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Fabrication of $Y_3Al_5O_{12}$:Eu thin films and powders for field emission display applications

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Abstract

Thin films of $Y_3Al_5O_{12}$:Eu (YAG) were spin coated on different substrates from sols. The precursor solution was made from organic precursors by combining stoichiometric ratios of Y(III) iso-propoxide, Al(tri Sec-butoxide) and Eu(III) acetyl acetonate. Sol–gel derived thin films and powders are non-crystalline. Powder samples calcined at 650°C for 5 h show the characteristic X-ray diffraction pattern for the YAG phase. Similarly, the thin film samples annealed at 600°C for 5 h also show YAG phase in the XRD. The emission spectra were measured for both the powder and thin-film samples. Scanning electron microscopy for the powder samples show that the particles are reasonably crystallized with a particle size of 5 μm. The spectral response and out gassing characteristic of the new, low voltage YAG thin films mainly used for application in the field emission flat panel displays are also measured. The cathodoluminescent materials were tested with electron beam excitation at currents of up to 50 μA within the 3000–8000 V range (medium voltage range). The spectral coordinates with minimal optimization as compared with industrially manufactured P22 phosphors at low voltage operation are reasonable.

Keywords: Thin films; YAG; Garnets; Phosphors; Sol–gel and display materials

1. Introduction

Suitable characteristics of phosphor materials are important in cathode ray tube (CRT) and field emission display (FED) fabrications [1]. Phosphors based on $Y_3Al_5O_{12}$:Eu (YAG) are used extensively because of their optical emission intensity and long life [2]. The choice of phosphor materials is one key factor which significantly determines the future success of field emission display (FED) technology. The proper phosphor must perform satisfactorily with the currents and voltages accessible in flat panel displays. New materials are now being developed and tested for low- and medium-voltage ranges [3–5]. The operating voltage in a field emission display depends on factors such as (a) the construction of the field emitter array (single or multiple gate emitters), (b) focusing technique (proximity focusing, focusing grid, co-planer focusing) and the addressing type such as addressable pixel in the emitter array or on the screen (c) the

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anode–cathode spacing (0.1–0.5 mm) (d) the excitation energy of the phosphor. The limitations and constraints concerning the applicability of low- and high-voltage phosphors for flat panel displays were studied [6, 7].

In this paper, $Y_3Al_5O_{12}$:Eu (1 and 2 at%) powder and thin films were made by sol–gel processes from the organic precursors. The thin films were made by a spin coating technique. Garnets of both the powders and thin films show reasonable luminescence intensity. However, garnet thin-film samples showed a broad band in the emission spectrum with satellite peaks. The brightness seems to be linear in the medium voltage range with visibility initiated near 200 V.

2. Experimental

YAG:Eu^{3+} phosphor powders and thin films were fabricated using metal organic precursors, such as Y(III) iso-propoxide, Al(tri sec-butoxide), Eu(III) acetyl acetonate (Aldrich chemicals 99.99% purity). At first Y(III) iso-propoxide was dissolved in 2 methoxyethanol. In order to obtain complete dissolution, 5–10 ml of CH_3COOH was added and refluxed at 125°C for 6 h in a three-neck flask in the presence of argon gas (inert gas). The Eu(III) acetyl acetonate was weighed stoichiometrically and refluxed with 10–15 ml of 2 methoxyethanol at 125°C for 6 h in an argon gas atmosphere. The solution was cooled to room temperature and reacted with $Y(OCH_2CH_2OCH_3)_3$ and further refluxed at 125°C for 12 h in an inert gas atmosphere (Ar or N_2 gas). In a similar manner the Al(tri sec-butoxide) was dissolved in 2 methoxyethanol and refluxed at 125°C for 6 h in an argon gas atmosphere. The solution was cooled to room temperature and reacted with Y–Eu complex sol and further refluxed at 125°C for 12 h. The resulting pH of the clear homogeneous sol was found to be ~3. The sol was hydrolyzed with the theoretical amount of H_2O and 2-methoxyethanol in the ratio 1:4 and placed in a 60°C oven for 6–8 h to produce a xerogel. The clear transparent xero-gel was dried and fired between 600°C and 650°C to produce the garnets [8]. Another portion of the solution was concentrated to 0.3 M and hydrolyzed with 2-methoxyethanol in the ratio 1:2. To obtain crack free films, 4% by volume formamide was added and stirred well prior to spin-coating. Fig. 1 shows the schematic reaction sequence for the formation of YAG gel and thin films.

