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RESEARCH ARTICLE

A facile route to synthesize β-Ga_2O_3 nanoparticles from γ-polymorph through a rapid microwave route and their optical properties

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Abstract

Due to the wide bandgap, monoclinic structure and thermodynamic stability, β-polymorph form of Ga_2O_3 nanomaterials is well-received for various applications. However, as the γ-Ga_2O_3 is difficult to synthesize, less attention has been paid towards it and its conversion to β-polymorph. This paper reports the single-step synthesis of γ-Ga_2O_3 using a microwave-assisted procedure. In this regard, γ-Ga_2O_3 powders are synthesized in minutes using benzyl alcohol as the solvent using gallium acetylacetone as the precursor. The XRD of the as-prepared powders indicates the formation of the γ-Ga_2O_3 phase, the very broad peaks indicative of the small crystallite size as confirmed by TEM. The γ-Ga_2O_3 powders were annealed at different temperatures and the complete phase conversion of γ-Ga_2O_3 phase to β-Ga_2O_3 phase happens at 700 °C. The TEM analysis shows the crystallite size to be ≈10 nm for the annealed β-Ga_2O_3 phase. The as-prepared nanopowders show very weak luminescence under excitation and in contrast, a blue-green emission is observed in case of annealed powders. This confirms the presented strategy as having the potential to use β-Ga_2O_3 nanopowders for different optoelectronic applications.

KEYWORDS
FTIR, Ga_2O_3, luminescence, microwave-synthesis, nanoparticles

1 | INTRODUCTION

New synthesis techniques that enable scientists to perform more experiments within a given time would be very beneficial to scientific community as well as the R&D enterprise. Microwave-assisted solution-based chemistry, which makes fast synthesis possible, is such a technique.[1,2] Microwave-assisted synthesis (MAS) of inorganic materials is considered a nascent technology which dramatically reduces reaction times due to the solvent superheating effect, improving reaction yields, avoiding byproducts and simplifying/shortening reaction procedures for combinatorial chemistry. Furthermore, MAS uses a safe heating source that can turned "on" and "off" instantaneously and can be applied in solvent-free environment. This often offers better product quality, sustainability and chemical yield, which is the advantageous compared to traditional heating sources.[3] Therefore, the MAS technique is expected to play an significant role in the environmentally friendly "synthetic nanotechnology" of the future.[1] Microwave-enhanced chemistry is based on the efficient heating of molecules by two main mechanisms: dipole rotation and ionic conduction which has been widely discussed by several authors.[1,3] The microwave technique greatly contributes to all areas of synthetic chemistry, particularly in the fabrication of nanostructures. The field of

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microwave-assisted synthesis of inorganic nanomaterials is growing rapidly, and almost all classes of functional materials have been targeted.[1]

Gallium based materials have been used for a wide variety of applications.[4–8] Gallium (III) oxide (Ga_2O_3) is a critical wide-band-gap semiconductor (E_g = 4.9 eV) that has various potential applications. These include semiconductor lasers, switching memories and high-temperature gas sensors.[9,10] In its nanometric form, Ga_2O_3 is expected to be extensively used as photocatalyst in water-splitting, CO_2 photoreduction, and waste-water treatment.[11–14] As such, among the various wide-band-gap transparent semiconducting oxides, Ga_2O_3 has garnered considerable interest in the scientific community.[14–18] Although there are several reports on the synthesis of β-Ga_2O_3 nanopowders; however, limited information on the synthesis of γ-Ga_2O_3 is available.[19–22] Previous reports for γ-Ga_2O_3 nanopowder synthesis indicate the reaction conditions used are harsh, reaction times very long, requiring dedicated setups for synthesis, which are not readily available everywhere.[21,23–26] In this article, we report a facile microwave-based synthesis route for the preparation of ultra-small nanoparticles of γ-Ga_2O_3, thermal conversion to β-Ga_2O_3 phase and their optical properties.

