Structural and optical properties of chromium doped zinc gallate long persistent phosphor prepared by surfactant assisted hydrothermal method

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Abstract. Herein, CTAB surfactant aided hydrothermal reaction was carried for preparing Cr³⁺ doped ZnGa₂O₄. Urea was used as fuel to continue the reaction. By fixing Cr³⁺ ions conc. to 0.5 mol%, the molar ratio of CTAB was varied. We used XRD, TEM, FTIR, PL, UV-VIS spectroscopy, decay kinetics, and afterglow decay experiments to characterize the samples. XRD data suggested a cubic phase matching with JCPDS card no. 00-038-1240. TEM images confirmed the formation of nanoparticles within the range 20-80 nm. The estimated band gap was around 4.8 eV. Excited by 227 nm UV lights elaborated a wide emission band extended from 600 to 800 nm and peaking at 696 nm. The afterglow decay curve showed a long persistent signal up to 1 hour after ceasing off the excitation source.

1. Introduction

Long persistent phosphors are widely investigated because of their various applications in different fields. The exclusive feature of dark glow makes these materials suitable for night vision applications, safety indicators, security applications, traffic signals, decoration, luminous watch and many more [1, 2]. After excitation, the emission from these materials can be observed for a long time in naked eyes. These materials contain an emitter centre and traps. Emitters are responsible for emission and traps store the excitation energy and helps in persistent properties [3]. For some practical applications such as bio imaging, the materials must have dimensions in nm range and should have long persistent NIR emission as the NIR (600-800 nm) signal easily penetrate into the animal body and hence this range is considered as biological optical window [4]. Hydrothermal synthesis is a suitable method for nanomaterials synthesis. Recently surfactant assisted hydrothermal synthesis method is found to be an effective approach for nanomaterial synthesis. Surfactants are used to lower the surface tension of liquids. CTAB (Cetyl Trimethyl Ammonium Bromide) is a famously known surfactant which usually acts as template in preparation of nanomaterials[5]. Yuan et al. have prepared ZnGa₂O₄ nanoparticles by CTAB aided microwave assisted hydrothermal synthesis method [6]. Liu et al. also have synthesized uniform ZnGa₂O₄ nanoparticles by the CTAB surfactant assisted hydrothermal process [7].

As per our survey, the preparation of uniform Cr³⁺ doped ZnGa₂O₄ nanoparticles with the addition of urea and cationic surfactant CTAB is seldom discussed. In this context, we have demonstrated the preparation of ZnGa₂O₄:Cr³⁺ by CTAB assisted hydrothermal technique and its structural and optical
effects have been investigated in detail. TEM images showed uniform morphology with small particle sizes (20-80 nm range). The spectroscopic property of this phosphor is discussed in details.

2. Experimental

2.1. Preparation of samples

Hydrothermal synthesis method is opted for the preparation of the samples. Zn(NO₃)₂.6H₂O, Ga(NO₃)₃, Cr(NO₃)₃.9H₂O; CO(NH₂)₂, cetyltrimethylammonium bromide (CTAB) were used in four different molar ratios: 1:1.99:0.01:10:0; 1:1.99:0.01:10:0.01; 1:1.99:0.01:10:0.1; 1:1.99:0.01:10:1, respectively. Molar concentration of the dopant (Cr³⁺) was fixed at 0.5 mol%. A stoichiometric quantity of above mentioned ingredients were dissolved in deionised water in a flask by stirring for approximately one hour. The as obtained transparent suspension then transferred in an autoclave. The sealed autoclave had been retained at 125°C for 25 hours inside of an oven. The sample then brought to room temperature naturally followed by filtering, and the obtained precipitate was collected after thorough washing by ethanol as well as D.I. water. Finally, the collected samples were dried at 70°C for 6 hours followed by grinding and then heating at 700°C for 2 hours before taking them for structural and optical characterizations.

2.2. Characterization:

The phase analysis was carried by X-ray diffractometer (PANalytical). JEOL JEM-2100 was utilized to collect HRTEM for morphological analysis. A Perkin Elmer FTIR was utilized to collect the FTIR spectra in the range of 450-4000 cm⁻¹. An UV-Vis spectrometer from Agilent Cary-500 was used for recording UV-visible diffuse reflectance spectra. The Fluorescence Spectrophotometer from Agilent Cary Eclipse was employed for recording photoluminescence excitation, emission and luminescence decay curves.

