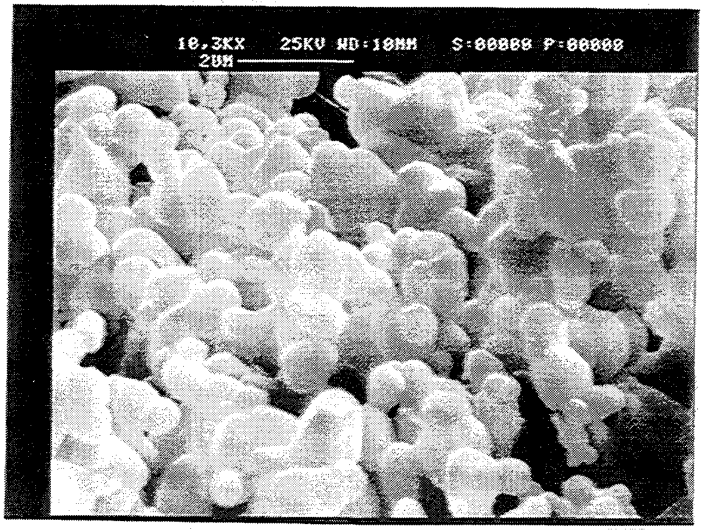
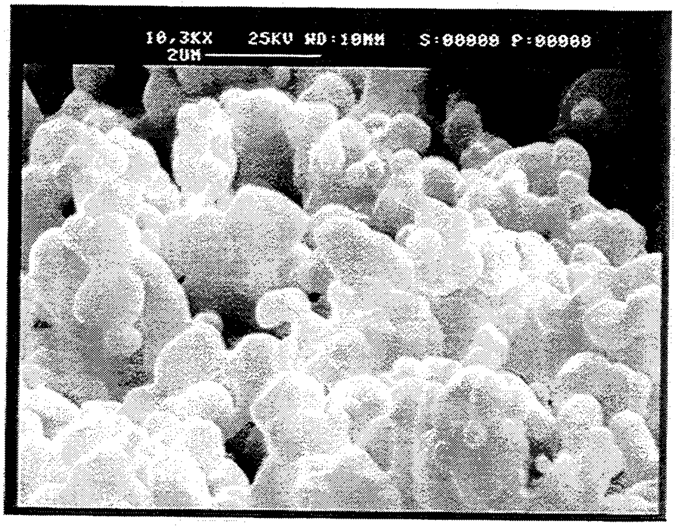


Fig. 23 **Maintenance of H_2O_2 etched ZnO:Zn phosphor (1500V, 5 uA beam current, e-beam 1.41mm dia).**