2 | MATERIALS AND METHODS

2.1 | Synthesis

All the chemicals used for synthesis were of AR grade and were used as such without any purification. Commercial gallium oxide powder was procured from Merck and was used as received. For the synthesis of Ga_2O_3 nanoparticles, Gallium acetylacetone was used as a precursor which was prepared as follows. In a typical synthesis 50 mL of 10 mM $Ga(NO_3)_3$ solution and 30 mmol of acetyl acetone (in 30 mL 1:1 H_2O:EtOH) were mixed together and after 10 min of stirring, KOH was added dropwise till the pH reached ≈6.7, which resulted in a white precipitate. The resulting white precipitate was filtered, washed repeatedly with water and dried at 50 °C for several hours. The obtained powder was dissolved in acetone to get single crystals of gallium acetylacetone.

For the synthesis of Ga_2O_3 nanoparticles, 0.5 g of $Ga(acac)_3$ taken in a round bottom flask was dissolved in 100 mL benzyl alcohol (Rankem, AR) and then subjected to microwave-irradiation for 5 min (at 800 W power) in a modified domestic microwave oven (LG) fitted with a water-cooling condenser. The irradiation results in a white precipitate which was separated from the solution by centrifugation, washed first with DI water and then several times with ethanol. The final powder was dried at 70 °C for 12 h in a hot air oven for further studies. The synthesis scheme for the preparation of $Ga(acac)_3$ precursor and Ga_2O_3 nanopowders is shown in Figure 1.

2.2 | Characterization

All the samples were characterized by powder XRD diffractometer (Philips's, Model 3710 MPD Cu-Kα radiation). XRD patterns were recorded from 20° to 80° (2θ) with a scanning step of one degree per minute. XPS measurements were conducted using an MK II photoelectron spectrometer, employing Al-Kα (1486.6 eV) as the X-ray source. Morphology, size, and crystallinity analyses of the nanoparticles were performed via transmission electron microscopy (TEM) using a Technai-G20 high-resolution electron microscope (HRTEM) with an accelerating voltage of 200 kV. The TEM samples were prepared by slowly evaporating a dilute solution of the powder sample dispersed in ethanol and depositing it onto a formvar-coated copper grid (300 mesh). Photoluminescence (PL) spectra were obtained at room temperature using an excitation wavelength of 325 nm (He-Cd laser, Horiba Jobin-Yvon LabRAM HR 100, CCD detector) with an acquisition time of 5 s, and the LMU-40×-NUV objective was utilized for data recording.

3 | RESULTS AND DISCUSSION

The XRD pattern of the as-prepared powders and the samples annealed in air at different temperatures together with the reference XRD patterns of cubic γ-Ga_2O_3 phase (JCPDS File-No. 00-041-1012) and the monoclinic β-Ga_2O_3 phase (JCPDS File-No. 00-041-1103) are shown in Figure 2. In case of the as-prepared powders, the two very broad peaks in the 2θ range of 30°–40° and 60°–70° indicating small crystallite size can be identified, and these can be indexed to γ-Ga_2O_3 phase. After the sample were annealed, the peaks become intense and sharp both as a result of crystallite growth and improvement in the degree of crystallinity. The phase conversion starts at 500 °C and the complete conversion of γ-Ga_2O_3 phase to β-Ga_2O_3 phase happens at 700 °C evidenced by all the peaks being indexable to the β-Ga_2O_3 phase.

The morphology and microstructure of the as-prepared and annealed β-Ga_2O_3 nanopowders were analyzed by transmission electron microscopy (TEM) and the results are shown in Figure 3. The low and high-magnification TEM images of the as-prepared powders are shown in Figure 3a–c and indicate very small-sized nanoparticles with no fixed morphology. Most of the nanoparticles have sizes < 10 nm (Figure 3a,b). The high-resolution electron micrographs (HR-TEM images) of individual nanoparticles (nanocrystals) show clear lattice fringes, as encircled in white color (Figure 3c). The typical size ranges from ≈5 to 8 nm for the nanoparticles. In contrast, the TEM results of annealed β-Ga_2O_3 powder samples (annealed at 700 °C) are shown in Figure 3d–f. These results show agglomerated nanoparticles with overall increase in size due to annealing (Figure 3e,f). Moreover, the SAED pattern (Figure 3e inset) reveals their polycrystalline nature; the diffraction rings are