3. Result and discussions

![Figure 1](image)

Figure 1. XRD patterns of the CTAB assisted ZnGa₂O₄:0.5Cr³⁺ samples synthesized with various mole contents of CTAB.
Figure 1 depicts the XRD results of polycrystalline ZnGa$_2$O$_4$:0.5Cr$^{3+}$ phosphors. The indexed diffracted peaks matched well with standard ICDD no. - 00-038-1240 of ZnGa$_2$O$_4$ spinel having cubic phase and the space group of the sample is Fd3m. Some impurity peak of ZnO were found at 2θ = 31.7°. The sharp peaks indicate the high crystallinity of the samples. No impurity peaks due to Cr$^{3+}$ ion is observed which indicates that the doping of small percentage of Cr$^{3+}$ did not affect the basic crystal nature of the host material. The important lattice parameters, evaluated by Unit Cell Win software, are listed in Table 1. Meanwhile, the crystallite sizes of the samples are also evaluated using Debye Scherer Formula;

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

Where $\beta$ standing for the full width at half maximum intensity

$K$ (shape factor) = 0.9

$\lambda$ (wavelength used of X-ray)=1.54 Å [8]

The sharp intense diffraction lines were used to calculate the crystallite sizes of the samples. The results obtained are shown in Table 1. From the results obtained, it can be seen that the average crystalline sizes are slightly reduced with increasing concentration of CTAB. This may be due to the fact that, at lower surfactant concentration, the particle-particle interactions are not controlled which leads to the higher crystallite size whereas at higher surfactant concentration, the inter particle interaction is significantly controlled which results reduced crystallite sizes [9].

Table 1. Crystallite sizes and lattice parameters of the CTAB assisted ZnGa$_2$O$_4$:0.5 mol% Cr$^{3+}$ samples.

| Sample    | Crystallite Sizes (nm) | Lattice parameters (a=b=c) Å | Cell Volume V (Å$^3$) |
|-----------|------------------------|-----------------------------|----------------------|
| 0 mol CTAB| 23-27                  | 8.33                        | 578.08               |
| 0.01 mol CTAB | 24-29              | 8.32                        | 577.10               |
| 0.1 mol CTAB | 23-28              | 8.33                        | 577.42               |
| 1 mol CTAB | 23-28                 | 8.33                        | 578.32               |

Figure 2. TEM images of ZnGa$_2$O$_4$: 0.5Cr$^{3+}$ synthesized with various mole contents of CTAB ((a) 0.0 (b) 0.01(c) 0.1 (d) 1.0).
Figure 2 elaborates the TEM images ZnGa$_2$O$_4$:0.5%Cr$^{3+}$ samples produced with various mol contents of CTAB. The particles are found to be spherical in shape having sizes between 20-80 nm. The average sizes for 0.0, 0.01, 0.1 and 1.0 mole CTAB aided ZnGa$_2$O$_4$:0.5%Cr$^{3+}$ samples are calculated to be 45, 47, 43 and 47 nm, respectively. Thus the particle sizes were nearly equal with the variation of CTAB concentrations.

![Figure 2. TEM images of ZnGa$_2$O$_4$:0.5%Cr$^{3+}$ samples produced with various mol contents of CTAB.](image)

The FTIR spectra, demonstrated in the figure 3, mainly shown the stretching absorption bands of Ga-O and Zn-O stretching bands at 470 cm$^{-1}$ and 590 cm$^{-1}$, respectively [10]. Band at 1096 cm$^{-1}$ corresponds to C-H bending and 2926 cm$^{-1}$ corresponds to C-H stretching vibration respectively. Peak due to the bending C-O-H band was observed at 1261 cm$^{-1}$[11]. The absorption peak at 1384 cm$^{-1}$ can be attributed to the N-O stretching [12, 13]. The band obtained at 1651 cm$^{-1}$ are due to H-O-H bending and that situated at 3448 cm$^{-1}$ is for the O-H stretching vibration [14]. Due to low doping concentration of Cr$^{3+}$ ion no peak due to Cr was found. The FTIR study revealed the presence of less organic and inorganic impurities and its suitability for performing the photoluminescence measurements.

![Figure 3. FTIR spectra of ZnGa2O4: 0.5Cr$^{3+}$ synthesized with various mole contents of CTAB.](image)
Figure 4. UV-Vis DRS of ZnGa$_2$O$_4$: 0.5mol%Cr$^{3+}$ synthesized with various mole contents of CTAB.

