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CHARACTERIZATION OF $ZnGa_2O_4$ DOPED WITH Zr^{4+} OBTAINED BY HYDROTHERMAL SYNTHESIS

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Abstract. The aim of this paper is to present the results of the synthesis of $ZnGa_2O_4:Zr^{4+}$ nanoparticles by the hydrothermal method. The suspension containing Ga_2O_3, $Zn(NO_3)_2*6H_2O$ and N_2O_7Zr (27%Zr) have been sealed tightly in a Teflon-lined stainless steel autoclave kept at 210^0C for 5h. The size of obtained particles, their distribution, phase homogeneity and morphology were well controlled. The nanoparticles were characterized by X-ray diffraction (XDR) and scanning electron microscopy (SEM), energy dispersive spectroscopy (EDAX) and atomic force microscopy (AFM).
Keywords: $ZnGa_2O_4$: Zr^{4+}, hydrothermal, nanoparticle

1. Introduction

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

The spinels are generally regarded as versatile materials of great technological importance and physical behavior [1-2], which have crystal structure, related $A^{+2}\,B^{+3}{}_2\,O_4$ and the spinel unit cell belong to the cubic space group $O_h{}^7$ (Fd_{3m}), with eight formula units per cell. The A site (Zn^{2+}) has tetrahedral coordination with full T_d site symmetry, while the B site (Ga^{3+}) has sixfold distorted octahedral coordination belongs to the D_{3d} point group [3]. The unit cell contains 8 tetrahedral cations, 16 octahedral cations and 32 oxygen anions. In this case of the Zr^{4+} ion in spinel $ZnGa_2O_4$, the Zr^{4+}, which has high octahedral site preference energy, are preferred to occupy octahedral B sites in spinel and form normal spinel. When transition metal ion (Fe^{3+}, Cr^{3+}, Zr^{4+}) doped in the spinel, there are great controversy on the assignation of point symmetry (D_{3d} or C_{3v}) of B site [3].

Synthesis of $ZnGa_2O_4$ spinel powders was accomplished by hydrothermal method using as precursors Ga_2O_3 and $Zn(NO_3)_2$ x $6H_2O$ in basic medium (pH=12). Were used Merck reactants with 99.99% purity. The precursors and obtaining method act on microstrucure and

physical properties of the resulting materials [4]. Hydrothermal method is one of the most promising solution chemical methods. The particles size and 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 aim of this paper is to present the results of the synthesis of $ZnGa_2O_4$: Zr^{4+} nanoparticles by hydrothermal method.

2. Experimental procedure

For obtaining of $ZnGa_2O_4$ nanocrystalline samples by 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 and sealed tightly and was introduced in an oven at 210^0C for 4 h [4]. It results a white precipitate that was filtrated and washed for many times with distillated water and ethylic alcohol, then dried in oven at 105°C for 4hours. Powder phosphors of $ZnGa_2O_4$: Zr^{4+}, was prepared by hydrothermal method. Hydrothermal method synthesis involves mixing ions (nitrates, acetates or oxides) acting as oxidizing reagents with filler that acts as the reducing agent. This redox mixture consisted in $ZnGa_2O_4$ and N_2O_7Zr (27%Zr). The proportion of each reagent was defined according to its respective molar ratio. Stoechiometric compositions of metal nitrates and N_2O_7Zr (27%Zr) were calculated based on the components total oxidizing and reducing coefficients for the stoechiometric balance, so that the equivalence ratio (Fc) was equal to the unit and the energy released was maximum.

After drying was achieved characterization of obtained material 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 was used field emission-scanning electron microscopy (SEM; Model INSPECT S), energy dispersive spectroscopy (EDAX) and atomic force microscopy (AFM; Model Nanosurf easy Scan).

3. Results and Discussions

Hydrothermal method is a success method regarding nanomaterials obtaining with a high degree of crystalinity and also homogeneity of particle's size.