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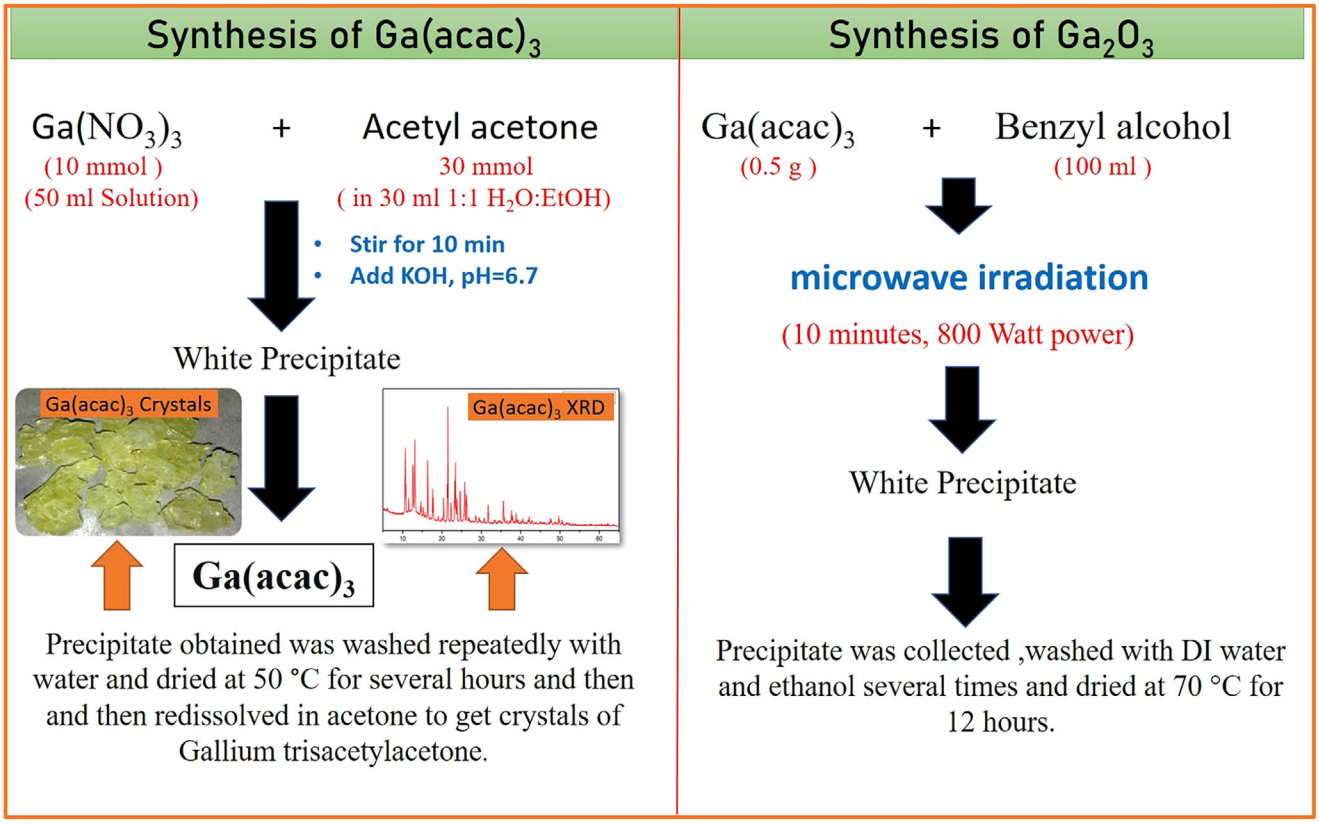
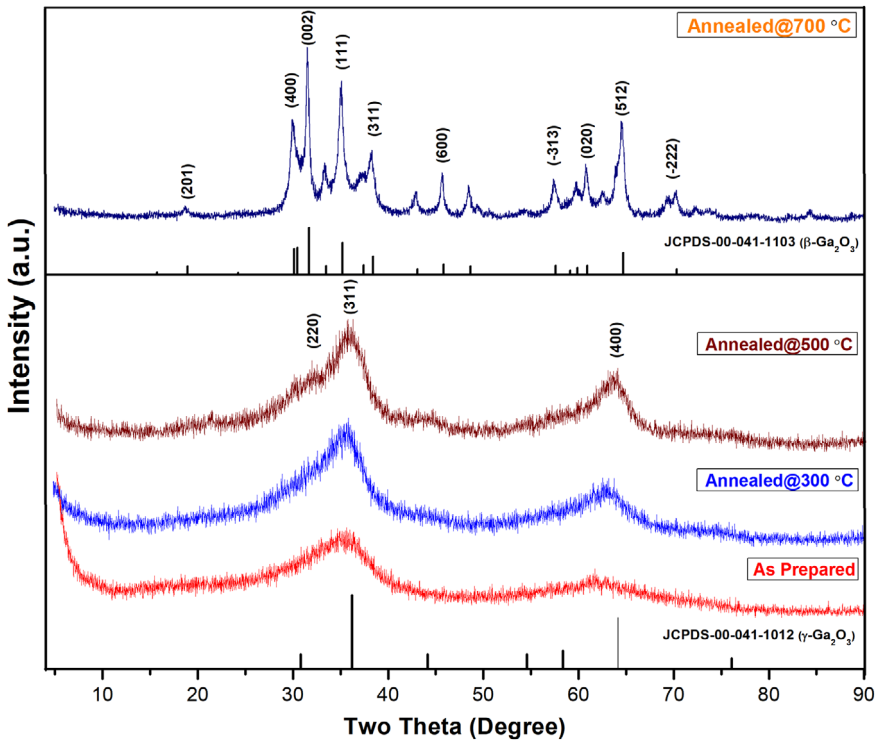


