THE PROPERTIES OF $ZnGa_2O_4$ NANOPARTICLES WITH SPINEL STRUCTURE OBTAINED BY THE HYDROTHERMAL METHOD

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Abstract

Zinc gallate ($ZnGa_2O_4$) is a normal spinel crystal structure (space group Fd_{3m}). $ZnGa_2O_4$ has attracted much attention due its multitude of possible applications regarding field emission display, electroluminescent devices, and in the last decade mostly sensor domain. $ZnGa_2O_4$ nanoparticles were obtained by the hydrothermal method using Ga_2O_3 and $Zn(NO_3)_2$ x $6H_2O$ precursors in basic medium using a Teflon-lined stainless steel autoclave tightly sealed. The synthesys was effectuated at 210°C for 4 h. The hydrothermal method is one of the most promising solution chemical methods. Thus, the size of particles and their distribution, phase homogeneity, and morphology could be well controlled. These powders were characterized by X-ray diffraction (XDR), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDAX), and atomic force microscopy (AFM). Photoluminescence (PL) measurements were obtained with a conventional lamp as an excitation source.

1. Introduction

Due phosphorescent properties of $ZnGa_2O_4$ this compound was used in various applications: field emission display, electroluminescent devices, sensors, etc.

Zinc gallate ($ZnGa_2O_4$) has a normal spinel crystalline structure (space group Fd_{3m}), with Zn^{2+} ions in the tetrahedral sites and Ga^{3+} ions in the octahedral sites. The unit cell contains 8 tetrahedral cations, 16 octahedral cations, and 32 oxygen anions. Synthesis of $ZnGa_2O_4$ spinel powders was accomplished by the hydrothermal method using as precursors Ga_2O_3 and $Zn(NO_3)_2$ x $6H_2O$ in basic medium (pH=12). Merck reactants with 99.99% purity were used. The precursors and obtaining method act on microstrucure and physical properties of the resulting materials [1, 2].

In the recent decade, there is a strong trend towards the application of solution routes for direct synthesis of crystalline ceramic particles at low temperatures [3, 4].

The hydrothermal method is one of the most promising solution chemical methods. The size of particles, their distribution, phase homogeneity, and morphology can be well controlled [5-7].

For higher resolution in display emission devices, nanosize phosphor powders are employed [8].

Densely packed phosphor layer improves the aging problem because of its nanosize, spherical shape, and self-assembly ability [9].

The $ZnGa_2O_4$ phosphor shows various emission colors from green to red when is doped with Mn^{2+} and Cr^{3+}, respectively [10, 11]. The undoped $ZnGa_2O_4$ emits blue color [4]. For this reason, the studies on luminescent properties of nanosize $ZnGa_2O_4$ have attracted extensive interests.

The aim of this paper is to present the results of the synthesis of $ZnGa_2O_4$ nanoparticles by the hydrothermal method.

2. Experimental procedure

For obtaining of $ZnGa_2O_4$ nanocrystalline samples by the hydrothermal method we used $Zn(NO_3)_2 \cdot 6H_2O$ and Ga_2O_3 as reactants, with molar ratio Zn:Ga of 1:2. The resulting mixture was then adjusted to a special pH=12 with sodium hydroxide solution under vigorous stirring. The resulting suspension was transferred into a Teflon-lined stainless steel autoclave, sealed tightly, and was introduced in to a furnace at 210°C for 4 h. The resultant white precipitate was filtrated and washed for many times with distillated water and ethylic alcohol, then dried in oven at 105°C for 4 hours. After drying, the obtained material was analyzed by X-ray diffraction (XRD) on an X'pert Pro MPD X-ray diffractometer, with monochromatic Cu Kα (λ = 1.5418 Å) incident radiation. Regarding identification of the morphology, dimension, and composition of the sample, field emission-scanning electron microscopy (SEM; Model INSPECT S), energy dispersive spectroscopy (EDAX), and atomic force microscopy (AFM; Model Nanosurf easy Scan) were applied. The photoluminescence (PL) measurement was carried out by using spectrofluorophotometer at room temperature. A xenon lamp 150 W was used as the excitation source.

