



Zinc gallate and its starting materials in solid state reaction route- A comparative study



T.A. Safeera^a, N. Johns^b, K. Mini Krishna^c, P.V. Sreenivasan^d, R. Reshmi^a, E.I. Anila^{a,*}

^a Optoelectronic and Nanomaterials' Research Lab, Department of Physics, Union Christian College, Aluva 683 102, Kerala, India

^b Dept. of Metallurgical Engineering and Material Science, IIT, Mumbai 400076, India

^c Department of Physics, Vimala College, Thrissur, Kerala, India

^d Department of Chemistry, Union Christian College, Aluva 683102, Kerala, India

HIGHLIGHTS

- ZnGa₂O₄ nanoparticles were prepared by solid state reaction at low temperature.
- A comparative study of ZnO, Ga₂O₃ and ZnGa₂O₄ was done.
- Due to the Porous nature, photocatalytic activity of ZnGa₂O₄ will improve.

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ABSTRACT

ZnGa₂O₄ belonging to the class of inorganic compounds with spinel structure is a self activated phosphor having wide applications in display devices. We report the synthesis and characterization of ZnGa₂O₄ using conventional solid state reaction method and a comparative study of its properties with commercial ZnO and Ga₂O₃ fired under similar conditions. XRD results proved that the zinc gallate phosphor is cubic in structure with an average grain size of 25 nm. Rectangular porous nature of zinc gallate phosphor is obtained from the SEM analysis. From the diffuse reflectance spectrum, the band gap of zinc gallate (4.74 eV) was evaluated to be between that of ZnO and Ga₂O₃. This ternary phosphor showed a bluish green emission with Commission International d'Eclairage (CIE) coordinates $x = 0.26$ and $y = 0.36$ under the excitation by UV light.

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1. Introduction

In the present era, researches based on metal oxides has increased due to their inevitable applications in various optoelectronic fields. ZnO and Ga₂O₃ are two important metal oxides, based on which many researchers developed fruitful results [1,2]. Zinc gallate, a combination of these metal oxides, is a II-III-VI direct bandgap semiconductor material having wide range of applications in display and photovoltaic devices. It is a self activated phosphor with high purity, exhibiting blue emission under excitation by UV light and low voltage electrons. The Ga-O group present in the zinc gallate is responsible for this emission [3–6]. ZnGa₂O₄ possess better mechanical, chemical and thermal stability under high electric field and high vacuum conditions, compared to the sulfide

phosphors, which emits corrosive gas under electron bombardment [7–9]. Thus it finds wide applications in low voltage field emission displays (FEDs), high definition television (HDTVs), electroluminescent devices (ELDs) and vacuum fluorescent displays (VFDs) [10,11]. Grafting SnOx on the surface of zinc gallate makes it an excellent photocatalyst [12]. The wide band gap (4.4 eV) of Zinc Gallate makes it an excellent host material for optoelectronic applications. ZnGa₂O₄ possess normal cubic spinel structure with the Zn²⁺ ions occupying the tetrahedral site whereas Ga³⁺ at the octahedral site [3,13]. Various preparation techniques like sol gel synthesis [3] solid state reaction [7,14–18] hydrothermal method [19–21] etc can be employed for the synthesis of zinc gallate phosphor. Among these, solid state reaction method is the most common method employed for the synthesis of gallates for the past several years. Apart from the necessity of high temperature, it is a simple, low cost, environmental friendly technique which involve the usage of simple chemicals whereas some chemical methods require variety of non-eco-friendly chemicals for low temperature

* Corresponding author.

E-mail address: anilaei@gmail.com (E.I. Anila).

production.

In this work we synthesized the ZnGa_2O_4 phosphor by solid state reaction of ZnO and Ga_2O_3 at 1000°C whereas in the previous reports, the synthesis temperature is above 1000°C [2–4]. The prepared powder was characterized by using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Diffuse Reflectance Spectroscopy (DRS), Fourier Transform Infrared Spectroscopy (FTIR) and Photoluminescence (PL). A comparative study of the zinc gallate with the starting compounds, ZnO and Ga_2O_3 fired at the same condition is also done.

2. Experimental

We synthesized zinc gallium oxide phosphor by conventional solid state reaction method. 1 mol% of Zinc oxide [ZnO , 99%, MERCK] was mixed with 1 mol% of Gallium oxide [Ga_2O_3 , 99.99%, ALDRICH] with 2-propanol as the mixing agent. This mixing is continued for half an hour to get a fine paste of the sample. This mixture was dried in the oven for 24 h at 70°C , transferred into alumina crucible and fired in the furnace at 1000°C for 12 h. ZnO and Ga_2O_3 were under the same conditions. To eliminate impurity peaks observed in XRD one more sample of zinc gallate was prepared by adding 5 wt % of ammonium chloride as a flux agent during the synthesis.

The crystallographic structure of ZnO , Ga_2O_3 and ZnGa_2O_4 were analyzed with Bruker AXS D8 advance X-ray Diffractometer using $\text{Cu-K}\alpha$ lines ($\lambda = 1.5406\text{\AA}$). Morphological study of phosphor was done by JEOL JSM 7600F Field Emission Scanning Electron Microscope. FTIR Spectrophotometer (Shimadzu) was used for the FTIR Analysis. The Absorption and Diffuse Reflectance spectra were recorded with Varian, Cary 5000 UV-VIS-NIR Spectrophotometer. Photoluminescence analysis was done using Horiba Fluoromax-4C Spectrofluorometer.

