



ZnGa₂O₄ Nanophosphors: Rapid Synthesis, Characterization and Luminescence Properties

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Abstract

Nanocrystalline ZnGa₂O₄ spinel powders were prepared through a simple and facile microwave-irradiation assisted solution-based route, using ethylene glycol as the reaction medium and, without using any structure-directing agents. The as-prepared product consists of ZnGa₂O₄ nanoparticles, which are crystalline as revealed by X-ray diffraction studies and TEM analysis. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) studies also show that the size of these as-prepared nanoparticles is less than 10 nm. The annealed nanopowders show intense blue luminescence, under UV excitation, which makes these nanopowders important in the field of phosphor applications.



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Introduction

ZnGa₂O₄ is a transparent conductive oxide with a wide energy band gap of ~ 4.4 eV^{1,2}. Being a ternary oxide that can be formed by the reaction between ZnO and Ga₂O₃, ZnGa₂O₄ crystallizes in the cubic spinel-type (AB₂O₄) structure. The tetrahedrally coordinated A-sites are occupied by Zn²⁺ ions, whereas, Ga³⁺ ions fill the octahedrally

coordinated B-sites³. ZnGa₂O₄ shows emission in the blue region without any dopant via excitation of self-activated optical centers linked to Ga–O groups, which are tetrahedrally coordinated⁴. Because of its improved stability than sulphide phosphors, it has received a lot of interest in the domain of field-emission and fluorescent vacuum displays, and also in electroluminescent devices⁵. ZnGa₂O₄ has

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also been investigated for its excellent cathodoluminescence properties at lower voltages. Pure zinc gallate shows a characteristic blue emission peak in the wavelength range of 430–450 nm, and this peak has been ascribed to the presence of defect states within the host lattice. However, it is well known that the emission characteristics of undoped ZnGa_2O_4 are relatively sensitive to various factors, such as the conditions of synthesis, (and the consequent) distortion around Ga^{3+} ions which, apparently, lead to the observed unexpected line profiles. For example, Kim *et al.*, attributed the presence of 360 nm emission in reduced ZnGa_2O_4 powders to distorted GaO_6 octahedra, that are responsible for the oxygen vacancies within the crystal lattice⁶. It was also observed that, when a sample is heated in a reducing environment, the oxygen vacancies created in the lattice lead to the distortion of GaO_6 octahedral geometry. Such distortion can increase the energy gap between Ga^{3+} and O^{2-} energy levels, which leads to a decrease in the emission wavelength. Furthermore, oxidizing this sample in air leads to the disappearance of 360 nm peak, confirming the contribution of oxygen vacancies to the observed emission.

In the recent years, microwave-assisted route has been used to synthesize a variety of inorganic materials from different classes^{12,13}. In this paper, we present a simple, facile microwave-irradiation based surfactant-free synthesis route for the preparation of ultra-small ZnGa_2O_4 nanoparticles using the acetylacetonates of Zn and Ga as the starting precursors, and ethylene glycol as the reaction solvent. It is worthwhile to mention here that, the whole reaction completes in just 22 minutes, make this a rapid and energy efficient process, in comparison to solid-state route or other solution-based methods like hydrothermal/solvothermal, which can take hours to days for synthesising such materials. In case of these metal acetylacetonates, the fragile M-O bonds, that can break easily in a chemical reaction, makes them very good starting materials for the preparation of various metal oxides^{7–10}. Ethylene glycol as the reaction medium has its own advantages like high boiling point (197 °C) and very high $\tan \delta$ value of 1.35 (highly efficient in converting microwave energy into thermal energy). A further advantage of using ethylene glycol can be its growth-directing ability, because of the presence

of lone pair of electrons on the two oxygen atoms that may bind to nanoparticle surface, stabilising them, thus performing the dual function of solvent and surfactant. Furthermore, the microwave-assisted solution based method can be a preferred route for nanomaterial synthesis because of its various attributes like increased reaction rates, homogenous heating and energy efficiency¹¹. Also in the reaction medium, the thermal energy is distributed uniformly because the microwave field energy is transferred directly to it, which results in ubiquitous nucleation that promotes nanocrystallinity and monodispersity in the product.