Figure 1 shows the XRD patterns of $ZnGa_2O_4:Zr^{4+}$ samples obtained from Ga_2O_3, $Zn(NO_3)_2 \cdot 6H_2O$ and N_2O_7Zr (27%Zr) by hydrothermal method of at 210^0C for 4 h.

It is seen from the form of the peaks in the XRD pattern that the $ZnGa_2O_4:Zr^{4+}$ spinel particles have a high degree of crystallinity.

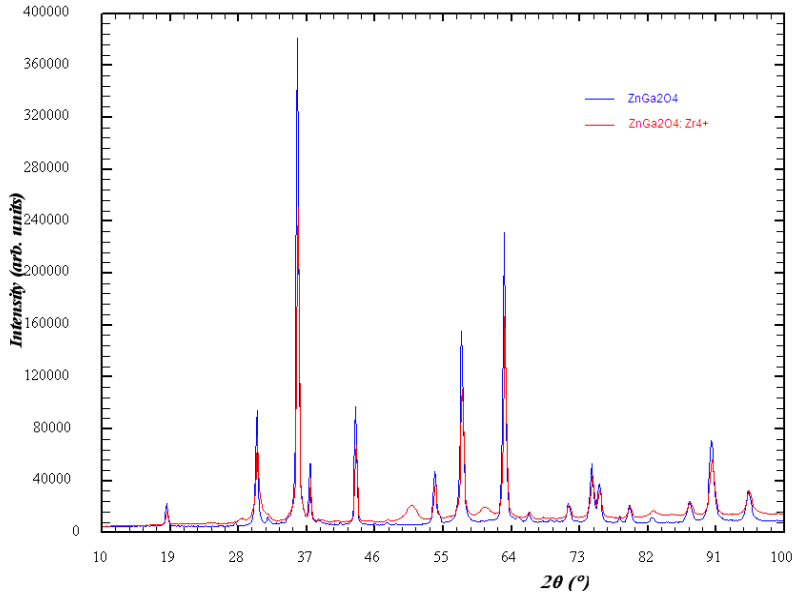

Fig.1. XRD patterns of $ZnGa_2O_4:Zr^{4+}$ samples obtained by hydrothermal method.

Fig.2. shows AFM surface morphology of $ZnGa_2O_4:Zr^{4+}$ obtained by hydrothermal method. The roughness and surface morphology of the $ZnGa_2O_4:Zr^{4+}$ thus obtained by hydrothermal method are different according to autoclavation conditions.

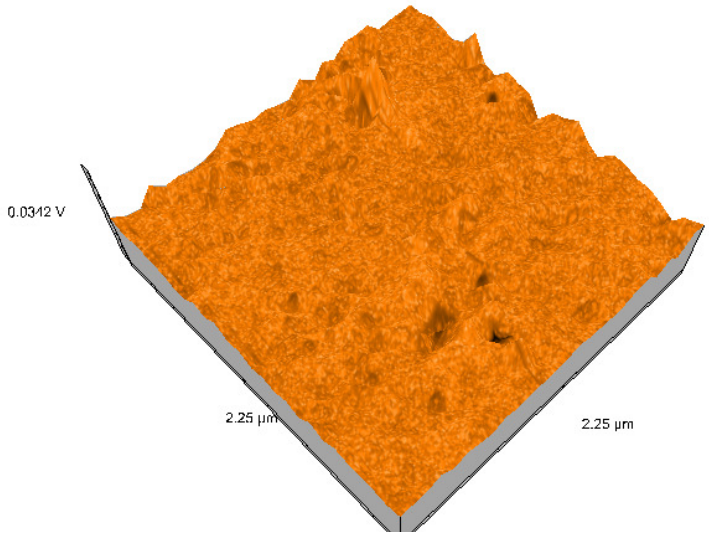

Fig. 2. AFM image of $ZnGa_2O_4:Zr^{4+}$ obtained by hydrothermal method.

The SEM image shown in Fig. 2 provides direct information about size and morphology type of the $ZnGa_2O_4:Zr^{4+}$ compound obtained by hydrothermal method.