3. Results and discussions

Fig. 1 represents the XRD patterns of ZnO , Ga_2O_3 and ZnGa_2O_4 with and without flux. It is evident from XRD that on adding flux, the unwanted peaks disappeared. Addition of flux agent helped in improving the crystallinity by producing defects in the host lattice thereby enhancing the atomic diffusion. The XRD of ZnO , Ga_2O_3 and ZnGa_2O_4 are in well agreement with their standard diffraction patterns as per JCPDS file numbers 79–0208, 74–1776 and

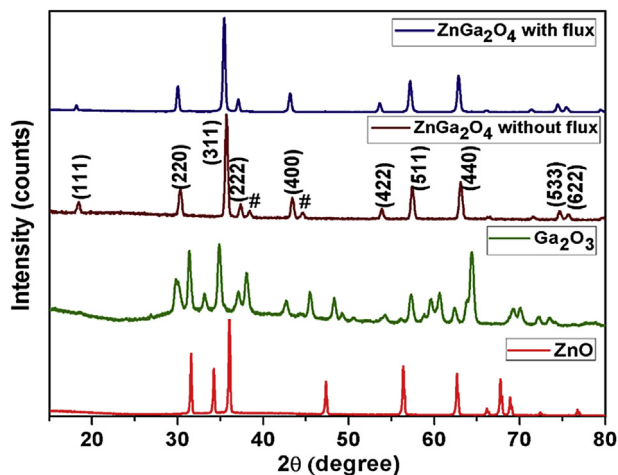


Fig. 1. XRD patterns of ZnO , Ga_2O_3 and ZnGa_2O_4 (with and without flux) fired at 1000°C . [# denotes unidentified peaks].

86–0415 with hexagonal, monoclinic and cubic structures respectively. The sharpness of peaks in the zinc gallate phosphor reveals that the prepared sample is highly crystalline with major reflections from (311), (440), (511) and (440) planes and no peaks of the starting materials are observed.

Properties of ZnO , Ga_2O_3 and ZnGa_2O_4 synthesized without flux were analyzed. The cell parameters of the zinc gallate phosphor were evaluated by using the relation $d_{hkl} = a/(h^2+k^2+l^2)^{1/2}$ and we obtained the value as $a = b = c = 8.37\text{\AA}$. The grain size (D) was estimated as 25 nm, using the Debye-Scherrer formula, $D = 0.9\lambda/\beta\cos\theta$ where λ is the wavelength of X-ray radiations (1.5406\AA), β is the full width at half maximum of the diffraction peak and θ is the glancing angle.

The FESEM image of the zinc gallate fired at 1000°C is depicted in Fig. 2 which consists of porous natured rods with length ranging from 1 to 5 μm and rectangular cross section. Some rods may be even hollow as observed in the cracked rod shown in Fig. 2. These rods have an average width of $\sim 382\text{ nm}$ and are formed by combining semispherical nanoparticles. These factors increases the surface area of contact on applying this material in photocatalytic applications. Packing of semispherical nanoparticles to form one dimensional rods with rectangular cross section is due to the anisotropic growth of cubic structured zinc gallate nanoparticles [22].

Fig. 3 is the FTIR spectra of ZnO , Ga_2O_3 and ZnGa_2O_4 . The spectra for the range $400\text{--}3500\text{ cm}^{-1}$ is studied. From the figure we can see that the band from $1000\text{ to }3500\text{ cm}^{-1}$ of all the samples are approximately identical. The peaks around 2925 cm^{-1} and 2847 cm^{-1} can be attributed to the stretching vibration of H-O-H group [23]. The band at 2350 cm^{-1} corresponds to antisymmetric stretching vibrations of CO_2 which might have been caused by the CO_2 in the ambient air [24]. The peak at 1600 cm^{-1} represents the bending vibrations of O-H group [23]. In the low frequency range the metal oxides shows their characteristics vibrations and the graphs are different. For the ZnO sample the peak around 530 cm^{-1} represents the Zn-O stretching vibration [25]. In the case of Ga_2O_3 the strong peak around 675 cm^{-1} represents the Ga-O-Ga bending vibration and the peak at 459 cm^{-1} can be assigned to Ga-O bending vibration [23]. For the zinc gallate sample, there are two major bands at 586 and 463 cm^{-1} , and they are attributed to the Zn-O and Ga-O stretching vibrations in the Zinc Gallate lattice [24].

The diffuse reflectance spectrum (DRS) of the zinc gallate phosphor along with ZnO and Ga_2O_3 is shown in Fig. 4. It shows the absorbing tendency of the phosphor and initial compounds in the UV region and then after reflection in the visible range. From the DRS we can calculate the absorption coefficient using the Kubelka-Munk equation [26,27]. The bandgap values can be estimated by extrapolating the linear portion of the $h\nu$ versus $[(k/s)h\nu]^2$ graph [Fig 5], where k and s denotes the absorption and scattering coefficients respectively and $h\nu$ is the photon energy. Here the bandgap values are found to be 3.32 eV, 4.95 eV and 4.73 eV for ZnO , Ga_2O_3 and ZnGa_2O_4 respectively. From the observed values it can be seen that the bandgap of ZnGa_2O_4 is lies between that of ZnO and Ga_2O_3 . There is a blue shift in bandgap value of zinc gallate with the bulk value of 4.4 eV [3,13], which may be attributed to the nano grain formation.

The PL emission spectrum of ZnO , Ga_2O_3 and ZnGa_2O_4 for an excitation wavelength of 310 nm is represented in Fig. 6. The ZnO shows two peaks, one intense emission at 381 nm which attributed to the near band edge emission and another broad emission centered at 497 nm which can be related to the ionized oxygen vacancy from the zinc oxide compound [28]. The peak at 466 nm is due to the zinc vacancy [29].

The emissions from the gallium oxide are mainly in the blue region. The peaks at 377 nm, 420 nm and characteristic emission

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