

A.c. powder electroluminescence devices using $\text{ZnGa}_2\text{O}_4\text{:Mn}$ phosphor

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Zinc gallate, ZnGa_2O_4 was recently investigated for the application to vacuum fluorescent displays (VFDs) utilizing low-voltage cathodoluminescence. The ZnGa_2O_4 host lattice without dopant shows blue emission [5, 6]. The phosphor shows green [1–3] and red [4] emission when it is doped with Mn^{2+} and Cr^{3+} activators. A high luminous efficiency had been obtained when the phosphor was operated at low voltage (10–300 V). The results of low accelerating voltage and high luminous efficiency led us to study the electroluminescence (EL) characteristics of the $\text{ZnGa}_2\text{O}_4\text{:Mn}$ phosphor. There are a few papers reporting the electroluminescence (EL) of the $\text{ZnGa}_2\text{O}_4\text{:Mn}$ phosphor. Thin film electroluminescence devices (TFEL) had been developed using $\text{ZnGa}_2\text{O}_4\text{:Mn}$ phosphor thin films which were deposited by RF magnetron sputtering on polished BaTiO_3 ceramic sheets [7]. In this paper, we report the fabrication of the a.c. powder electroluminescence (ACPEL) devices. The $\text{ZnGa}_2\text{O}_4\text{:Mn}$ ACPEL device was developed by the printing technique.

First, ZnO (99.999%), Ga_2O_3 (99.999%) and MnO (99.9%) powders were mixed in 1 : 1 : 0.001 mole ratio and ball-milled with alcohol for 24 h. The mixed powders were dried at 100 °C and sintered at 1375 °C for 5 h in air to form the doped zinc gallate ($\text{ZnGa}_2\text{O}_4\text{:Mn}$) phosphor powder. The phase identification of the phosphor powder was carried out on a Siemens D5000 X-ray diffraction (XRD) equipment with $\text{CuK}\alpha$ radiation. Fig. 1 shows X-ray diffraction patterns of $\text{ZnGa}_2\text{O}_4\text{:Mn}$ and ZnGa_2O_4 powders. There are no ZnO -phase or Ga_2O_3 -phase peaks discernible in any of the samples. The subsolidus equilibria study of the ZnO - Ga_2O_3 system showed no appreciable solid solubilities of ZnO or Ga_2O_3 in the ZnGa_2O_4 compound [1]. All the sintered powders exhibit the spinel structure of the ZnGa_2O_4 powder. The lattice constant of the $\text{ZnGa}_2\text{O}_4\text{:Mn}$ powder was calculated to be 0.8365 nm. The result is consistent with the value of 0.837 nm [8]. It is shown that the concentration of Mn dopant is much less so that it cannot influence the crystal structure of host lattice.

The a.c. powder electroluminescence (ACPEL) devices were prepared by the printing method. The cross-sectional structure of the $\text{ZnGa}_2\text{O}_4\text{:Mn}$ ACPEL device is shown in Fig. 2. The device consisted of the indium tin oxide (ITO) coated glass, $\text{ZnGa}_2\text{O}_4\text{:Mn}$ emitting layer, BaTiO_3 insulating layer, and Ag paste electrode. Initially, an ITO coated glass substrate was etched in the requisite manner. Secondly, the $\text{ZnGa}_2\text{O}_4\text{:Mn}$ phosphor powder was mixed with the dielectric organic binder