Materials and Methods

For the preparation of ZnGa_2O_4 nanopowders, 1 mmol (0.28 g) of zinc (II) acetylacetonate monohydrate and 2 mmol (0.73 g) of gallium tris-acetylacetonate (corresponding to a Zn:Ga mole ratio of 1:2) were dissolved in 50 ml of ethylene glycol in a sealable 80 ml glass vessel. A clear solution obtained after 5 minutes of continuous stirring was microwave-irradiated in a mono-mode microwave synthesiser (operating at 2.45 GHz, CEM-Discover, USA). This clear solution is heated to 200 °C and then held at this temperature for another 20 minutes. The microwave power is switched off after 20 minutes, and the reaction vessel was allowed to cool to room temperature. A white precipitate is obtained, which is isolated from the solution by centrifugation at 4000 rpm. The precipitate is washed several times with acetone, and the obtained powders are dried in a hot-air oven at 70 °C for 10 h for further studies.

The phase purity of products was examined by powder X-ray diffraction (XRD) using a PANalytical X'Pert PRO diffractometer (Cu-K α radiation, $\lambda=1.54$ Å). Field-emission scanning electron microscopy (FE-SEM, SIRION XL-40) and transmission electron microscopy (TEM, Technai-G20, 200 kV) were used to study morphology and the crystallinity of the nanopowders. Selected area electron diffraction (SAED) patterns were recorded in TEM to study the structure of the nanoparticles, and elemental analysis was carried out by using EDAX (attached to SEM and TEM). Fourier transform infrared (FT-IR, Bruker) transmittance spectra in the range of 4000–400 cm^{-1} were collected in KBr pellets. The photoluminescence (PL) emission spectra of the powder samples were collected at room temperature

with an excitation wavelength of 325 nm (He-Cd laser, Horiba Jobin-Yvon), and the Raman spectra were obtained using an argon ion laser of wavelength 514 nm using the same instrument (accumulation time is 25 seconds).

Results and Discussions

Fig. 1 shows the XRD patterns of the as-prepared product and the powder material annealed at 700 °C for 2 h in air. The results indicate that the samples are well crystallized, and all the XRD peaks in the

as-prepared and the annealed powder samples are in good agreement with cubic ZnGa_2O_4 (JCPDS 00-038-1240). However, there is a marked difference between the peak shapes of as-prepared and annealed powders. The diffraction peaks are very broad in case of as-prepared powders, indicating that the particle size is very small. By applying the Scherrer equation to calculate the particle size using peak broadening (full width at half maximum), the particle size of the as-prepared powders is deduced to be 3.5 nm whereas, as a result of annealing, the

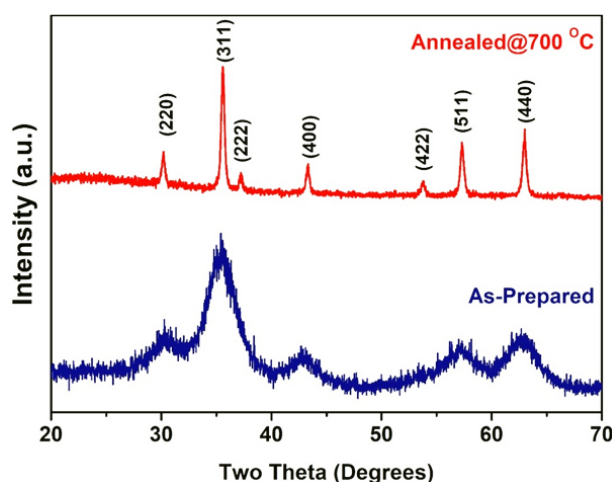


Fig. 1: XRD patterns of the as-prepared (blue) and annealed (red) ZnGa_2O_4 powder samples

crystallite size in the annealed powder is significantly larger at 19 nm. No impurity phases were present that can be observed in the experimental range.

The as-prepared ZnGa_2O_4 powders were analysed by SEM and TEM. Fig. 2(a) represents the SEM image and 2(b) shows the high magnification TEM image of the as-prepared powders; it can be readily seen that the as-prepared powders contains aggregates of nanoparticles of very small sizes. High-resolution TEM images (HRTEM) shown in Fig. 2(c) and 2(d) show that the size of these nanoparticles is considerably less than 10 nm and that they are of different shapes. The nanoparticles are indeed crystalline, as they display clear lattice fringes as seen in the red circled areas of Fig. 2(d), thus supporting the XRD data. Fig. 2(e) shows the SAED pattern of the as-prepared ZnGa_2O_4

nanopowders. A ring-type diffraction pattern is observed, and these diffraction rings gave d-spacing value corresponding to the most intense reflections of cubic ZnGa_2O_4 , viz., the (311), (400), (511) and (440) crystal planes.

