

Green Synthesis and Characterization of Gallium(III) Sulphide (α -Ga₂S₃) Nanoparticles at Room Temperature

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Abstract. Two different batches of Gallium(III) sulphide nanocrystals, (α -Ga₂S₃)₁ and (α -Ga₂S₃)₂ were synthesized at room temperature by the reaction of Gallium(III) chloride with sodium thiosulphate in water for 10 and 20 min respectively. The resultant nanoparticles were characterized by different spectroscopic techniques. TEM micrographs showed well-defined, close to hexagonal particles, and the lattice fringes in the HRTEM images confirmed their nanocrystalline nature. The sizes of (α -Ga₂S₃)₁ and (α -Ga₂S₃)₂ were 12 and 35 nm respectively with similar morphologies. Optical band gap energies (3.43 eV/3.41 eV) and photoluminescence peaks 635/641 nm (red shift) and 414/420 nm (blue shift) of the synthesized α -Ga₂S₃ nanocrystals suggest that they may be promising photocatalysts. Raman spectra for the α -Ga₂S₃, shows very sharp bands at 119, 135 and 148 cm⁻¹ due to Ga-S₂ scissoring.

Introduction

Synthesis of shape and size control semiconductor nanoparticles has been intensively pursued because of their size-dependent characteristics, and their novel electronic, magnetic, optical, chemical, and mechanical properties that cannot be obtained in their bulk counterparts [1-4]. A wide range of approaches for synthesis of nanoparticles have been reported, such as the hydrothermal method, solvothermal methods and low temperature synthesis (co-precipitation, sol-gel encapsulation), which are not environmentally friendly [5-6]. Researcher are evaluating different green synthesis routes to synthesize nanoparticles. Group III sulphides are an interesting class of

materials with promise in photovoltaic and optoelectronic applications [7]. Gallium sulfide (Ga_2S_3) is an important semiconducting material because of its wide band gap (3.05 eV at 300 K), which leads many valuable properties, making it attractive in photoelectric device, electrical sensor, and nonlinear optical applications. Many synthetic routes have been reported for the synthesis of gallium sulphide, Hu et al. [8] synthesized gallium sulphide nanotubes by annealing the natural lamellar precursor in argon, whereas, Gautam et al., [9] used laser irradiation and thermally induced exfoliation method to get the nanocrystals from bulk gallium sulphide. Ga_2S_3 nanoclusters encapsulated in Zeolite Y have also been synthesized [10]. Both the groups of Shen and Panda have used thermal evaporation process to synthesized Ga_2S_3 nanobelts [11]. However, there is no published report or controlled research data on synthesis of Ga_2S_3 nanoparticles in aqueous medium (green solvent) at room temperature. In this study, we have synthesized $\alpha\text{-Ga}_2\text{S}_3$ nanoparticles at room temperature by the reaction of gallium(III) chloride and sodium thiosulphate without using any toxic organic surfactants and solvents.

Experimental

Gallium (III) chloride and sodium thiosulphate were purchased from Sigma-Aldrich. Deionized water from a MilliQ® system was used in all the experiments. Synthesis was carried out inside a glove box under N_2 atmosphere. An ice cooled aqueous solution of gallium(III) chloride 3.82 g (0.02 mol) and ice cooled aqueous solution of sodium thiosulphate 4.74 g (0.03 mol) were mixed together in a round-bottomed flask, placed in an ice-water bath. After mixing the solution, the round bottom flask was removed from the ice-water bath and stirred at room temperature for 10 min. Resulting light yellow colour colloidal solution was centrifuged at 12000 rpm for 20 min. The light yellow powder of gallium sulphide (Ga_2S_3)₁ was washed several times with deionized water and dried in a vacuum oven. A similar method has been used to synthesize (Ga_2S_3)₂, but here the round bottom flask was stirred for 20 min. The synthesized nanoparticles were characterized by XRD using a PANalytical X'Pert Pro X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda=1.54 \text{ \AA}$) and field emission transmission

electron microscope (FETEM-JEM 2100F). Raman spectra over the spectral range $100\text{--}800\text{ cm}^{-1}$ were taken at room temperature using an LABRAM Dilor spectrometer (Jobin Yvon Horiba Group) equipped with a triple monochromator; liquid nitrogen cooled charge-coupled device (CCD) detector. The UV-Vis absorption spectra were recorded using a Perkin Elmer spectrometer. The photoluminescence spectra were measured on a Perkin Elmer LS-55 fluorescence spectrometer.