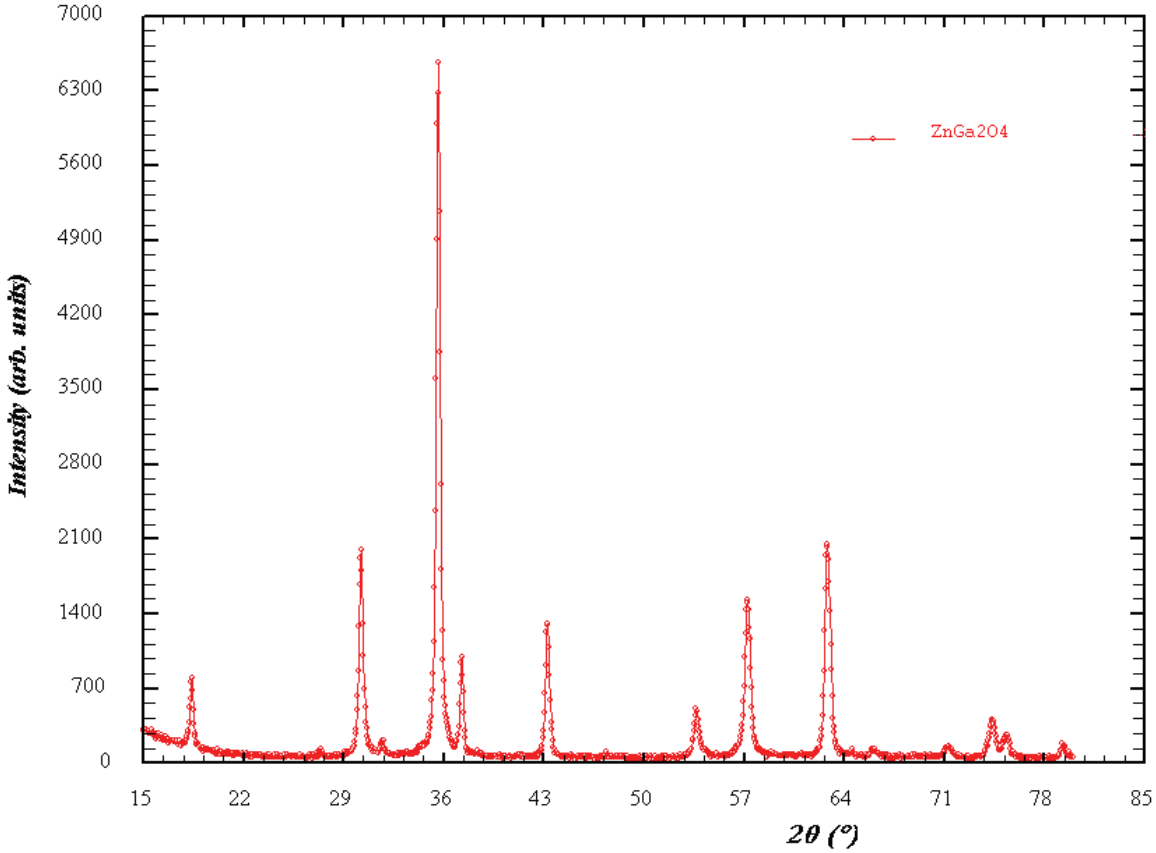


Fig. 1. XRD patterns of $ZnGa_2O_4$ samples obtained from Ga_2O_3 and $Zn(NO_3)_2 \cdot 6H_2O$ by the hydrothermal method.

3. Results and discussion

3.1. X-ray diffraction

The hydrothermal method is a successful method for obtaining of nanomaterials with a high degree of crystalinity and also homogeneity of particle size.

Figure 1 shows the XRD patterns of $ZnGa_2O_4$ samples obtained from Ga_2O_3 and $Zn(NO_3)_2 \cdot 6H_2O$ by the hydrothermal method of at 210°C for 4 h.

It is seen from the form of the peaks in the XRD pattern that the $ZnGa_2O_4$ spinel particles have a high degree of crystallinity.

3.2. SEM-analysis

The SEM image shown in Fig. 2 provides direct information about size and morphology type of the $ZnGa_2O_4$ compound obtained by the hydrothermal method.

By SEM images, we can observe that particles have oblong form (bars) and dimension within 600-900 nm.