Photograph 7 Standard ZnO:Zn phosphor



Photograph 8 H_2O_2 etched ZnO:Zn phosphor

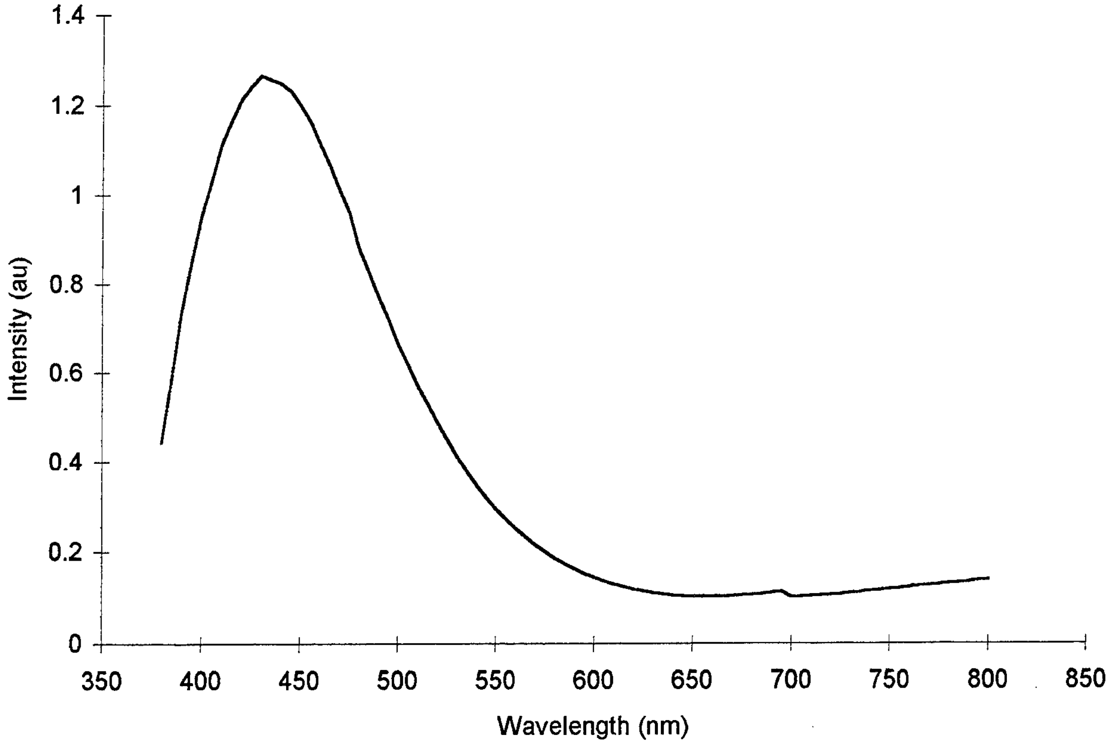


Fig. 24 CL spectral emission of ZnGa2O4

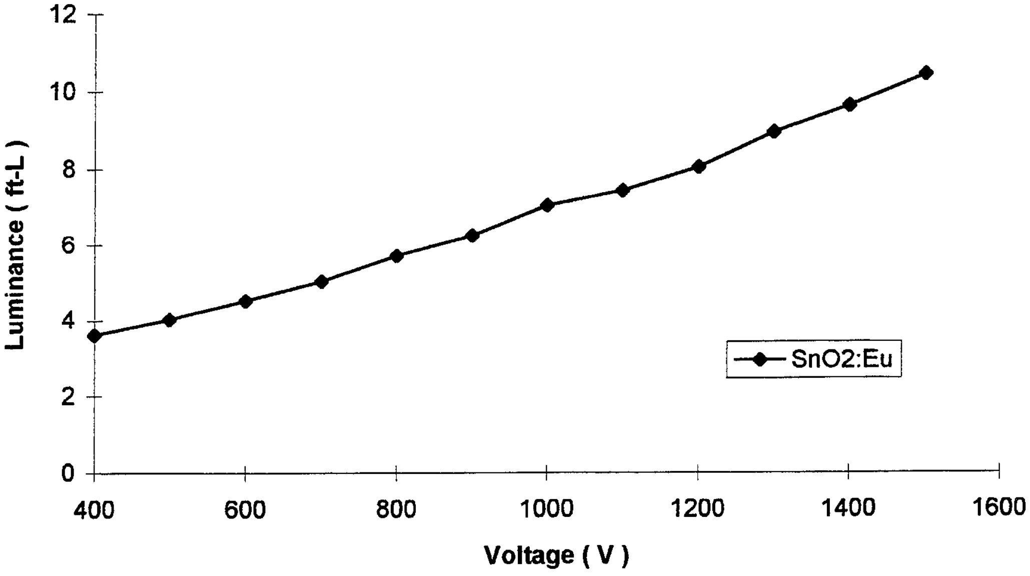


Fig. 25 V/L Characteristics of SnO_2:Eu
(at 5 uA beam current , e-beam 1.41mm dia.)