Results and Discussion

$(\alpha\text{-Ga}_2\text{S}_3)_1$ and $(\alpha\text{-Ga}_2\text{S}_3)_2$ nanoparticles were prepared by the reaction of gallium chloride and sodium thiosulphate for 10 and 20 minutes respectively, at room temperature. Fig. 1a and 1b shows TEM images of both types of GaS nanocrystals. The sizes of $(\alpha\text{-Ga}_2\text{S}_3)_1$ and $(\alpha\text{-Ga}_2\text{S}_3)_2$ were 12 nm and 35 nm respectively with similar morphologies. The particle size distribution histogram of nanoparticles was obtained and shows that the size ranges from 6 nm to 40 nm in diameter with an average size of 12 nm and 35 nm for $(\alpha\text{-Ga}_2\text{S}_3)_1$ and $(\alpha\text{-Ga}_2\text{S}_3)_2$ respectively. The HRTEM images of $(\alpha\text{-Ga}_2\text{S}_3)_1$ and $(\alpha\text{-Ga}_2\text{S}_3)_2$ displaying clear fringes with interlayer spacing measured to be $0.53 \pm 0.005\text{ nm}$, very close to the lattice spacing of the (110) planes of wurtzite in hexagonal $\alpha\text{-Ga}_2\text{S}_3$ nanocrystals. The corresponding EDS results indicate that the nanoparticles consist of Ga and S with a ratio of 2:3.