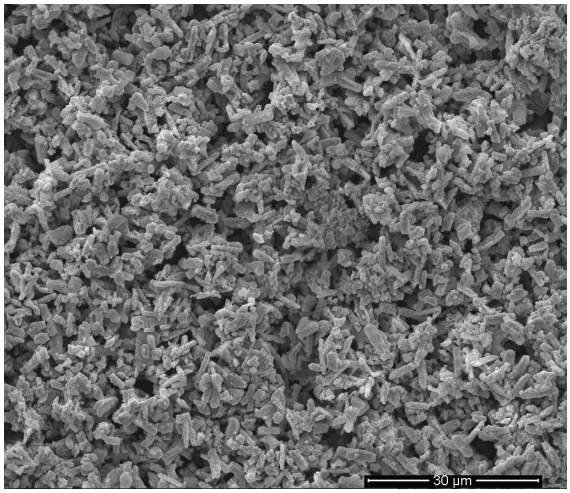
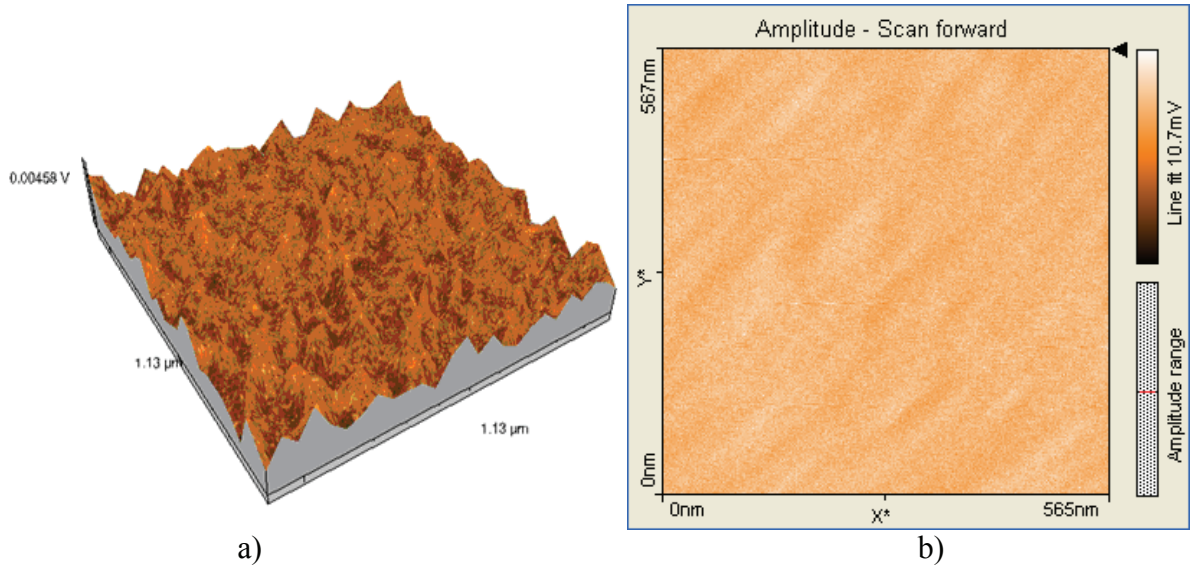


Fig. 2. SEM image of $ZnGa_2O_4$ compound obtained by the hydrothermal method.



a) b)

Fig. 3. AFM image of $ZnGa_2O_4$ obtained by the hydrothermal method.

3.3. AFM-analysis

Figures 3a and 3b show AFM surface morphology of $ZnGa_2O_4$ obtained by the hydrothermal method. The roughness and surface morphology of the $ZnGa_2O_4$ thus obtained are different according to autoclavation conditions.

3.4. Photoluminescence

The luminescence characteristic of the samples obtained by the hydrothermal method from different precursors is studied.

Figure 4 presents the room temperature emission spectra of all the samples under excitation at 488 nm. The emission spectrum of all the samples shows a broad-band emission, but the maximum emission peak and intensity are different. The $ZnGa_2O_4$ phosphors obtained from Ga_2O_3 and $Zn(NO_3)_2 \cdot 6H_2O$ emit lower intensity light, being closer to pure blue light at around 608 nm. It is clear that the wavelength characteristic to emission peak is blue-shifted with decreasing particle size.