FIGURE 1 A schematic for the synthesis of $Ga(acac)_3$ precursor and Ga_2O_3 nanoparticles. The insets show the $Ga(acac)_3$ crystals and the corresponding PXRD pattern.

FIGURE 2 The XRD pattern of the as-prepared powders, powders annealed at 300 °C for 3 h, 500 °C for 3 h, 700 °C for 3 h.



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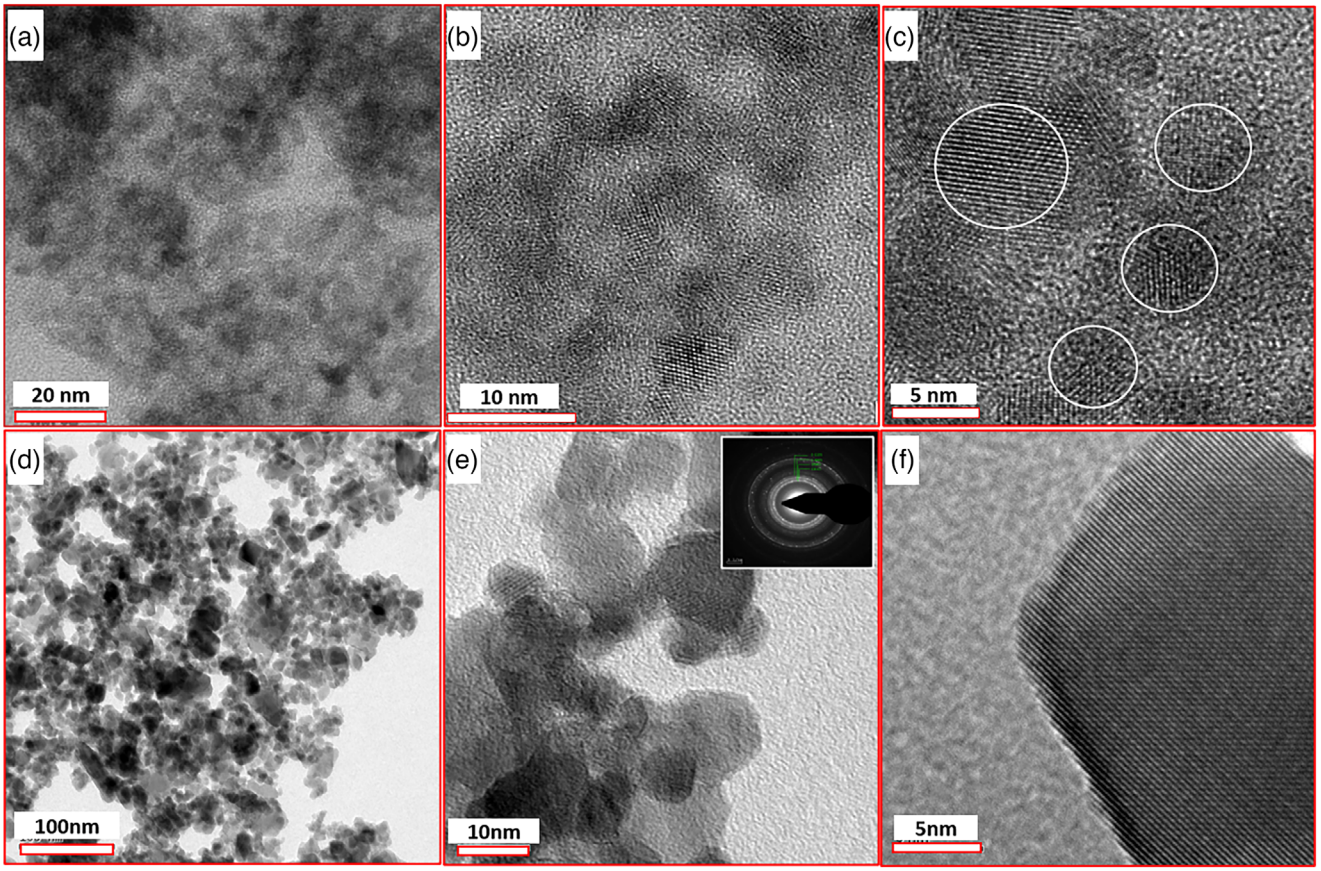