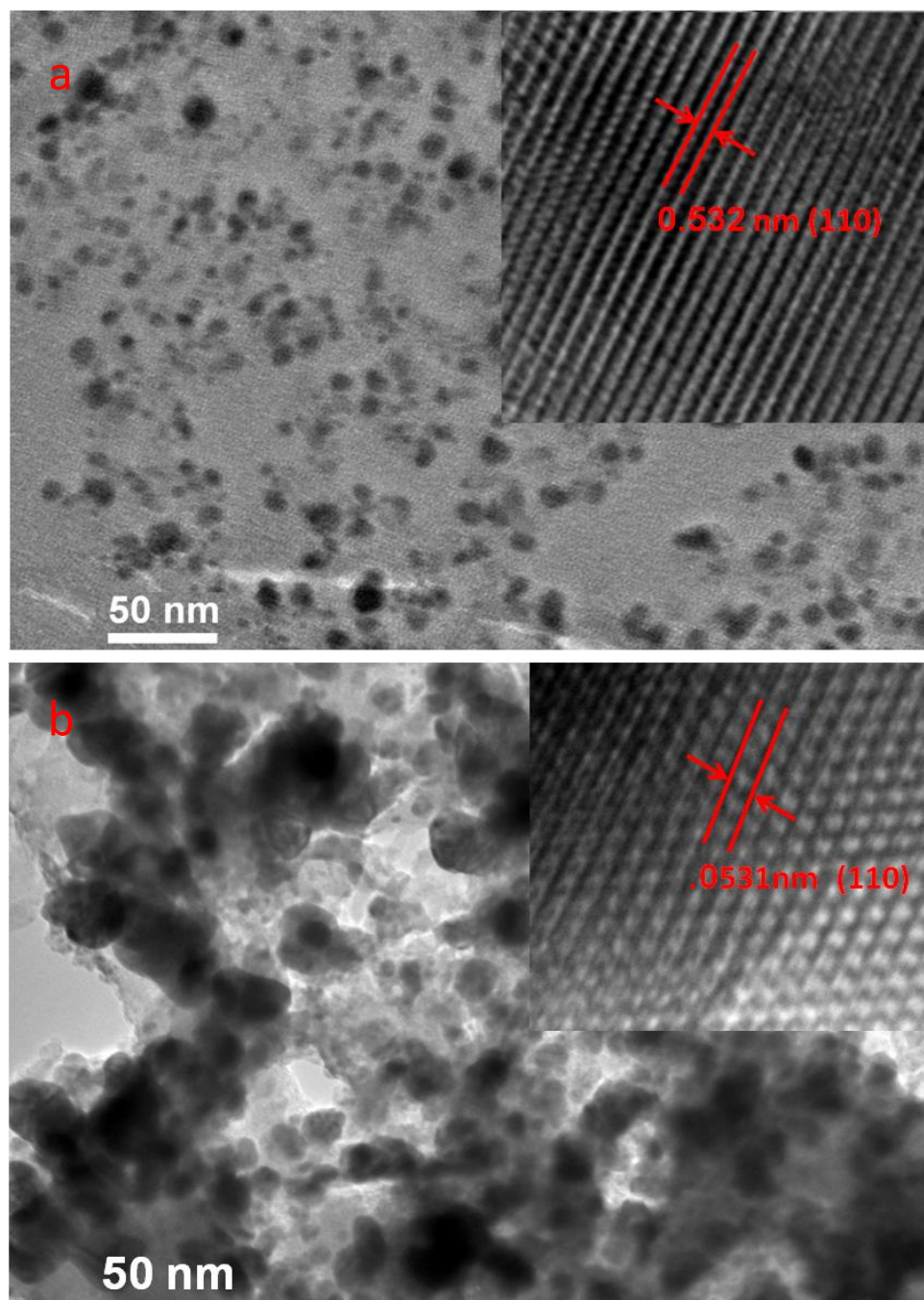


Fig. 1. TEM and HRTEM spectra of (a) (α-Ga₂S₃)₁ (b) and (α-Ga₂S₃)₂.

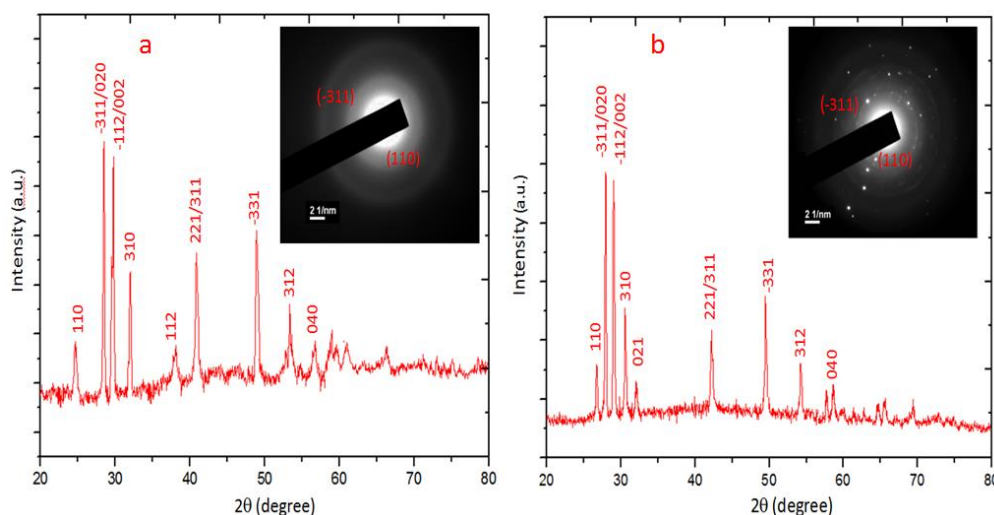


Fig. 2. XRD spectrum of (a) $(\alpha\text{-Ga}_2\text{S}_3)_1$ (b) and $(\alpha\text{-Ga}_2\text{S}_3)_2$.

The XRD patterns, in Fig. 2a and 2b can be indexed to the hexagonal Ga_2S_3 nanocrystals with lattice constants of $a = 11.120 \text{ \AA}$, $b = 6.395 \text{ \AA}$ and $c = 7.002 \text{ \AA}$, which are consistent with the data in the standard card (JCPDS 16-0500). The (110), (-311), (020), (310), (021), (221) and (312) planes of wurtzite $\alpha\text{-Ga}_2\text{S}_3$ are clearly distinguishable in the pattern [12]. The SAED pattern consists of broad diffuse rings, which are indicative of the small size of the particles. The diffraction rings can be indexed to the (110) and (-311) planes, confirming the wurtzite phase of $\alpha\text{-Ga}_2\text{S}_3$ nanoparticles. Average particle size of nanocrystal is estimated according to Scherrer equation [13]

$$D = \frac{K\lambda}{\beta_{2\theta} \cos 2\theta}$$

Where $K = 0.94$, λ is the X-ray wavelength and $\beta_{2\theta}$ is the full width at half maximum of the XRD selected diffraction peak and θ is diffraction angle. The particle size of the synthesized nanocrystal is found to be 12 nm and 30 nm for $(\alpha\text{-Ga}_2\text{S}_3)_1$ and $(\alpha\text{-Ga}_2\text{S}_3)_2$ respectively.