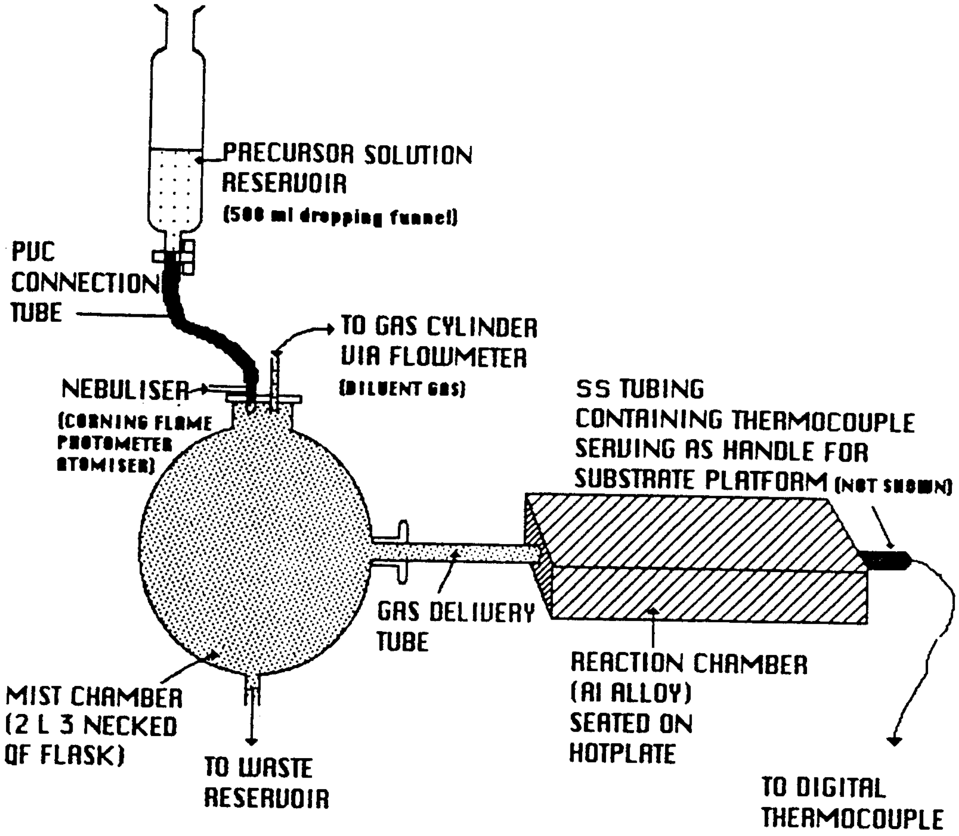
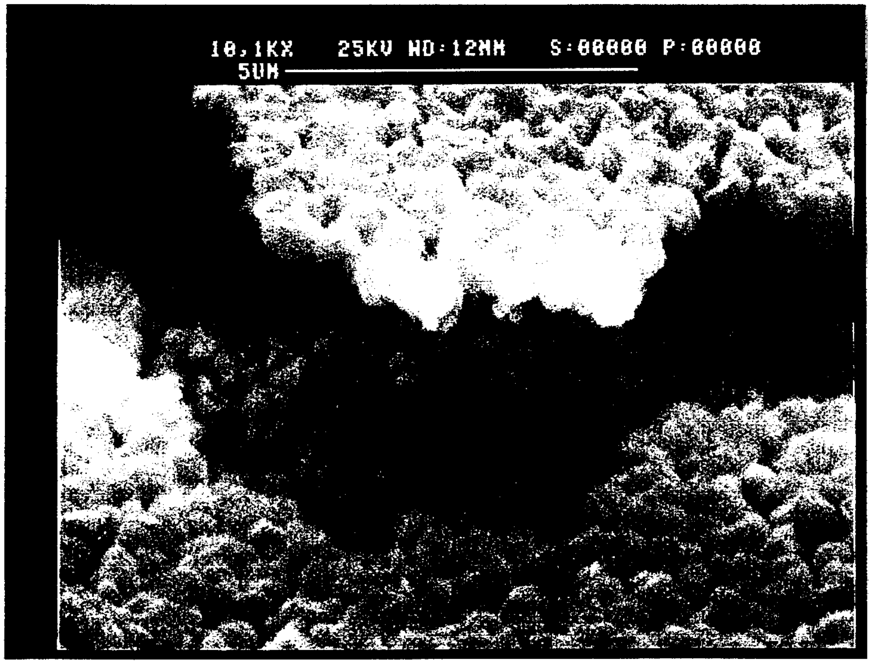