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

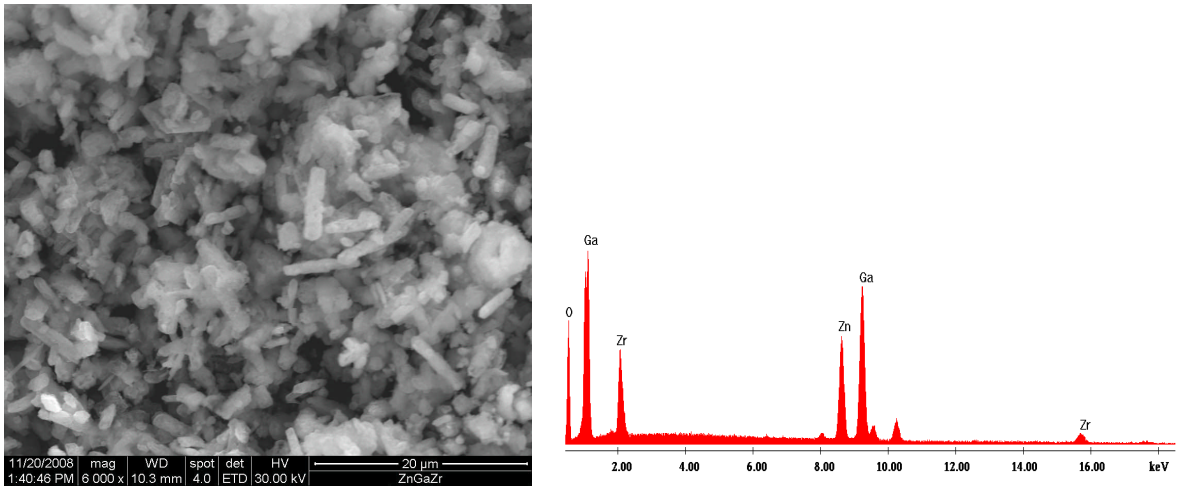

Fig.3. SEM image of $ZnGa_2O_4:Zr^{4+}$ compound obtained by hydrothermal method. The qualitative EDAX analysis (0.0892%)

4. Conclusions

$ZnGa_2O_4$ powders were synthesized by the hydrothermal method using as reactants Ga_2O_3, $Zn(NO_3)_2 \cdot 6H_2O$ and N_2O_7Zr (27%Zr). The reagent concentration and reaction medium have a particularly importance regarding hydrothermal synthesis. The X-ray diffraction shows a high crystallization degree for $ZnGa_2O_4$ and $ZnGa_2O_4$: Zr^{4+} nanoparticles. SEM analyses suggest that particles have oblong from and dimensions between 700-900 nm. The assignments of luminescent spectra to crystal field levels are given and a tentative to modulate these energy levels has been made. These observations indicate the low probability of transition metal ions incorporation into the octahedral sites of the spinel type structure, which is explained by the big difference between the ionic radii of Ga and transition metal elements.

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References

1. H. Richter, T. Posch, M. N. Taran, H. Mutschke, Mineral. Petrol 85, (2005), 53.
2. H. Aizawa et al., Rev. Sci. Instrum. 73 (8), (2002), 3089.
3. D. Bravo, F.J. Lopez, J. Phys. 4 (1992) 10335.
4. M. Vasile, P. Vlazan, A. Ioitescu, N. Avram, I. Grozescu, E. Rusu, 4th International Conference on Materials Science and Condensed Matter Physics, Chisinau, Sep 23-26, (2008)
5. X. Wang, Y. Li, J. Am. Chem. Soc. 124, (2002), 2880.
6. Y. Li, J. Wang, Z. Deng, J. Am. Chem. Soc. 123, (2001), 9904.
7. X. Li, J. Liu, Y. Li, Appl. Phys. Lett. 81, (2002), 4832.
8. S.K. Sampsth, J.F. Cordaro, J. Am. Ceram. Soc. 81, (1988), 649.
9. T. Omata, N. Ueda, H. Kawazoe, Appl. Phys. Lett. 64, (1994), 1077.