The substrate was thoroughly ultrasonicated in 2-methoxyethanol and iso-propanol and then dried and spin coated with the precursor solution to get the desired thickness. The powder samples were characterized using a Scintag PAD-V/VAX 3100 powder X-ray diffractometer interfaced with a computer for data acquisition. Photoluminescence measurements were carried with a HITACHI fluorescence spectrometer (model F-4010). In all the measurements, both the excitation and emission band pass were fixed at 5 nm. The spectrometer was operated with minimum scan speed for a response time of 2 s. Morphology and grain size were observed by a scanning electron microscope (SEM model ISI-DS 130, Akashi Beam Tech, Japan). In the case of thin-films coated on ITO (indium tin oxide) glass substrate and those with Pt coated Si (100) single crystals, the luminescence measurements were made with an ultra high vacuum (UHV) system equipped with a thermal electron gun operated at medium-voltage range (3000–8000 V). The system has a base pressure of 10^{-9} torr and it is equipped with a quick access load lock mechanism. An unfocused electron beam with a current up to 50 μA was used with a spot diameter of about 3 mm for brightness and chromaticity measurements.

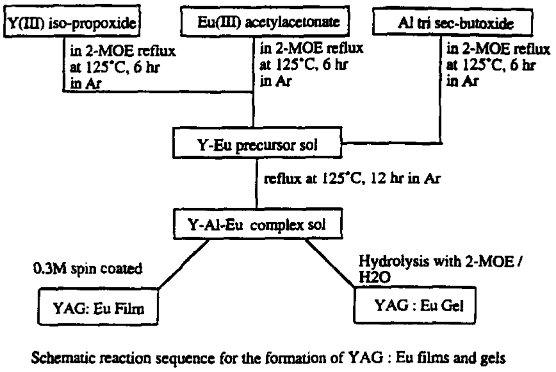

Fig. 1. Schematic reaction sequence for the formation of YAG gel and thin films

3. Results and discussions

3.1. *YAG:Eu phosphor in powder form*

The phosphor samples prepared by the sol–gel processes show reasonable emission characteristics for the garnet phase. It is well known that the purity of the host matrix as well as the homogeneity of impurities are extremely important to obtain efficient phosphor materials. Normally, it takes several days for complete gelation when the sols are stored at room temperature. However, the gelation process could be increased by increasing the temperature up to 70°C.

The gel samples were found to be non-crystalline by X-ray analysis. To achieve better crystallinity, the gel powders were calcined between 600°C and 650°C in an air atmosphere for 6–12 h. Figs. 2 and 3 shows the powder X-ray diffraction patterns for the YAG:Eu phase.

All diffraction peaks could be indexed on the garnet structure without any impurity phases. This indicates that 600°C is a suitable crystallization temperature for the gel samples. The thermogravimetric analysis of the gel samples dried at 60°C is shown in Fig. (4). The gel samples show rapid weight loss around 240°C, indicating the decomposition of the organic matter and transformation into the appropriate inorganic oxide phase. Beyond 330°C the thermogram shows negligible weight loss indicating complete removal of the water and organic matter present in the gel samples. The crystallization of the gel samples, was determined by differential thermal analysis. Fig. 5 shows the differential thermogram of a gel sample dried at 60°C. At the onset temperature 220°C, the thermogram shows an endothermic peak corresponding to organic burnout, which is in agreement with the TG analysis. At still higher temperature, with an onset temperature of 375°C there is an exothermic peak indicating initial crystallization of the gel samples into the garnet phase. The exothermic peak at 950°C in DTA associated with a small weight loss in TGA shows crystallization of the $YAlO_3$ phase [9]. The same garnet phase was also obtained at 1200°C by using inorganic precursors to form the gels. Their samples show the crystallization temperature of the garnet phase to be 915°C by DTA. Yan et al. [10] had obtained the garnet phase at 1300°C. This clearly shows that by choosing organic precursors as the starting materials,