Fig. 26 Simplified sketch of apparatus used for ASP



Photograph 9 **SEM of a 1.2μm ZnO:Zn thin film .**

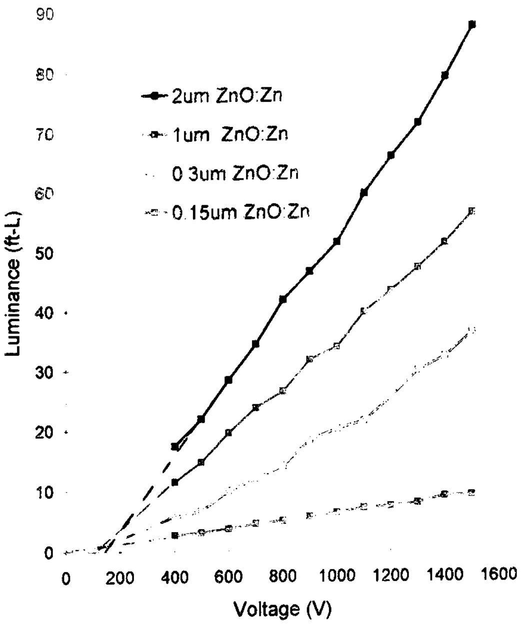


Fig. 27 V/L characteristic for simple ZnO:Zn layers, at 5uA, e-beam 1.41mm dia.