FIGURE 3 TEM images of (a–c) as-prepared and (d–f) annealed β-Ga_2O_3 nanopowders at different magnifications, (c) HRTEM showing lattice-fringes of very fine crystals; (e) the SAED pattern (inset) reveals polycrystallinity, however some nanocrystals as shown by (f) HRTEM can also be present.

easily indexed to the (−1 1 3), (−2 0 2), (0 0 4), (1 1 1) crystal planes of β-Ga_2O_3.

Figure 4 represents the analysis performed by Fourier transform infrared spectroscopy (FTIR) in the 4000−400 cm^{-1} region obtained for the as-prepared and Ga_2O_3 powders annealed at 700 °C. The FTIR spectrum of commercially available Ga_2O_3 is also shown for reference. A very broad peak over 2850 cm^{-1} in the annealed samples of β-Ga_2O_3 nanopowders can be assigned to the H—O—H stretching resulting from adsorbed moisture and O—H stretching of GaOOH. In case of as-prepared sample, the broadness in this region may be enhanced by the presence of some organic moieties encapsulating the nanoparticles. Further, the IR spectrum of the commercial Ga_2O_3 powder shows two intense peaks centered at 695 and 448 cm^{-1} and these peaks can be assigned to the vibrations involving the GaO_4 tetrahedra and GaO_6 octahedra, respectively, as reported in the literature.[27,28] These two corresponding peaks appear at 665–680 cm^{-1} for as-prepared powders and 460–475 cm^{-1} for nanopowders annealed 700 °C. The broadness of these peaks with respect to the commercial powder sample shows that the particle size in case of microwave-synthesized is particularly small, which leads to a distribution of Ga—O distances in the crystallites.

It is well known that Ga_2O_3 nanopowders show a diverse array of PL signatures which, in turn, depend on the shape/size of nanopowders, the synthetic protocol and surfactant used, and the annealing atmosphere.[21,23–26] Figure 5 represents the room temperature photoluminescence spectra of the annealed β-Ga_2O_3 nanocrystalline powder and the commercial grade β-Ga_2O_3 powder sample under excitation at 325 nm. A typical blue-green emission centered at 426 and 536 nm is observed in case of the annealed β-Ga_2O_3 nanopowders, which represents a blue shift of 10–15 nm from the commercial powder sample, which can be due to size-related effects. This emission can be attributed to an electron-hole recombination process resulting from an acceptor formed by gallium vacancies (V_{Ga}) and a donor formed by oxygen vacancies (V_O), respectively.[11] In addition, a weak UV emission band centered at ≈366 nm present in case of the annealed sample can only be assigned to the recombinations in a self-trapped excitation.[11] Moreover, very weak luminescence was observed in case of as-prepared powders, which may be attributed to the small crystallite size (numerous surface defects) or to the presence of any organic moieties on the surface (due to the method of synthesis) that led to the luminescence quenching.

