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Nanoparticle properties of $ZnAl_2O_4$ obtained by hydrothermal method

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Nanocrystallines $ZnAl_2O_4$ particles with a spinel structure were prepared by hydrothermal method. XRD analysis shows the high quality of spinel grains constituting the powder. The morphological structure of the resulting powders was examined by SEM, and the micrographs reveal the formation of soft agglomerates composed of nanometric scale particles. The AFM data for $ZnAl_2O_4$ show uniform surface without any valleys.

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1. Introduction

During the last decades, much attention has been focused on the rational synthesis of nanocrystals ranging in size from 1 to 100 nm, which can exhibit very interesting size-dependent electrical, optical, magnetic, and chemical properties compared with those of bulk counterparts [1]. These novel properties and the resulting applications are strongly related with their geometrical parameters [2]. At present, all the strategies for control of the preparing nanocrystals, by solution-phase methods have the advantages of environment friendly characteristics and low cost as well. Furthermore, the size and shape of nanocrystals in solution can be manipulated as we expect by precisely varying the chemical conditions, including the reaction temperature, the reaction time, surfactants, composition of solution, etc. [3, 4].

$ZnAl_2O_4$ phosphors have gained much attention for use in field emission displays (FEDs) and vacuum florescent displays (VFDs) [5, 6]. They exhibit higher chemical stability than commonly used sulfide phosphors. Since $ZnAl_2O_4$ are oxide based phosphors, many of the degradation problems associated with sulfide-based phosphors are avoided. $ZnAl_2O_4$ has attracted considerable interest for electroluminescent thin film displays and opto-mechanical sensors [7-9]. $ZnAl_2O_4$ is a well-known wide-band gap semiconductor, an active component of catalysts, and also acts as a convenient support for other metal oxides and dispersed metals [10–12]. Moreover, the optical band gap of polycrystalline $ZnAl_2O_4$ is 3.8 eV, indicating that $ZnAl_2O_4$ is transparent for light possessing wavelengths >320 nm.

The normal spinels $ZnAl_2O_4$ are a typical example of the general formula $(M)[N]_2O_4$, where M and N stands for divalent and trivalent ions, respectively. The ( ) and [ ] refer to 8 tetrahedrally coordinated A sites and 16 octahedrally coordinated B sites within the close-packed face-centered cubic unit cell with Fd3m space group symmetry. In normal spinels $ZnAl_2O_4$ structure the lattice constant is a=8.0912Å [13] and the divalent cations Zn^{2+} are at the A sites and the trivalent cations Al^{3+} at the B sites. $ZnAl_2O_4$ powders are easily prepared by solid phase reactions [14, 15], or by chemical reactions from solutions [16, 17].

2. Experimental procedure

Powder phosphors of $ZnAl_2O_4$ were 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 zinc nitrate-$Zn(NO_3)_2 \cdot 6H_2O$ (Merck 99,99%), and aluminum oxide-Al_2O_3 (Merck 99,99%). The proportion of each reagent was defined according to its respective molar ratio Zn:Al 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. 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. In the hydrothermal synthesizes of $ZnAl_2O_4$ precipitates with spinel structure is formed at temperature less than 210^0C as a result of the following reactions:

$$Zn(NO_3)_2 + Al_2O_3 + H_2O \rightarrow ZnAl_2O_4 + 2HNO_3$$

After drying, the characterization of the obtained material was achieved by X-ray diffraction XRD on an X'pert Pro MPD X-ray diffractometer, with monochromatic Cu Kα (λ = 1.5418 Å) incident radiation.

For the identification of the morphology, dimension and composition of the sample, field emission-scanning electron microscopy SEM and energy dispersive spectroscopy EDAX (Model INSPECT S) and atomic force microscopy AFM (Model Nanosurf® EasyScan 2 Advanced Research) were used.

3. Results and discussion

The X-ray patterns confirmed that the samples prepared by hydrothermal method consist of single phase of the $ZnAl_2O_4$ spinels. Fig. 1 shows the representative patterns, at room temperature, measured for $ZnAl_2O_4$. XRD patterns of the powder phosphors formed showed $ZnAl_2O_4$ crystalline phases of spinel structure in which the (311) plane indicating the standard powder diffraction pattern of $ZnAl_2O_4$ phase and the (220) peak of preferred orientation of powder were detected. All the specimens showed (311) peak with highest intensity in the XRD patterns. The diffraction peaks in the patterns are indexed to spinel (space group Fd3m) phases.

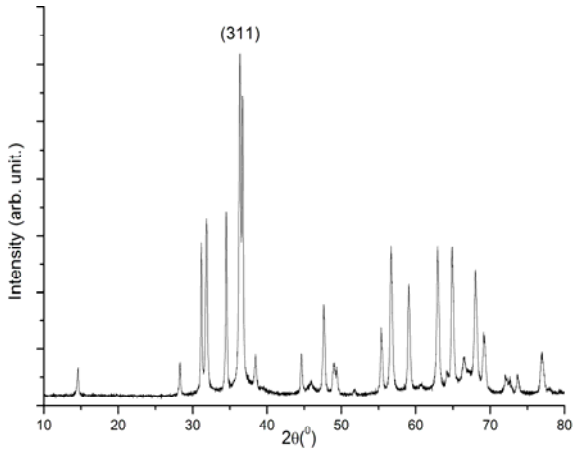


Fig. 1. XRD patterns of $ZnAl_2O_4$.