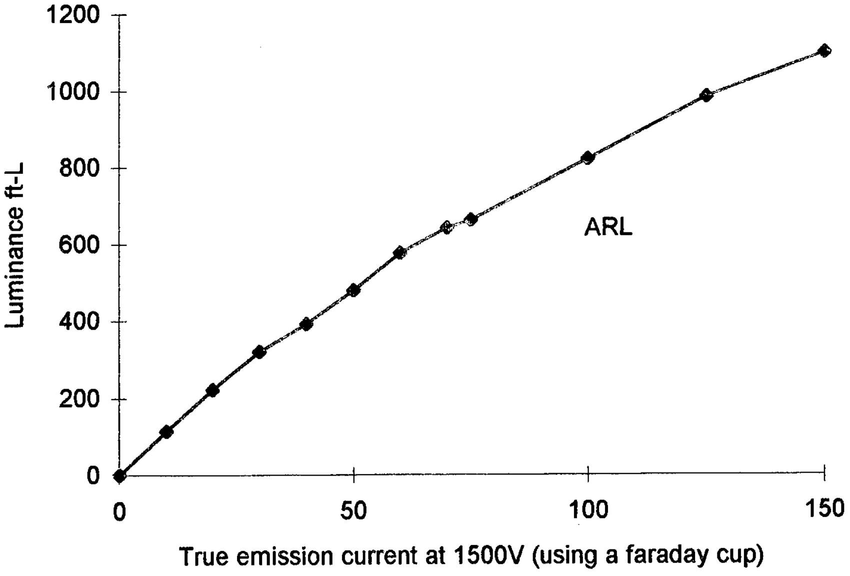


Fig. 28 C/L characteristics of ZnO:Zn thin film

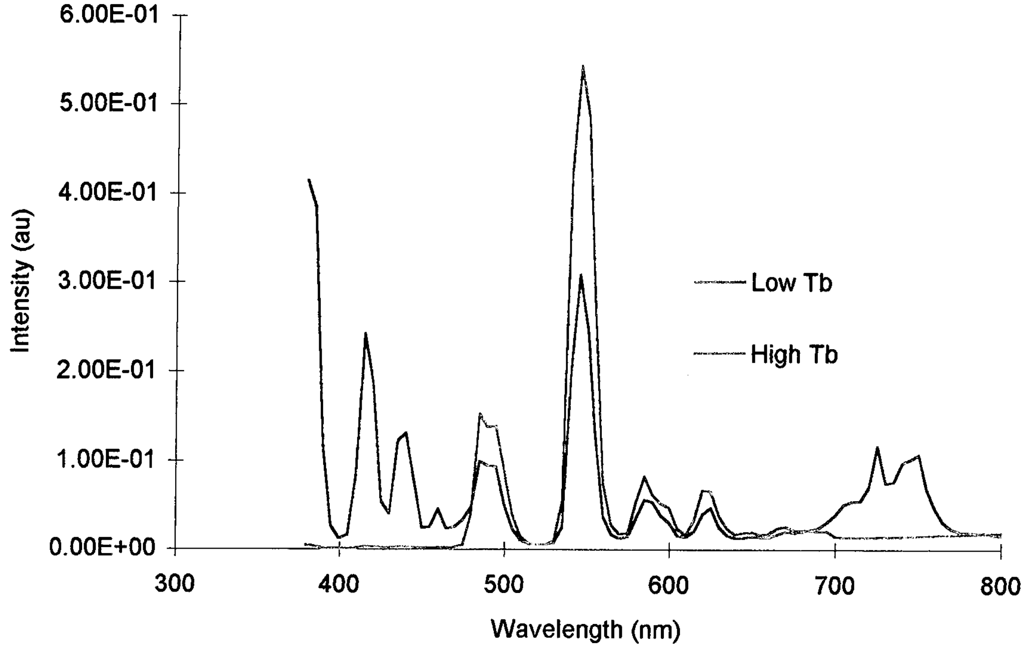


Fig. 29 Spectral emission of YAG at different Tb levels