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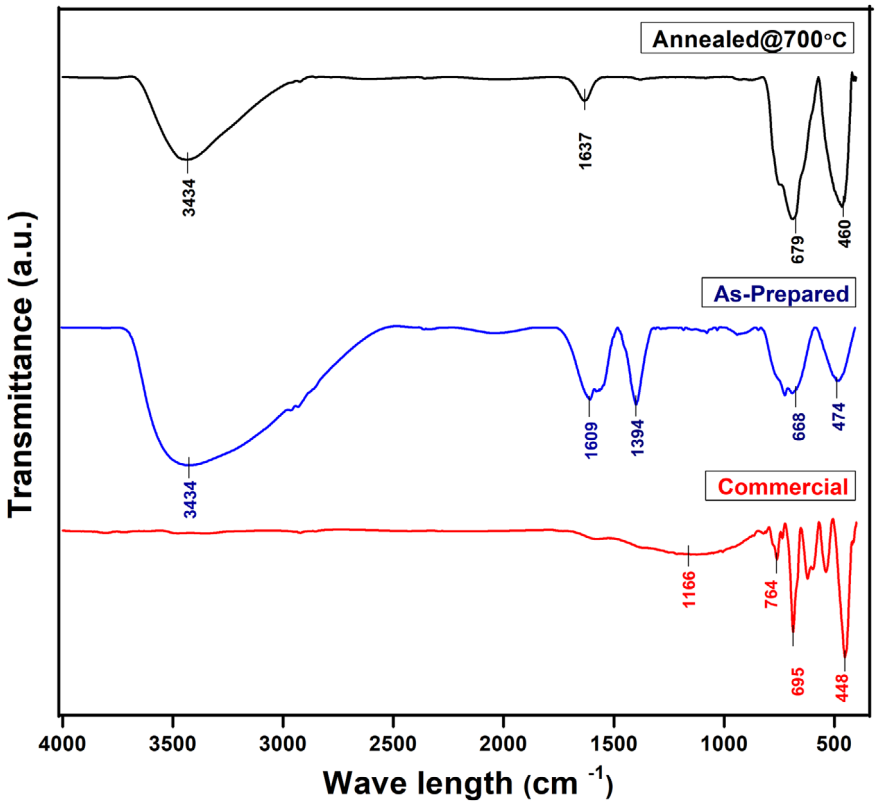

FIGURE 4 IR spectral spectra of commercial Ga_2O_3 powder, as-prepared γ-Ga_2O_3 powder and annealed β-Ga_2O_3 nanopowders.