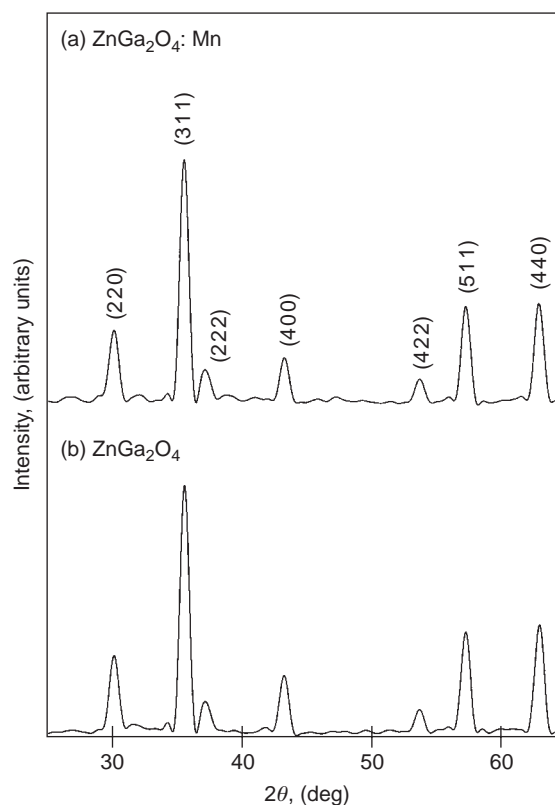


Figure 1 XRD patterns of (a) $\text{ZnGa}_2\text{O}_4\text{:Mn}$, and (b) ZnGa_2O_4 powder.

(cyanoethyl cellulose) and deposited on the ITO substrate by printing. The high dielectric material (BaTiO_3) was printed upon the phosphor film to protect against breakdown. Finally, the Ag paste was printed as an electrode film. Fig. 3 shows the scanning electron microscope (SEM) image and the corresponding cathodoluminescence (CL) image of the ACPEL device in its cross-sectional view. It is interesting to note that the interface between the $\text{ZnGa}_2\text{O}_4\text{:Mn}$ phosphor layer and the BaTiO_3 insulator layer cannot be apparently distinguished in the SEM image (Fig. 3a). In contrast, we can easily characterize the thicknesses of each of the layers of the ACPEL device with the CL image (Fig. 3b). The thickness of the phosphor, the BaTiO_3 and the Ag are evaluated to be ~ 10 , 13 and 6 μm respectively. We can calculate the electric field in the printed phosphor layer by evaluating the thickness of the phosphor layer.

Among transition-metal ions, Mn^{2+} ions are usually used as luminescent centres in the phosphor powder. Mn^{2+} centres in the ZnGa_2O_4 host lattices show green luminescence with a peak at 508 nm, which is due to $3d^5$ intra-shell transitions. The wave-

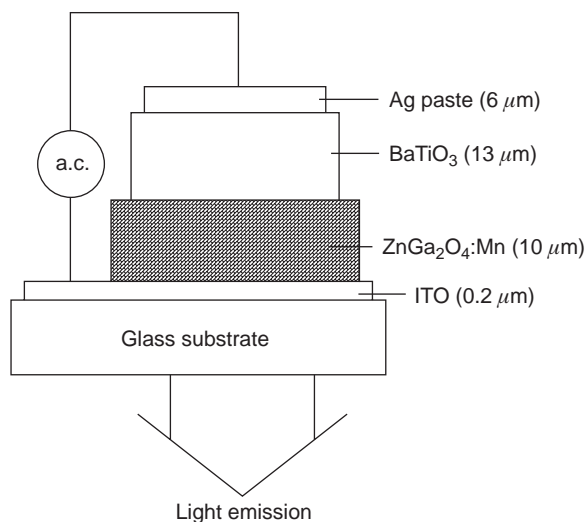
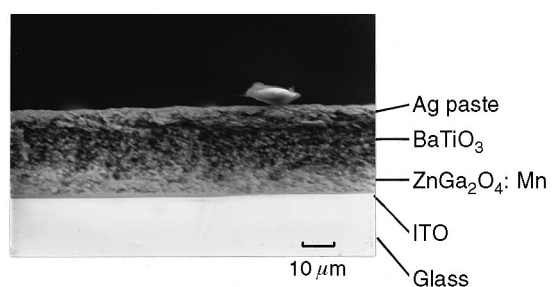
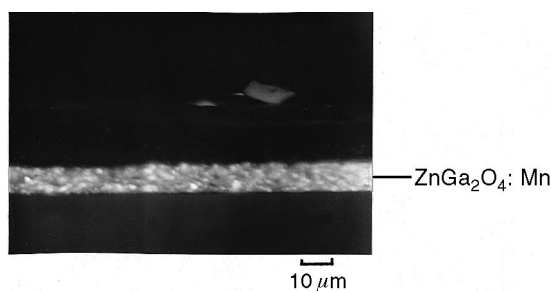