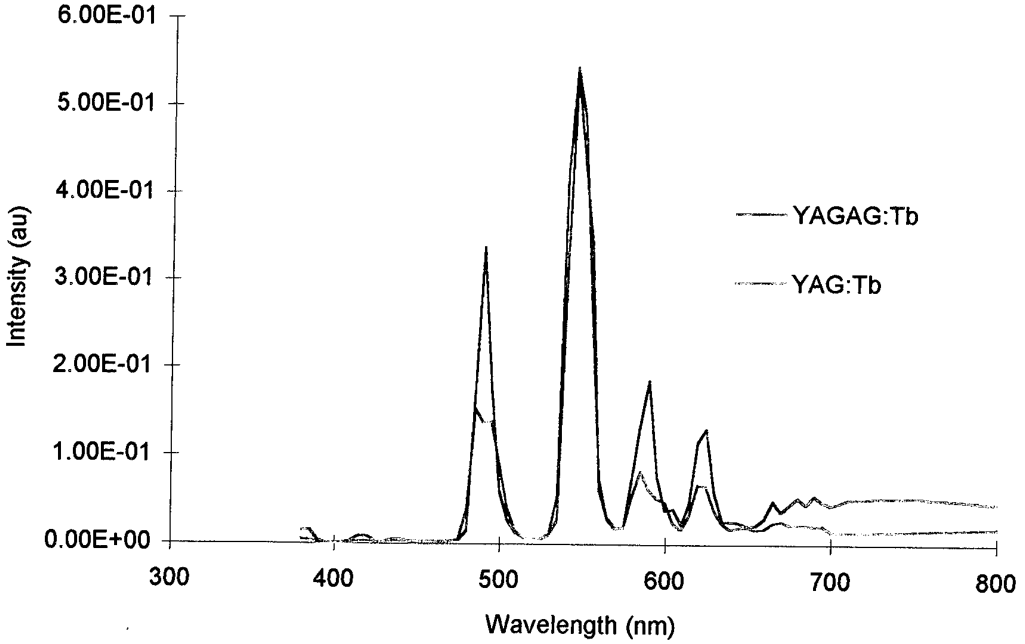


Fig. 30 CL Spectral emission of Tb activated YAG and YAGAG

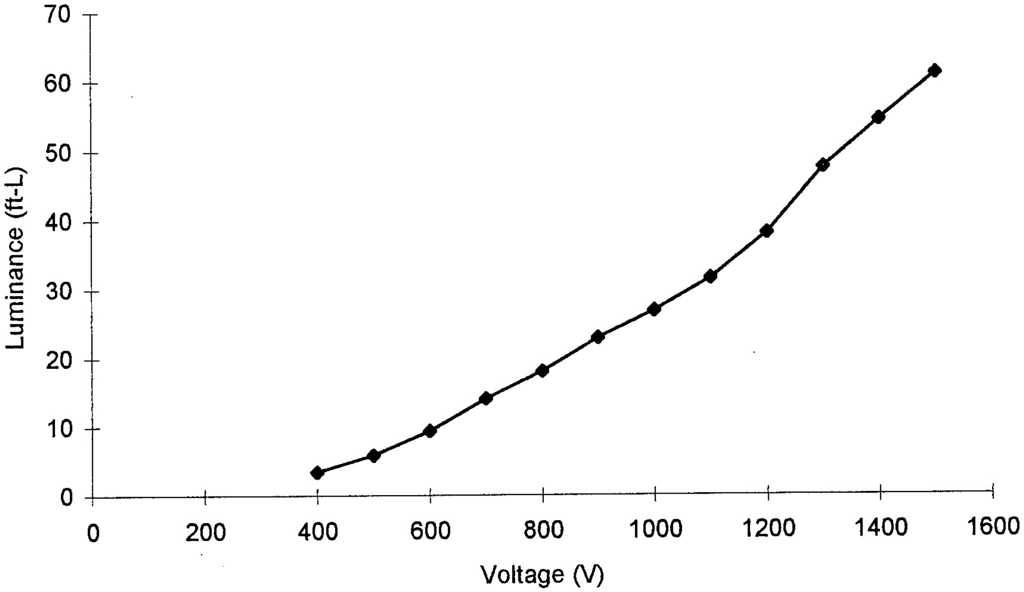


Fig. 31 V/L characteristics of YAGAG:Tb thin film at 5uA, e-beam 1.41mm dia.