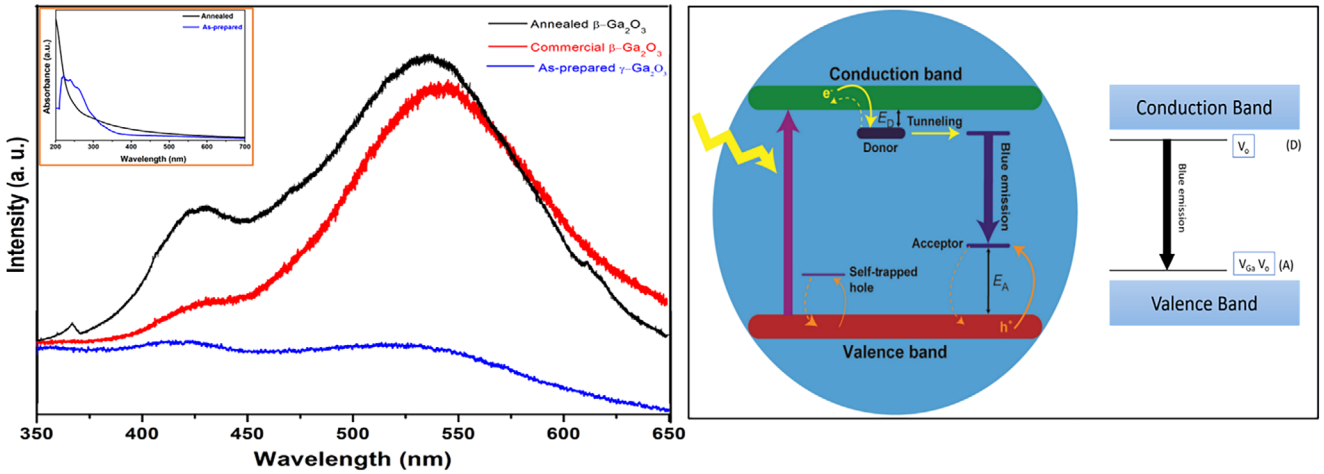

FIGURE 5 PL spectra of the as-prepared γ-Ga_2O_3, commercial and the annealed β-Ga_2O_3 nanopowders excited by 325 nm He–Cd laser and the schematic diagram depicting the pathways through which charge carriers travel, leading to the emission of blue photoluminescence in gallium oxide. The inset shows the UV–Vis absorption spectra of as-prepared and annealed powders.

4 | CONCLUSION

In conclusion, γ-Ga_2O_3 phase was synthesized through a rapid microwave assisted route and its thermal conversion to the oxide β-Ga_2O_3 phase was studied. The as-prepared γ-Ga_2O_3 powders consist of very small nanoparticles which show very weak luminescence under excitation. In contrast the annealed β-Ga_2O_3 nanopowders show a strong blue green emission. The lack of emission in case of as-prepared nanopowders can be attributed to minimal particle size and/or the presence any organic moieties capping their surface resulting in luminescence quenching.