Figure 4 depicts the diffused reflection spectra of CTAB assisted ZnGa$_2$O$_4$: 0.5 mol% Cr$^{3+}$ phosphors. Strong absorption at 250 nm is because of the band-to-band transition in the present host. The absorption fringe at 552 nm appeared because of Cr$^{3+}$ d to d transition.

The band gap (optical) of the phosphor was calculated using Kublka-Munk Theory as follows:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S}$$  \hspace{1cm} (2)

where $R$, $K$ and $S$ are standing for diffuse reflectance, absorption coefficient, and scattering coefficient, respectively.

Tauc has given relation between direct band gap ($E_g$) and linear absorption coefficient ($\alpha$) of the material which is written as

$$\alpha h\nu = c(h\nu - E_g)^{1/2}$$  \hspace{1cm} (3)

$h\nu$ is the energy of the photon and $c$ is the constant. The diffuse reflectance spectrum is converted into Kubelka-Munk function by substituting $F(R)$ in place of $\alpha$,

$$[h\nu F(R)]^2 = A(h\nu - E_g)$$  \hspace{1cm} (4)

$h\nu$ is in eV and it is related with the wavelength $\lambda$ as, $h\nu = \frac{1239.7}{\lambda}$ in eV.

When $[h\nu F(R)]^2$ vs. $h\nu$ graph is plotted a curve is obtained. If we extrapolate the linear portion of the curve then it meets horizontal axis at a certain point for zero value of $[h\nu F(R)]^2$. The point at which extrapolated line meet the x-axis is considered as optical band gap of the sample [15]. Figure 5 illustrates the Kubelka-Munk graph with band gap values.
Figure 5. Kubelka-Munk plot of ZnGa$_2$O$_4$: 0.5%Cr$^{3+}$ synthesized with various mole contents of CTAB ((a) 0.0 (b) 0.01 (c) 0.1 (d) 1.0).

Figure 6. Photoluminescence (a) excitation and (b) emission spectrum of ZnGa$_2$O$_4$: 0.5Cr$^{3+}$ synthesized with various mole contents of CTAB.

The PL excitation spectra (figure 6a), monitored at 696 nm, showing intense peaks at 227, 437 and 571 nm due to the $^4A_2(^4F)\rightarrow^4T_1(^4P)$, $^4T_1(^4F)$, and $^4T_2(^4F)$ transitions of Cr$^{3+}$, respectively. The corresponding spectra of PL emission for all the samples with the variation in molar ratio of CTAB are also shown in the figure 6(b). The intensities of all the samples are almost same as the doping concentration of Cr$^{3+}$ has been fixed at 0.5 mol%. The PL emission spectra at 227 nm excitation wavelength show a peak at 696 nm which is due to the spin forbidden transitions $^2E(^2G)\rightarrow^4A_2(^4F)$. The satellite peaks at 674 nm
and 708 nm corresponds to phonon side bands of zero phonon R-line. The wide luminescence band is because of the broad spin allowed $^4T_{2g} (^4F) \rightarrow ^4A_2 (^4F)$ transition [16].

Figure 7 depicting the decay curves of the studied phosphors investigated at excitation wavelength 227 nm and wavelength of emission 696 nm. The data were recorded within the range of 0-100 ms. Decay curves were fitted triple exponentially by the given equation:

$$I = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$$

(5)

Luminescence intensity is represented by $I$; $I_0$ is the intensity at $t = $ very large (infinity); $A_1$, $A_2$ and $A_3$ are constants; $\tau_1$, $\tau_2$ and $\tau_3$ are decay constants. The following formula is used to calculate the effective lifetime from the decay analysis [17],

$$\tau_{\text{eff}} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2 + A_3 \tau_3^2}{A_1 \tau_1 + A_2 \tau_2 + A_3 \tau_3}$$

(6)

Figure 7. Photoluminescence decay curve of ZnGa$_2$O$_4$: 0.5Cr$^{3+}$ synthesized with various mole contents of CTAB ((a) 0.0 (b) 0.01 (c) 0.1 (d) 1.0).

The values of estimated lifetimes are found to be 10.88, 9.89, 11.63 and 9.81 ms for 0.0, 0.01, and 1.0 mole CTAB contents, respectively. To check the afterglow behaviour of the material afterglow decay (figure 8) analysis of the 0.1 mol% CTAB assisted ZnGa$_2$O$_4$:0.5 mol% Cr$^{3+}$ phosphor was done. The sample was excited by a UV light source for few minutes and then the light source was ceased. The long lasting photoluminescence was observed for one hour.