The optical absorption spectra of dispersed $(\alpha\text{-Ga}_2\text{S}_3)_1$ and $(\alpha\text{-Ga}_2\text{S}_3)_2$ were measured in the region 200–800 nm at room temperature. The optical spectra can be used to calculate an approximate direct band gap using the Tauc relation [14].

$$\alpha = A(h\nu - E_g)/2h\nu$$

Where α is absorption coefficient, E_g is the absorption band gap, and A is a constant. The optical band gaps were obtained 3.43 eV and 3.41 eV respectively for (α -Ga₂S₃)1 and (α -Ga₂S₃)2. The band edges for both samples are blue-shifted in relation to the bulk material and agree with those reported values. The particle size of nanocrystals is also calculated using Brus equation [15]:

$$E^{eff} = E_g + \frac{h^2\pi^2}{2\mu R^2} - \frac{1.8e^2}{4\pi\epsilon\epsilon_0 R}$$

And ($1/\mu = 1/m_e^* + 1/m_h^*$), where m_e^* is the effective mass of the electron (0.19 m_e), m_h^* is the effective mass of hole (0.8 m_h), R is the radius of the particle, ϵ is the dielectric constant (5.7) and ϵ_0 is the permittivity of free space. The particle size of the Ga₂S₃ nanoparticles as estimated using the above equation are found to be 12 nm and 35 nm for (α -Ga₂S₃)1 and (α -Ga₂S₃)2 respectively as estimated from the XRD and TEM analysis.

The Raman spectra of the (α -Ga₂S₃)1 and (α -Ga₂S₃)2 were recorded at room temperature and shown in Fig 3. The strongest scattering lines are observed in the range of 100–450 cm⁻¹ for both the samples. The sharp bands at 119, 135 and 148 cm⁻¹ are mainly due to the Ga-S₂ scissoring [16] and the band at 238 cm⁻¹ is due to the ring out plane bending of (α -Ga₂S₃). The presence of Ga-S symmetric stretching is clearly identified with the large intense spectral band at 392.4 cm⁻¹.