Figure 2 Cross-sectional structure of the $\text{ZnGa}_2\text{O}_4\text{:Mn}$ ACPEL device.

function of 3d electrons is sensitively distorted by the crystal field. In other words, the 3d electrons are much affected by crystal field and the $3d^5$ excited energy levels depend on the strength of the crystal field. The luminescent transition is due to the ${}^4T_1({}^4G)\text{-}{}^6A_1({}^6S)$ transition [9, 10] for the $\text{ZnGa}_2\text{O}_4\text{:Mn}$ phosphor. ${}^4T_1({}^4G)$ is the lowest excited state of $3d^5$ intra-shell and ${}^6A_1({}^6S)$ is the ground state. The excitation and emission spectra of the $\text{ZnGa}_2\text{O}_4\text{:Mn}$ phosphor powder were obtained using a spectrofluorophotometer from Shimadzu RF-5301. The photoluminescence (PL) emission and excitation spectra of the $\text{ZnGa}_2\text{O}_4\text{:Mn}$ phosphor powder are shown in Fig. 4a. Under excitation of 254 nm UV light radiation, the emission spectrum exhibited a green emission band with a peak at 508 nm. The excitation spectrum, monitored at 508 nm exhibited two peaks at 245 and 290 nm. The excitation



(a) SEM image



(b) CL image

Figure 3 (a) SEM image of the ACPEL device in the cross-sectional view, and (b) CL image corresponding to (a).

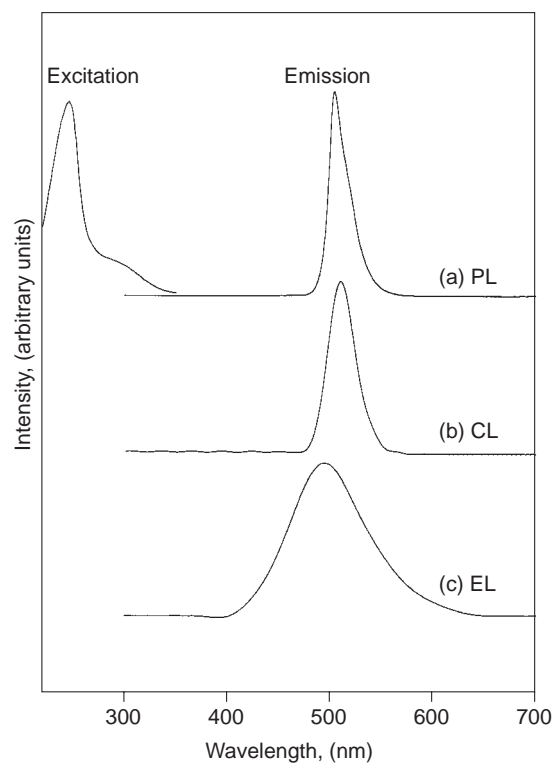


Figure 4 (a) PL emission and excitation, (b) CL emission, and (c) EL emission spectra of the $\text{ZnGa}_2\text{O}_4\text{:Mn}$ powder.

spectrum of the $\text{ZnGa}_2\text{O}_4\text{:Mn}$ phosphor powder is similar to the report by Shea *et al.* [3]. The appearance of the 245 nm peak in the excitation spectrum of the ZnGa_2O_4 host lattice. The excitation energy was transferred to Mn^{2+} centres and the phosphor emitted green light (508 nm). In addition, the 290 nm peak was due to the direct absorption of Mn^{2+} centres, which could cause the green luminescent efficiency increase.