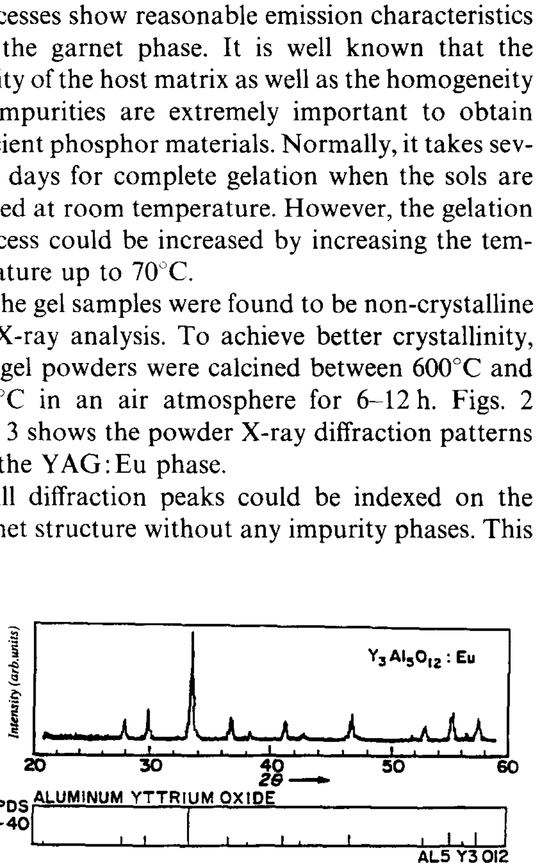

Fig. 2. Powder X-ray diffraction pattern of $Y_3Al_5O_{12}:Eu^{3+}$ (1 at%) gel calcined at 650°C in air.

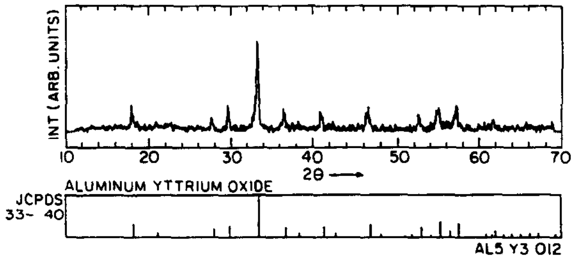

Fig. 3. Powder X-ray diffraction pattern of $Y_3Al_5O_{12}:Eu^{3+}$ (2 at%) gel calcined at 650°C in air.

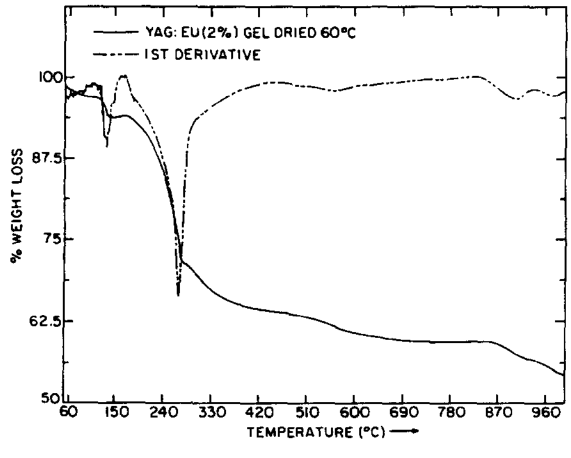

Fig. 4. TGA trace of $Y_3Al_5O_{12}:Eu^{3+}$ gel dried at 60°C showing rapid weight loss at 240°C.