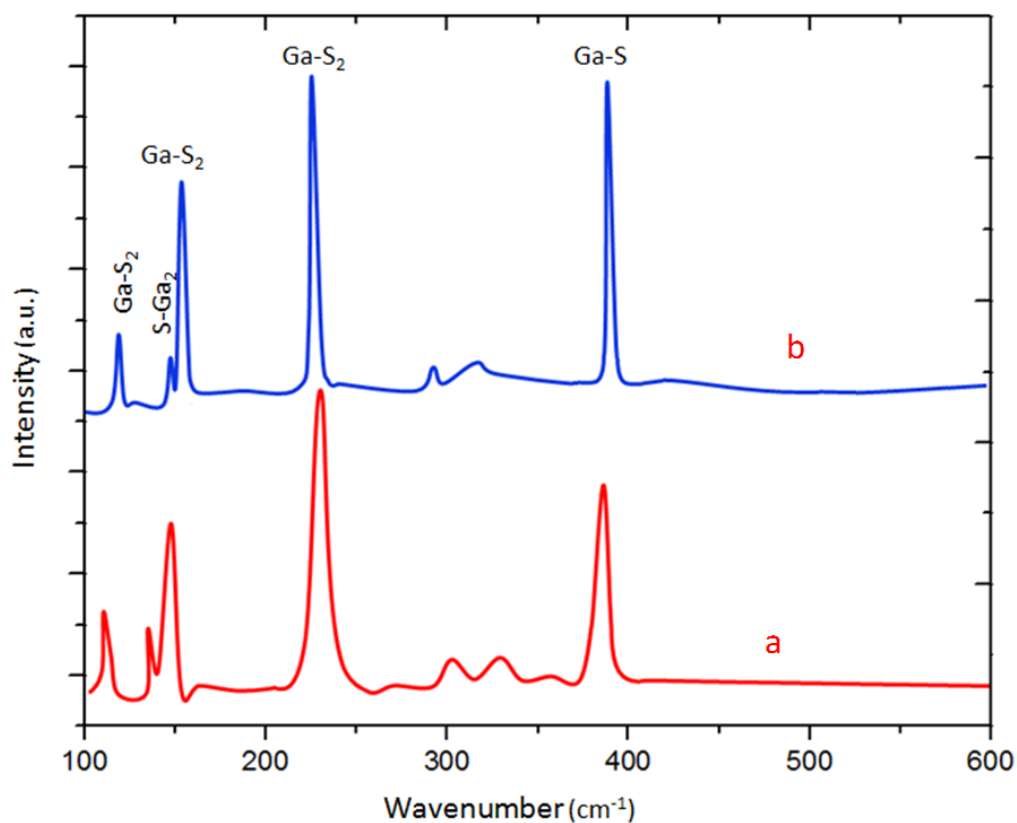


Fig. 3. Raman Spectrum of (a) $(\alpha\text{-Ga}_2\text{S}_3)_1$ (b) and $(\alpha\text{-Ga}_2\text{S}_3)_2$.

The photoluminescence spectras of $(\alpha\text{-Ga}_2\text{S}_3)_1$ and $(\alpha\text{-Ga}_2\text{S}_3)_2$ are shown in Fig. 4, and were measured at the wavelenght range of 300 to 800 nm. For $(\alpha\text{-Ga}_2\text{S}_3)_1$ two broad emission peaks at 414 (blue emission) and 635 nm (red emission) were observed. For $(\alpha\text{-Ga}_2\text{S}_3)_2$ two broad emission peaks were observed at 420 and 641 nm; the red emission is broader than blue emission, and the intensity of this emission peak is higher than red emission.

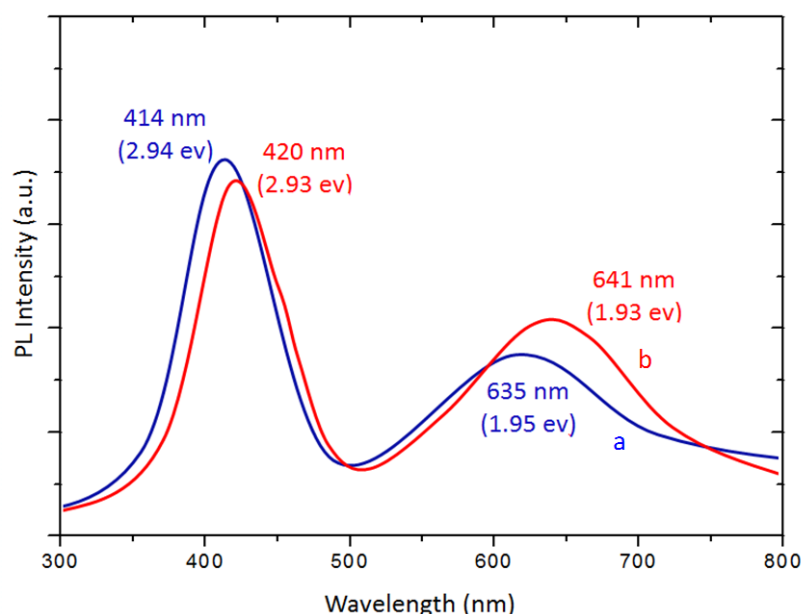


Fig. 4. Photoluminescence spectras (a) $(\alpha\text{-Ga}_2\text{S}_3)_1$ (b) and $(\alpha\text{-Ga}_2\text{S}_3)_2$.

Conclusion

Different techniques used to synthesize nanoparticles such as the hydrothermal method, solvothermal methods and low temperature synthesis (co-precipitation, sol-gel encapsulation), involve the use of toxic, hazardous chemicals (organic solvents, surfactants), high temperature treatment etc., which may pose potential environmental and biological risks. In the present study we synthesized pure $\alpha\text{-Ga}_2\text{S}_3$ nanocrystals by a simple reaction between gallium (III) chloride and sodium thiosulphate in water (green solvent) at room temperature (green environment). As expected, we observed the increasing particle size with the increasing reaction time. The optical properties of these gallium sulphide nanocrystals are similar to the other reported ones in the literature synthesized by conventional routes. So, these nano crystals can also be suitable for optoelectric application.

Acknowledgements

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