The mean crystallite grain size (d) of the powder samples was calculated using Scherrer's formula [18]:

$$d = \frac{K\lambda}{(\beta^2 - \beta_0^2)^{1/2}} \cos\theta$$

where β is the half-width of the diffraction peak in radians, β_0 corresponds to the instrumental broadening, K = 180/π, λ is the X-ray wavelength, and θ is the Bragg diffraction angle. The average grain size determined from XRD line broadening using Scherrer's formula is 46 nm for $ZnAl_2O_4$.

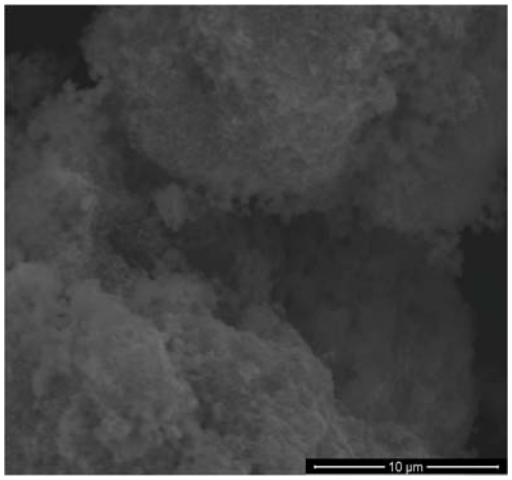
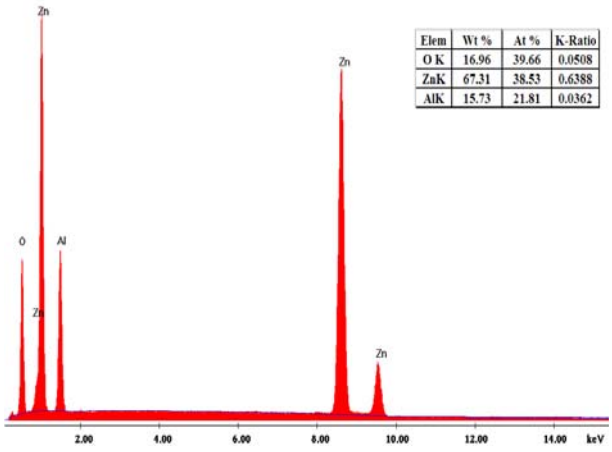


Fig. 2. SEM image for $ZnAl_2O_4$.

Fig. 2 shows SEM micrograph obtained for a typical $ZnAl_2O_4$ at room temperature. The surface feature reveals the uniformity of the powders. Higher magnification (250KV x 1000) of the surface reveled the presence of crystallites. The spherical crystallites are clustered around the etched pits. The grains were having an average size around a nanometric scale.



Elem	Wt %	At %	K-Ratio
O K	16.96	39.66	0.0508
ZnK	67.31	38.53	0.6388
AlK	15.73	21.81	0.0362

Fig. 3. The qualitative EDAX analysis for $ZnAl_2O_4$. Inset shows quantification of elements and weight (%).

The EDAX spectrum presented in Fig. 3 for $ZnAl_2O_4$ confirms the presence of elements Zn, Al and O, respectively.

The slight deviation from the ideal stoichiometry has been evidenced, also, by EDAX measurements on groups of crystallites. The qualitative EDAX analysis which confirms that results observed before in XRD analyses the presence of $ZnAl_2O_4$ respectively. Qualitative the Zn^{2+} ions are found to be about 67.31%, and the Al^{3+} ions are found to be about 15.73% of total mass of the analyzed compounds.

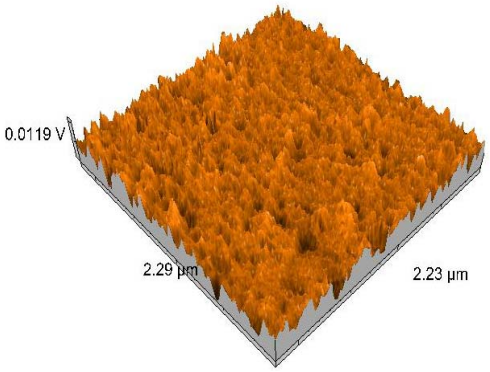


Fig. 4. AFM images for $ZnAl_2O_4$.

Fig. 4 shows the AFM of $ZnAl_2O_4$ measured at room temperature. The AFM studies revealed uniform surface without any valleys. The average grain size for $ZnAl_2O_4$ is about ~45nm.

4. Conclusions

The growth and characterization of $ZnAl_2O_4$ phosphors synthesized by hydrothermal route were investigated. $ZnAl_2O_4$ powders were grown by the hydrothermal method using as reactants $Zn(NO_3)_2 \cdot 6H_2O$ and Al_2O_3, respectively. The experimental results based on X-ray diffraction, scanning electron microscopy and atomic force microscopy indicate that the material consisting of $ZnAl_2O4$ particles, with the average grain size of about ~45nm.The obtained powder exhibits good crystalinity, with cubic spinel structure.

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