The EDAX (or EDS) spectrum of the as-prepared ZnGa_2O_4 powders show the presence of Zn, Ga, O, C (from the organic moieties of the precursors and the solvent) and Cu (TEM grid). The obtained weight percentage of Zn, Ga and O from EDS data matches favourably with the theoretical values calculated for ZnGa_2O_4 . Fig. 3 shows the morphology and microstructure of annealed ZnGa_2O_4 powders. Fig. 3(a) and 3(b) shows that the sample contains aggregates of nanoparticles forming mesh-like structures. The crystallite size has also increased (>20 nm) as a result of annealing, Fig. 3(c). Further,

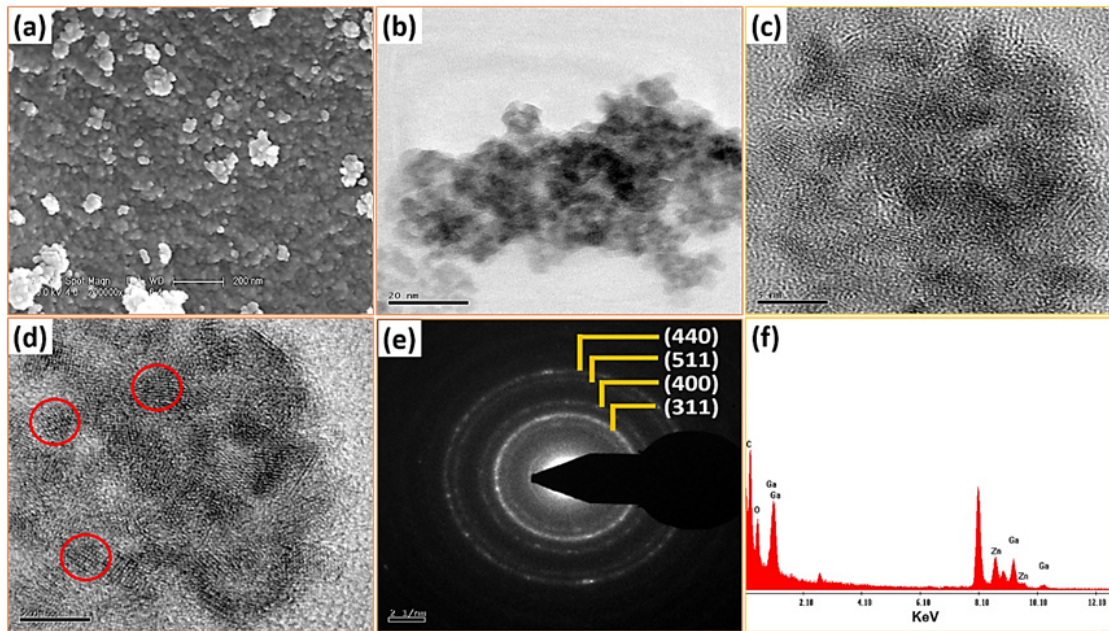


Fig. 2: A SEM (a) and a TEM (b) micrograph of the as-prepared powder sample; High resolution TEM (HRTEM) images of as-prepared nanoparticles (c) & (d); SAED pattern (e); and EDAX profile (f) of the as-prepared powders