When the material is excited by any source, then the ground state electrons absorbs this excitation energy and goes to the higher energy states. From the higher excited state, the electrons are captured by different traps which lie in the band gap of the material via conduction band. When the excitation source is removed then the electrons that are trapped at the shallow traps are de-trapped and repopulate the higher excited states through conduction band. Then they non-radiatively relax to the first excited state and then transit to ground state by emission of photons. The electrons in deep traps are released after some times but they do not follow the above steps rather they tunnel to the nearby Cr$^{3+}$ energy levels directly. Then they recombine and results in emission. This process is quite slow and hence leads to the long persistent luminescence [18].
4. Conclusion
ZnGa$_2$O$_4$:0.5 mol%Cr$^{3+}$ nanophosphor was prepared by CTAB assisted hydrothermal reaction method. The sharp intense peaks in the XRD pattern were utilized to calculate the crystallite size and lattice parameters. Spherical particles with particle size in the range of 20-80 nm were observed in the TEM images. The FTIR spectra showed the presence of different vibrational bands. Band gaps were found to be around 4.8 eV. The PL emission spectra showed $2E(2G)\rightarrow 4A_2(4F)$ transition of Cr$^{3+}$ at 696 nm. Lifetimes of the samples varied from 9.81 ms to 11.63 ms calculated from decay kinetics curve. Persistent light signal was being observed up to 1 hour after the excitation of the sample by 254 nm UV light. Tiny particle size in nanometer scale and long lasting luminescent emissions in NIR region makes the material to be applicable in various medical probes such as applications in bioimaging.

5. References
[1] Viana B, Sharma S K, GourierD, Maldiney T, Teston E, Scherman Da nd Richard C 2016 J. Lumin. 170 879.
[2] Das S, Manam J and Sharma S K, 2017 New J. Chem. 41 5934.
[3] Casillas-Trujillo L, Andersson D A, Dorado B, Nikl M, Sickafus K E, McClellan K J and Stanek C R, 2014 Phys. Status Solidi B – Basic Solid-State Phys. 251 2279.
[4] Smith A M, Mancini M C and Nie S, 2009 Nat. Nanotechnol. 4 710.
[5] Johnson C J, Dujardin E, Davis S A, Murphy C J and Mann S, 2002 J. Mater. Chem. 12 1765.
[6] Yuan Y, Huang J, Tu Wand Huang S, 2014 J. Alloy. Compd. 616 461.
[7] Liu L, Huang J, Cao L, Wu J, Fei J, Ouyang H, Ma F and Zhou C, 2013 Mat. Lett. 95 160.
[8] Baitha P K, Pal P P and Manam J, 2014 Nuclear Instru. and Methods in Phys. Res. A, 745 91.
[9] Vadivel M, Babu R R, Ramamurthi K and Arivanandhan M, 2016 Ceramics Int. 42 19320.
[10] Li Z, Zhang Y, Wu X, Hunag L, Li D, Fan W and Han G, 2015 J. Am. Chem. Soc. 137 5304.
[11] Snyder R G, Hsu S L and Krimm S, 1977 Spectrochimica Acta Part A: Molecular Spectroscopy, 34 395.
[12] Rintoul L, Micalef A S and Bottle S E, 2008 Spectrochimica Acta Part A, 70 713.
[13] Sinha S, Mahata M K, Swart H C, Kumar A and Kumar K, 2017 New J. Chem. 41 5362.
[14] Mondal A and Manam J, 2017 ECS J. Solid State Sci. Technol. 6 R88.
[15] Mondal A, Das S and Manam J, 2019 Physica B: Condensed Matter 569 20.
[16] Li Y, Zhou S, Li Y, Sharafudeen K, Ma Z, Dong G, Peng M and Qu J, 2014 J. Mater. Chem. C2 2657.
[17] Xu X, Chen J R G, Kong D, Gu C, Chen C and Kong L, 2013 Opt. Mater. Express 3 1727.
[18] Pan Z, Lu Y and Liu F, 2012 Nat. Mater. 11 58.

6. Acknowledgement
One of the authors Kumari acknowledges the collaborative research project having project id- 1-5736649073 of TEQIP-III, MHRD New Delhi for the research grant.