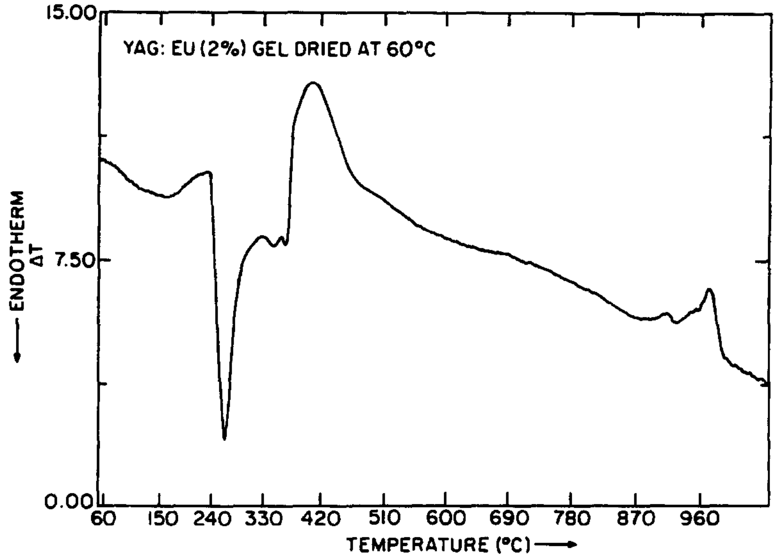

Fig. 5. DTA trace of $Y_3Al_5O_{12}:Eu^{3+}$ gel dried at 60°C with an exothermic peak onset temperature at 375°C due to crystallization of garnet phase.

better crystallized phases at low temperatures can be obtained. Fig. 6 shows the SEM image of the garnet phase. The particles are reasonably crystallized with a particle size of 5–10 μm. Depending on the phosphor requirements, it is always possible to optimize the preparation conditions to achieve the desired particle size. The samples activated with 1 at% Eu did not show any emission at all. However, the samples with 2 at% Eu showed reasonable emission characteristic of the garnet phase (Fig. 7). Most of the emission is concentrated in the 590 nm orange line from the $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+}. The 610 nm red line from the $^5D_0 \rightarrow {}^7F_2$ transition appears but is relatively weak. Eu^{3+} enters the garnet structure on the 8-coordinated Y^{3+} site with site symmetry D_2. However, the exact local symmetry is only a small distortion of the centrosymmetric D_{2h} point symmetry. As a result, the luminescent intensity is concentrated mainly in the magnetic dipole transition (590 nm) rather than the forced electric dipole transition (610 nm). The broad excitation band at 230 nm (5.4 eV) could be either due to the pumping of the Eu^{3+} d-orbitals or to a charge transfer transition.

3.2. *Thin-films phosphors of YAG:Eu*

The sol–gel precursor was made up to 0.3 M and spin coated on different substrates. To obtain crack-free films, formamide 0.4% by volume was added to the precursor sol. Prior to spin coating, the substrates were ultrasonicated in 2-methoxyethanol and iso-propanol for 30 min and dried. Finally, the substrates were spin coated using a spin coater. Multilayer coatings were made to get the desired thickness. After each coating the substrates were pyrolysed to remove the organic matter and finally annealed at 600°C for 5 h (Fig. 8). SEM micrographs show crack-free films with a film thickness of 0.3 μm and with a grain size of 0.1 μm as shown in Fig. 9.