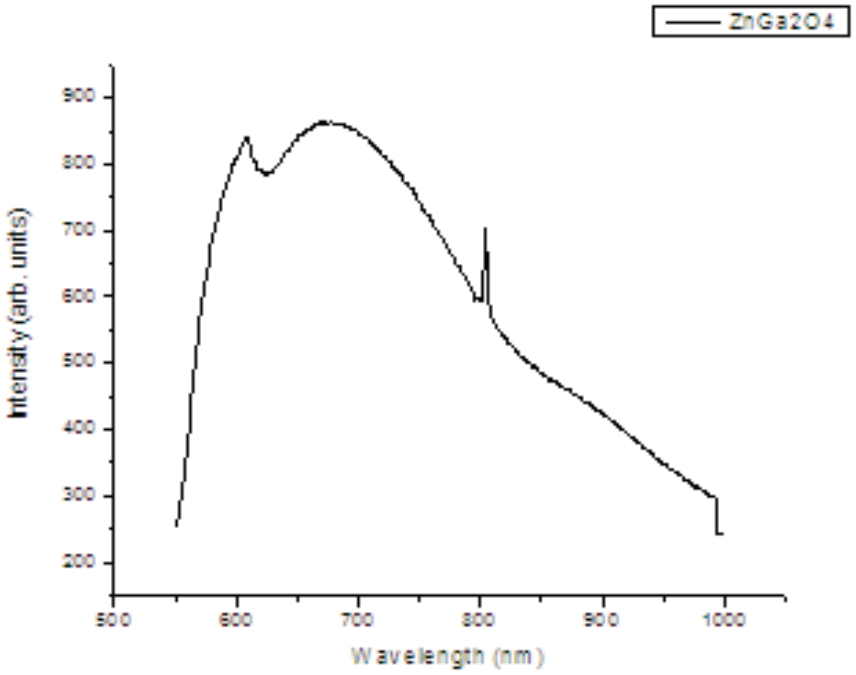


Fig. 4. Photoluminescence spectra of the samples obtained by the hydrothermal method.

Figure 5 shows the spinel crystalline structure of $ZnGa_2O_4$ which has Fd_{3m} space group. In the normal spinel (AB_2O_4) oxide structure, Zn^{2+} ions occupy the tetrahedral coordinated A sites, whereas Ga^{3+} ions occupy B sites that are octahedrally coordinated. The broad emission band at 608 nm can be assigned to self-activated centers originating from octahedral Ga – O group in the spinel lattice [5]. The oxygen vacancies are most probably associated with formation of Ga^{3+} ions. It was reported that the absorption and corresponding emission peaks originated from the self-activated optical centers of tetrahedral Ga – O groups shifted to a higher energy as compared to peaks originated from those of octahedral Ga – O groups. It is supposed that blue emission to be related with the formation of new self-activated optical centers due the tetrahedral Ga – O groups in the spinel lattice.

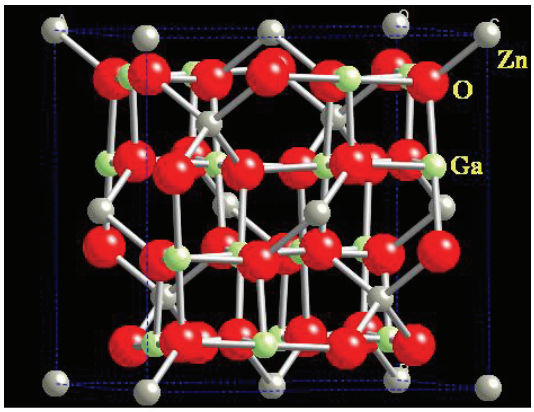


Fig. 5. Spinel crystal structure.

According to particle size decreasing, we can observe blue shift in the absorption and emission spectra; at the same time, it is supposed that the number of Ga^{3+} ions in tetrahedral sites increase with the decrease of those in octahedral sites.

Fujihara and co-workers had attributed the blue shift to the quantum-size effect (the increased bandgap) [12].

Some authors [13, 14] reported that the shape anisotropy could affect symmetry of crystal fields around the activation center, giving the different luminescence behavior. Although much work remains to be done to fully understand these phenomena of blue-shift for the as-synthesized ZnGa2O4 phosphors, it is speculated that these phenomena are also caused by the quantum-size effect.

4. Conclusions

In summary, $ZnGa_2O_4$ powders were synthesized by the hydrothermal method using different gallium precursors as reactants. It has been demonstrated that the hydrothermal technique is a suitable one-step method for the preparation of nanomaterials at relatively low temperature and by using not pollutant reagents. The concentration of the reactants in the solvent (water) plays a critical role for the successful synthesis of single-phase ternary nanocrystal products. The reactant concentration and reaction medium are of particular importance regarding the hydrothermal synthesis.

The morphology, size, composition, and the surface quality are of special importance for different types of applications [15].

In a future research, we propose to study the physical and chemical phenomena that appear during $ZnGa_2O_4$ nanoparticle synthesis.

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