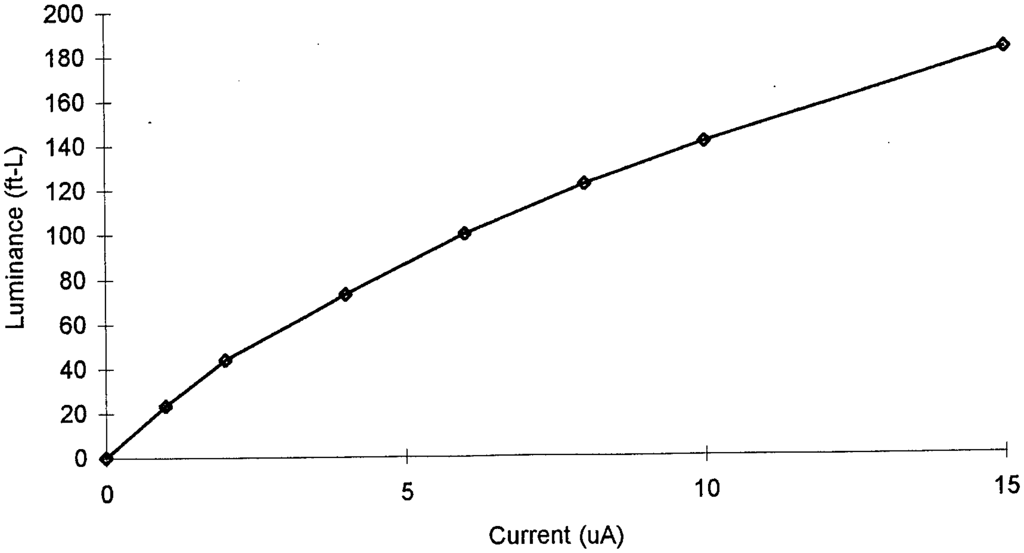


Fig. 32 I/L characteristic for Y2O3:Eu thin film, at 1500eV, e-beam 1.41mm dia

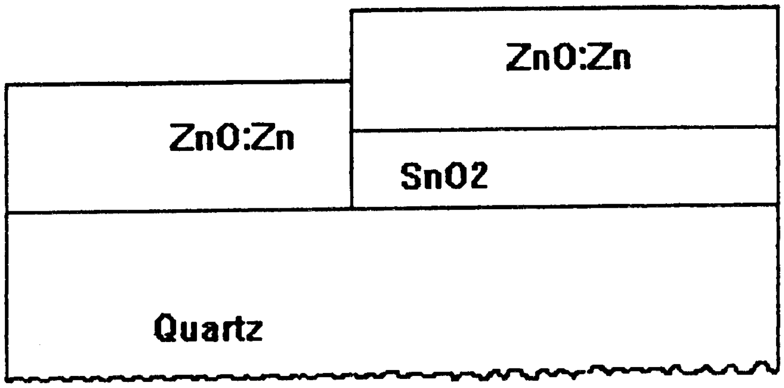


Fig. 33 **Structure of multilayer film**

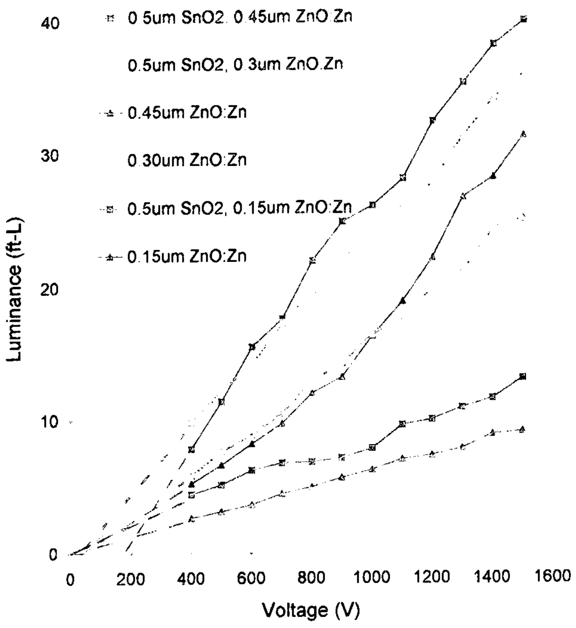


Fig. 34 V/L characteristic for ZnO:Zn multilayer films, at 5uA, e-beam 1.41mm dia.

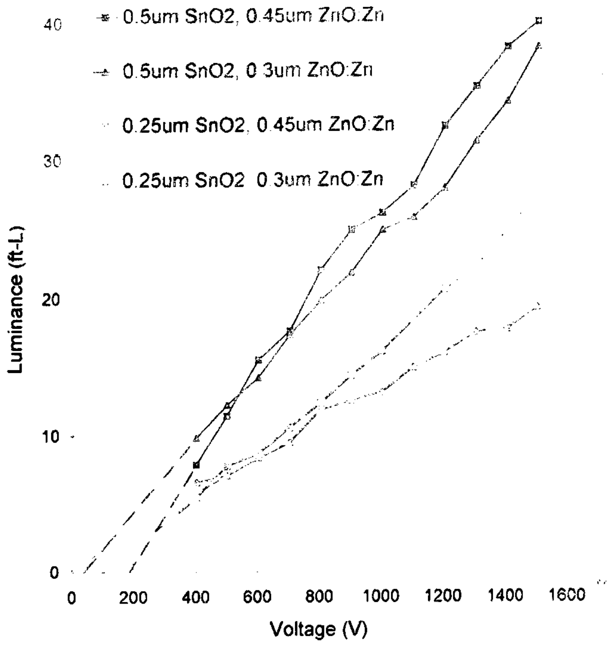


Fig. 35 V/L characteristic for ZnO:Zn multilayers, at 5uA, e-beam 1.41mm dia.

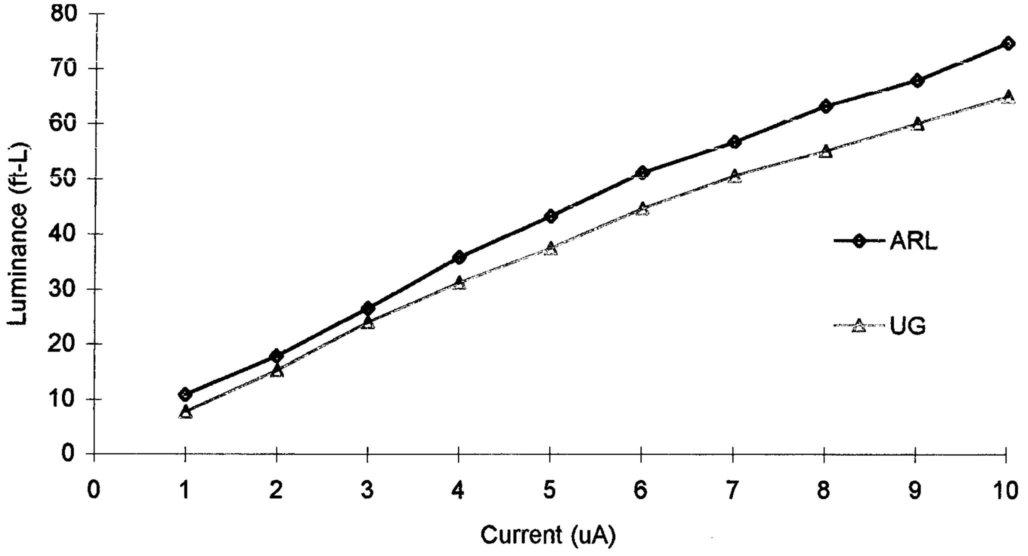


Fig. 36 I/Lcharacterristics of Y2O3:Eu thin film