Fig. 10 shows the luminescence spectrum for the YAG activated with 2 at% Eu-thin film phosphor screen coated on Pt-coated Si substrates. The measurement was made at an acceleration voltage of 7.5 kV and beam current of ~50 μA. The intensity of the emission obtained from the films deposited on the ITO-glass substrates was found to be insufficient for the spectral measurements. This is mainly due to poor crystallization of the YAG

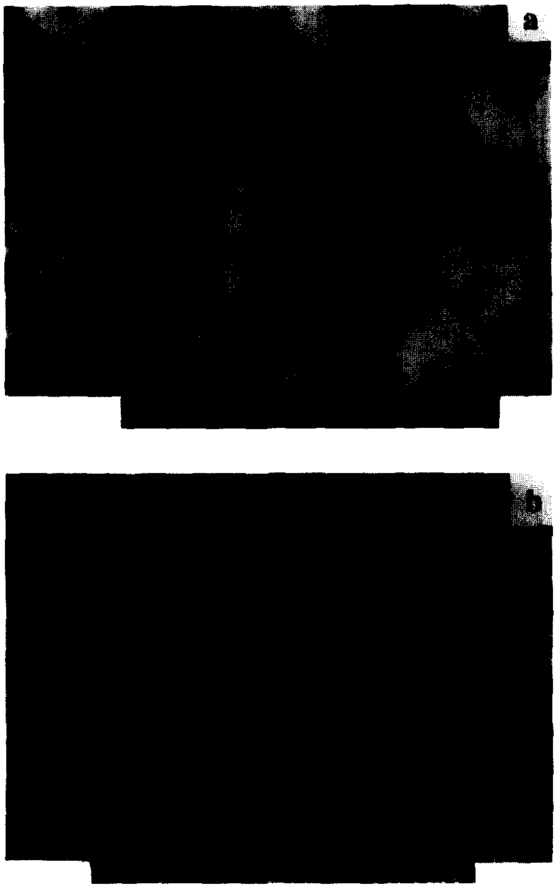

Fig. 6. SEM micrographs of garnet phase in powders showing well crystallized particles of 5 μm: (a) $Y_3Al_5O_{12}:Eu^{3+}$ (1 at%) (b) $Y_3Al_5O_{12}:Eu^{3+}$ (2 at%).

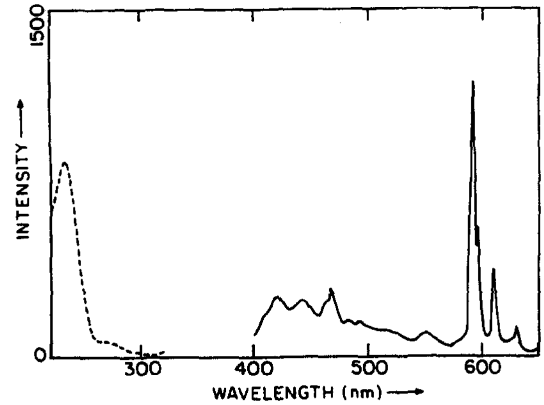

Fig. 7. Excitation (230 nm) and emission (590 nm) spectra of garnet phase with 2 at% of Eu.

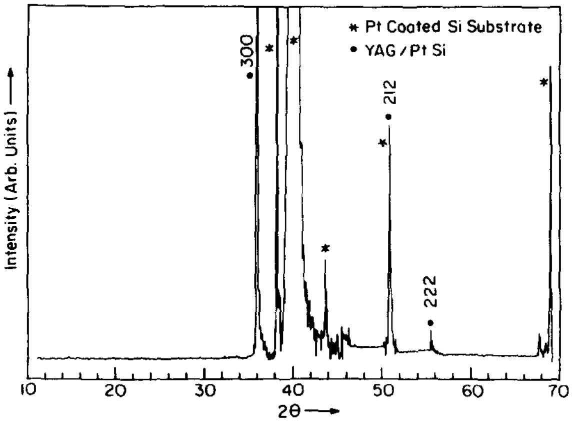

Fig. 8. Thin films of $YAG:Eu^{3+}$ coated on a Pt/Si substrate and annealed at 600°C – 5 h.