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REFERENCES

1. I. Bilecka, M. Niederberger, Microwave chemistry for inorganic nanomaterials synthesis, *Nanoscale* **2010**, *2*, 1358.
2. Y. J. Zhu, F. Chen, Microwave-assisted preparation of inorganic nanostructures in liquid phase, *Chem. Rev.* **2014**, *114*, 6462.
3. T. A. Saleh, S. Majeed, A. Nayak, B. Bhushan, Principles and advantages of microwave- assisted methods for the synthesis of nanomaterials for water purification, in *Advanced Nanomaterials for Water Engineering, Treatment and Hydraulics*, IGI Global, Hershey, PA **2017**, p. 40.
4. F. Shi, H. Qiao, Preparations, properties and applications of gallium oxide nanomaterials–A review, *Nano Sel.* **2022**, *3*, 348.
5. N. S Jamwal, A. Kiani, Gallium oxide nanostructures: A review of synthesis, properties and applications, *Nanomaterials* **2022**, *12*, 2061.
6. Z. K. Heiba, M. B. Mohamed, N. G. Imam, Structural, magnetic, and optical performance of Al and Mo doped $GaFeO_3$, *J. Supercond. Novel Magn.* **2016**, *29*, 1647.
7. K. Nguyen, P. V Radovanovic, Defects and impurities in colloidal Ga_2O_3 nanocrystals: New opportunities for photonics and lighting. *Can. J. Chem.* **2022**, *100*, 1.
8. S. Wani, H. S. Sofi, F. A. Sheikh, S. A. Shivashankar, S. Majeed, $ZnGa_2O_4$ nanophosphors: rapid synthesis, characterization and luminescence properties, *Mater. Sci. Res.* **2017**, *14*, 116.
9. M. Bartic, C. I. Baban, H. Suzuki, M. Ogita, M. Isai, β-Gallium oxide as oxygen gas sensors at a high temperature, *J. Am. Ceram. Soc.* **2007**, *90*, 2879.
10. M. Baldini, Z. Galazka, G. Wagner, Recent progress in the growth of β-Ga_2O_3 for power electronics applications, *Mater. Sci. Semicond. Process.* **2018**, *78*, 132.
11. L. Binet, D. Gourier, Origin of the blue luminescence of β-Ga_2O_3, *J. Phys. Chem. Solids* **1998**, *59*, 1241.
12. E. I. El-Sayed, A. A. Al-Ghamdi, S. Al-Heniti, F. Al-Marzouki, F. El-Tantawy, Synthesis of ultrafine β-Ga_2O_3 nanopowder via hydrothermal approach: A strong UV "excimer-like" emission, *Mater. Lett.* **2011**, *65*, 317.
13. Y. Lv, L. Yu, G. Zha, D. Zheng, C. Jiang, Application of soluble salt-assisted route to synthesis of β-Ga_2O_3 nanopowders, *Appl. Phys. A: Mater. Sci. Process.* **2014**, *114*, 351.
14. V. Zade, B. Mallesham, S. Shantha-Kumar, A. Bronson, C. V. Ramana, Interplay between solubility limit, structure, and optical properties of tungsten-doped Ga_2O_3 compounds synthesized by a two-step calcination process, *Inorg. Chem.* **2019**, *58*, 3707.
15. L. K. Ping, D. D. Berhanuddin, A. K. Mondal, P. S. Menon, M. A. Mohamed, Properties and perspectives of ultrawide bandgap Ga_2O_3 in optoelectronic applications, *Chin. J. Phys.* **2021**, *73*, 195.
16. T. Miyata, T. Nakatani, T. Minami, Gallium oxide as host material for multicolor emitting phosphors, *J. Lumin.* **2000**, *87-89*, 1183.
17. D. Guo, Q. Guo, Z. Chen, Z. Wu, P. Li, W. Tang, Review of Ga_2O_3-based optoelectronic devices, *Mater. Today Phys.* **2019**, *11*, 100157.
18. Y. Wu, S. Feng, M. Zhang, S. Kang, K. Zhang, Z. Tao, Y. Fan, W. Lu, Self-catalyst b-Ga_2O_3 semiconductor lateral nanowire networks synthesis on the insulating substrate for deep ultraviolet photodetectors, *RSC Adv.* **2021**, *11*, 28326.
19. Y. Takano, Y. Hayashi, J. Fukushima, H. Takizawa, Room-temperature synthesis of γ-Ga_2O_3 nanoparticles from gallium metal via ultrasound irradiation, *Adv. Powder Technol.* **2021**, *32*, 860.
20. V. Vasanthi, M. Kottaisamy, V. Ramakrishnan, Near UV excitable warm white light emitting Zn doped γ-Ga_2O_3 nanoparticles for phosphor-converted white light emitting diode, *Ceram. Int.* **2019**, *45*, 2079.
21. L. Cui, H. Wang, B. Xin, G. Mao, One-step rapid synthesis of ultrafine γ-Ga_2O_3 nanocrystals by microwave hydrothermal method in ammonium hydroxide medium, *Appl. Phys. A* **2017**, *123*, 1.
22. H. Y. Playford, A. C. Hannon, M. G. Tucker, D. M. Dawson, S. E. Ashbrook, R. J. Kastiban, J. Sloan, R. I. Walton, Characterization of structural disorder in γ-Ga_2O_3, *J. Phys. Chem. C* **2014**, *118*, 16188.
23. Y. Hou, J. Zhang, Z. Ding, L. Wu, Synthesis, characterization and photocatalytic activity of β-Ga_2O_3 nanostructures, *Powder Technol.* **2010**, *203*, 440.
24. L. Li, W. Wei, M. Behrens, Synthesis and characterization of α-, β-, and γ-Ga_2O_3 prepared from aqueous solutions by controlled precipitation, *Solid State Sci.* **2012**, *14*, 971.
25. R. Lorenzi, A. Paleari, N. V. Golubev, E. S. Ignat'eva, V. N. Sigaev, M. Niederberger, A. Lauria, Non-aqueous sol–gel synthesis of hybrid rare-earth-doped γ-Ga_2O_3 nanoparticles with multiple organic–inorganic-ionic light-emission features, *J. Mater. Chem. C.* **2015**, *3*, 41.
26. A. Sharma, M. Varshney, H. Saraswat, S. Chaudhary, J. Parkash, H.-J. Shin, K.-H. Chae, S.-O. Won, Nano-structured phases of gallium oxide (GaOOH, α-Ga_2O_3, β-Ga_2O_3, γ-Ga_2O_3, δ-Ga_2O_3, and ε-Ga_2O_3): fabrication, structural, and electronic structure investigations, *Int. Nano Lett.* **2020**, *10*, 71.
27. A. J. Hinchcliffe, J. S. Ogden, Matrix isolation studies on the gallium-indium-oxygen system. Infrared spectra and structures of molecular gallium(I) oxide, indium(I) oxide and indium gallium suboxide (InOGa), *J. Phys. Chem.* **2002**, *77*, 2537.
28. Y. Quan, D. Fang, X. Zhang, S. Liu, K. Huang, Synthesis and characterization of gallium oxide nanowires via a hydrothermal method, *Mater. Chem. Phys.* **2002**, *121*, 142.

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