The cathodoluminescence (CL) spectrum of the $\text{ZnGa}_2\text{O}_4\text{:Mn}$ phosphor powder was measured with a TOPCON ABT-150s type scanning electron microscope equipped with a Jobin Yvon H20UV monochromator and is shown in Fig. 4b. The CL spectrum shows a green emission with a peak at 508 nm, which is consistent with the PL spectrum (Fig. 4a). The electron beam heats the $\text{ZnGa}_2\text{O}_4\text{:Mn}$ lattices when the powder was excited. Due to the thermal effect, the full width at half maximum (FWHM) of the CL spectrum is wider than the FWHM of the PL spectrum as shown in Fig. 4a and b.

Electroluminescence (EL) properties of the $\text{ZnGa}_2\text{O}_4\text{:Mn}$ ACPEL device, which were driven by an a.c. sinusoidal power at different applied voltages and frequencies were measured using a DIGISEM monochromator. The threshold voltage of the ACPEL devices is about 50 V. Electroluminescence starts to occur above the threshold voltage. The electric field in the printed phosphor layer is calculated to be 10^5 V cm^{-1} . The EL spectrum of the ACPEL device is shown in Fig. 4c. It is observed that the peak of the EL spectrum of the ACPEL device is shifted to 490 nm (Fig. 4c). Many of the studies with a.c. electroluminescence were focused on determining brightness–voltage characteristics.

However, there were many difficulties in comparing them with one another. The characteristics of the EL devices, including EL spectrum, and brightness–voltage dependence are different due to the various fabrication methods of the active layers. The brightness–voltage characteristics for the conventional EL devices can be fitted to the relationship [11]

$$B = B_0 \exp(-bV^{-1/2})$$

where B is brightness, V is applied voltage, B_0 and b are constants which are determined by the phosphor material, device structure and exciting condition. Fig. 5 shows that the logarithm of B is directly proportional to $V^{-1/2}$. The experimental results in the figure are compatible with the above equation. This shows that the ACPEL device of $\text{ZnGa}_2\text{O}_4:\text{Mn}$ phosphor which was fabricated by the printing technique is similar to the conventional EL devices.

In summary, the PL emission spectrum of the $\text{ZnGa}_2\text{O}_4:\text{Mn}$ phosphor powder exhibited the green emission band with a peak at 508 nm under UV light excitation. The excitation spectrum monitored at 508 nm exhibited an absorption band with two peaks at 245 nm and 290 nm. The appearance of 245 nm and 290 nm peaks is due to the absorption by the ZnGa_2O_4 host lattice and Mn^{2+} activator, respectively. The ACPEL device of the $\text{ZnGa}_2\text{O}_4:\text{Mn}$ phosphor powder has been fabricated by a printing technique. The cross-sectional structure of the ACPEL device could be apparently distinguished by CL. Above the threshold voltage (50 V), the $\text{ZnGa}_2\text{O}_4:\text{Mn}$ ACPEL device gave blue-green emission with a peak at 490 nm. The relationship between brightness and applied voltage was similar to the conventional EL devices.

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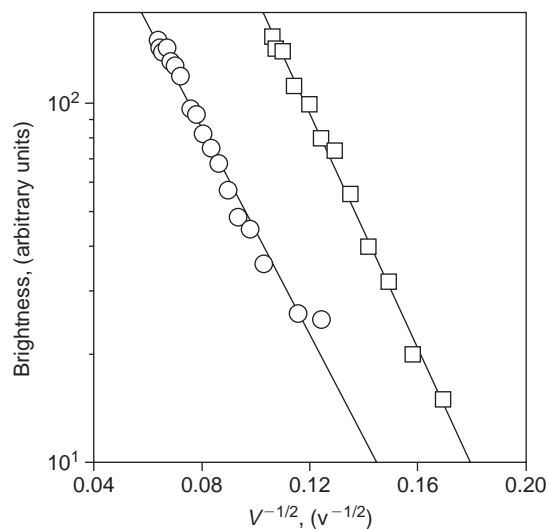


Figure 5 Brightness versus $V^{-1/2}$ for various operating frequencies. (□) 10714, (○) 5000 Hz.

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