phase. To obtain a well crystallized YAG phase, the samples are to be annealed at temperature around 600°C. The ITO-glass substrates could not be annealed at temperatures greater than 400°C, whereas the YAG phase (complete crystallization) crystallizes at ~600°C. As a result the emission intensity is poor on the ITO-glass substrates. In the case of Pt-coated Si substrates, the main $YAG:Eu^{3+}$ emission occurs at a band wavelength of 590 nm. In addition, its satellite peaks at 610 and 708 nm were also observed. The luminescence intensity drops significantly during the first minute exposure to the DC electron beam. Fig. 11 shows a set of spectra taken while exposing a fresh spot to the beam up to 5 min. No physical changes of the film surfaces were observed during this period of time, and no lifetime test for longer periods of time were made.

3.3. Brightness and chromaticity

The brightness and chromaticity characteristics of the phosphor were measured using a digital chroma meter with a data processor, enabling direct readings of the brightness in candelas per square meter. The color space of the phosphors were also measured. The changes in brightness were constant during the measurements. Fig. 12

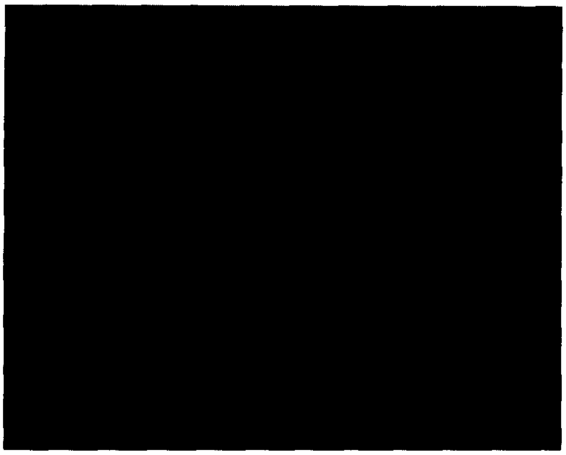

Fig. 9. SEM micrographs of thin films with a particle size of 0.1 μm.

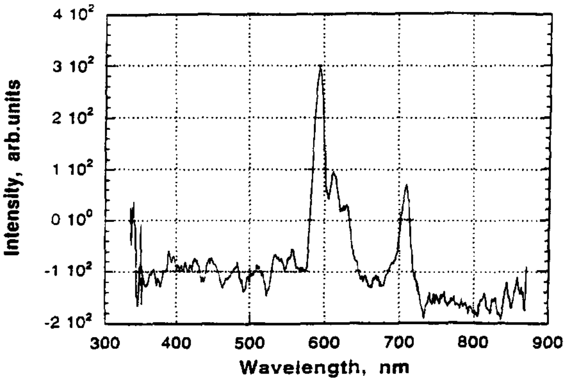

Fig. 10. Luminescence spectrum of garnet film coated on to a Pt/Si substrates with an emission at 590 nm.

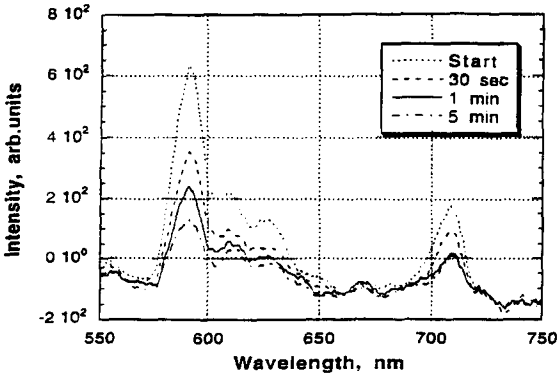

Fig. 11. Magnified part of the luminescence spectra: Intensity versus time during first 5 min.