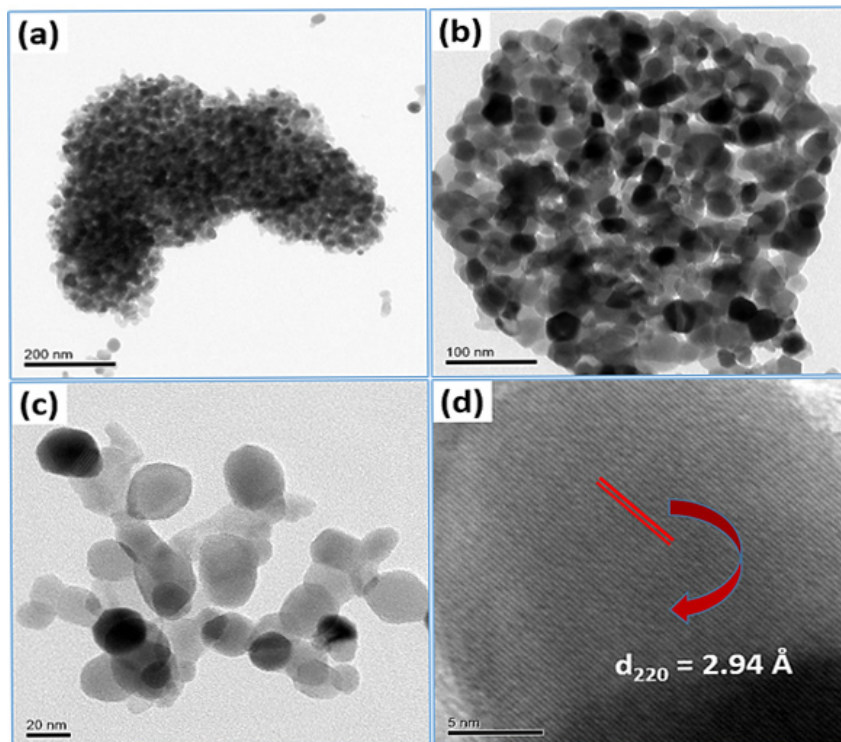


Fig. 3: TEM micrographs of annealed ZnGa_2O_4 powders (a), (b) and (c) HRTEM of a single ZnGa_2O_4 nanoparticle, showing that it is a single crystal (d)

as evident from Fig. 3(d), each of these nanoparticles is single crystal. The d-spacing calculated from the lattice fringes corresponds to the (220) interplanar distance.

The Raman spectrum of the annealed ZnGa_2O_4 powder is shown in Fig. 4. In case of spinel structures like ZnGa_2O_4 , the related phonon modes have been

assigned at $\Gamma = A_{1g} + E_g + T_{1g} + 3T_{2g} + 2A_{2u} + 2E_u + 5T_{1u} + 2T_{2u}$ ¹⁴⁻¹⁶. While the $4T_{1u}$ modes are infra-red active, the $A_{1g} + E_g + 3T_{2g}$ modes are Raman active¹⁴⁻¹⁶. These are the first order Raman modes and these modes have their origin in Zn^{2+} ions located in the tetrahedral holes, and doesn't depend on the motion of Ga^{3+} ions occupying the octahedral sites. The Raman peaks at 469 and 611 cm^{-1} are due

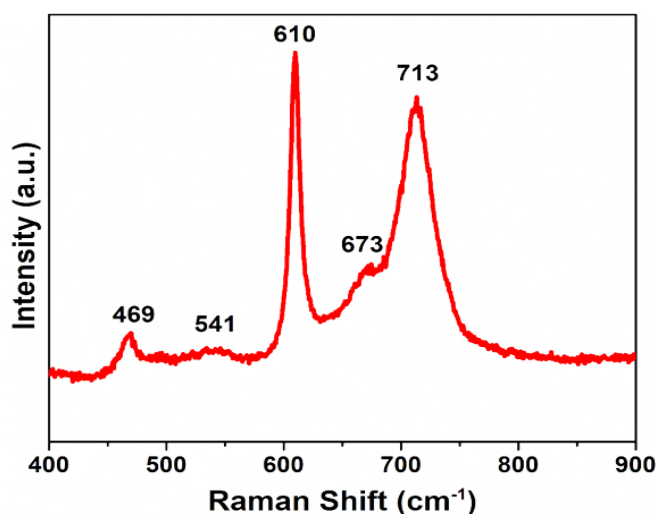


Fig. 4: Raman spectrum of the annealed ZnGa_2O_4 nanopowder

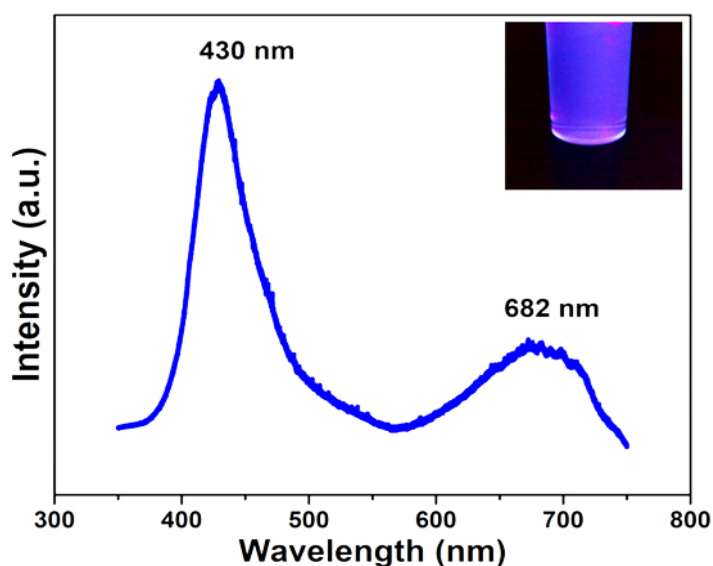


Fig. 5: Photo luminescence emission spectrum of annealed ZnGa_2O_4 nanopowders at room temperature; the inset shows a strong blue emission from ZnGa_2O_4 dispersed in ethanol, under UV excitation