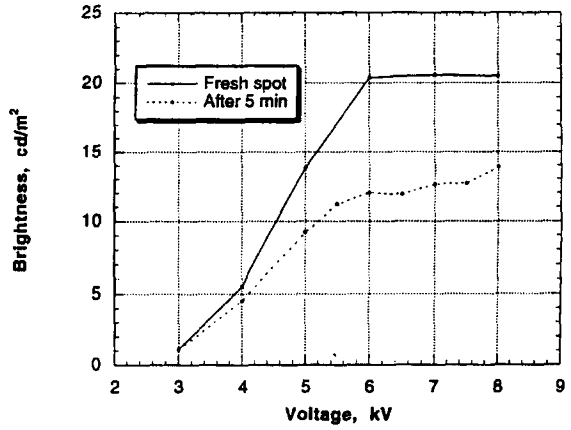

Fig. 12. Brightness as a function of beam energy. Note the changes in brightness for the same spot during 5 min exposure to DC-electron beam.

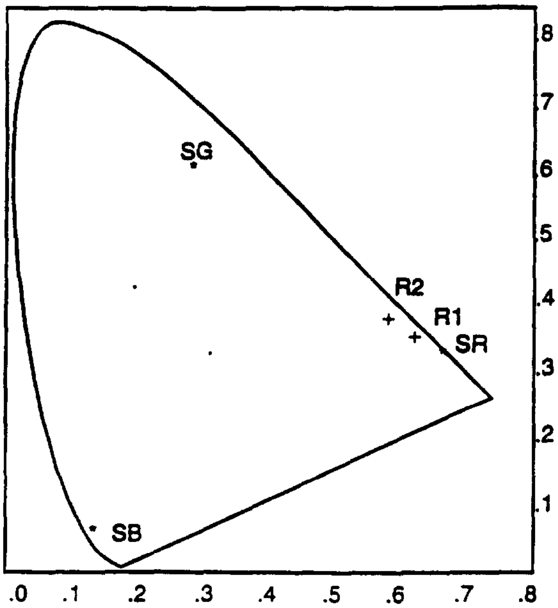

Fig. 13. Color coordinates of the examined phosphors on the 1931 CIE chromaticity diagram shown by + symbols. R_1 - Red $Y_3Al_5O_{12}:Eu^{3+}$ thin films deposited on the Pt/Si substrate. R_2 – thin-films deposited on ITO/glass substrate. The coordinates for PTCOE standard voltage RGB triplet (shown by * symbols) manufactured by Osram Sylvania [11] are given as a reference (SR - $Y_2O_2S_2$, SG- ZnS:Cu, Al; and SB – ZnS:Ag). The colors are reasonable of the examined phosphors are which clearly inside the PTCOE phosphor ranges, indicating the lower spectral range.

shows the changes in brightness in the medium voltage range below ~5 kV. Above ~6 kV a saturation of the brightness was observed. The brightness of the spot exposed for 5 min drops significantly compared to the brightness of the fresh spot. The brightness of the YAG:Eu^{3+} deposited on an ITO- glass substrate is about 2 cd/m^2 at 7.5 kV which is not sufficient to perform measurements versus acceleration energy.

Fig. 13 shows the color space of the tested triplet compared with the phosphor standard reference of the Phosphor Technology Center of Excellence (PTCOE) [11]. The colors are reasonable, however, the coordinates of the examined phosphors are well inside PTCOE limits, indicating the lower spectral range.

4. Conclusion

Powder and thin films of YAG:Eu red emission phosphor was made successfully using the sol–gel method. Lower crystallization temperature of the YAG phase and thin-films coated on to Pt-coated Si substrate was reported for the first time. Phase pure powders and thin films of garnet were made by sol–gel. Reasonable emission intensity was observed for the powders. Crack-free films were obtained with film thicknesses of 0.3 μm with a grain size of 0.1 μm. The spectral response and peak intensities of thin-film phosphors deposited on ITO coated glass and on Pt-coated Si substrates for application in field-emission flat panel display, have been measured. The colors are reasonable, however the emission band is associated with satellite peaks. The brightness is linear in the medium-voltage range, with visibility initiated near 200 V.

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