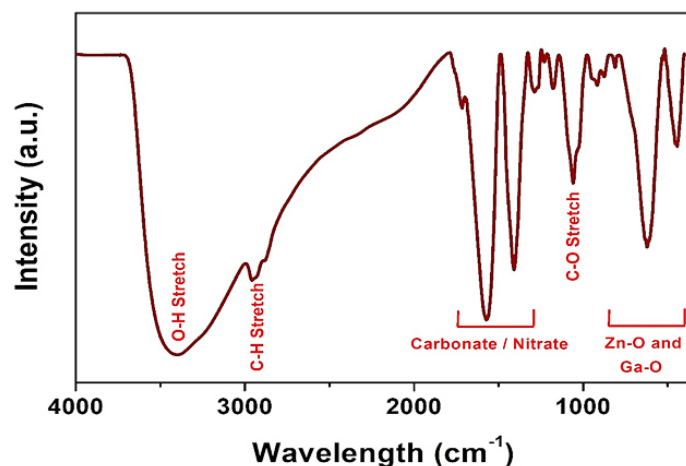


Fig. 6: Infrared spectrum of as-prepared ZnGa_2O_4 nanoparticles showing the presence of organic capping agents

to T_{2g} modes, and the A_{1g} mode is responsible for 713 cm^{-1} Raman peak. The weak second order Raman lines are present at 541 and 673 cm^{-1} . Moreover, the Raman peak around 673 cm^{-1} has been also shown to appear due to excess ZnO; the “disordered peak” well known in spinel compounds¹⁷.

Fig. 5 represents the photoluminescence emission spectrum of annealed ZnGa_2O_4 nanopowder at room temperature. The PL spectrum shows two broad peaks, viz., a strong blue emission peak centered at 430 nm and a weak broader peak centered at 682 nm . In case of undoped ZnGa_2O_4 phosphors, it is a well-established fact that the inherent blue emission originates from the self-activation center of Ga–O octahedral group. This process involves a transfer of charge between Ga^{3+} ions located at the center of octahedral sites and its six first-neighbor O^{2-} ions¹⁸. A blue shift observed in this work, vis-à-vis the usual emission shown at $450\text{--}470\text{ nm}$ by ZnGa_2O_4 phosphors prepared by various methods, may be due to the quantum-confinement effects stemming from the very small crystallite size of the present sample of ZnGa_2O_4 ¹⁹. It has also been suggested that the existence of singly charged oxygen vacancies (which depends on synthesis conditions and annealing environment) within the ZnGa_2O_4 nanoparticles may be responsible for the appearance of a small broad peak in the PL spectrum, centered at 682 nm ²⁰.

It must be noted that the as-prepared nanoparticles show no luminescence under UV excitation. This may be due to their extremely small size (hence a lot of unsatisfied bonds, leading to PL quenching), as well as the presence of organic capping agents, which have been found to be efficient quenching agents. Indeed, the IR spectrum of the as-prepared ZnGa_2O_4 powder (Fig. 6) confirms the presence of organic residues on their surface, as indicated by the presence of peaks at 2900 cm^{-1} (C–H stretch) and 1050 cm^{-1} (C–O stretch). The IR spectrum also shows the characteristic metal-oxygen vibrations of Zn–O and Ga–O at 616 and 445 cm^{-1} , respectively, in addition to absorptions due to O–H stretching at 3400 cm^{-1} and carbonates/nitrates at $1570/1400\text{ cm}^{-1}$. The very strong O–H absorption probably indicates the presence of ethylene glycol, the reaction solvent, which may effectively coat the surface of the nanoparticles formed.

Conclusion

In conclusion, nanocrystalline ZnGa_2O_4 powders having size $<5\text{ nm}$ were prepared through a simple, facile microwave-irradiation assisted method without utilising any structure-directing agents. The as-synthesised nanoparticles are crystalline, as shown by XRD and TEM analysis. Whereas the as-prepared nanoparticles don't show any luminescence due to their small size and the presence of quenching organic capping agents as (shown by the IR

spectrum), the annealed ZnGa_2O_4 nanopowder shows a strong blue emission under UV excitation, in addition to a weak emission in the red, making it potentially useful in luminescence applications.

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Conflict of Interest

We have no conflicts of interest to disclose and the manuscript has been approved by all authors.

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