Hydrothermal synthesis of $ZnAl_2O_4:Cr^{3+}$ nanocrystals

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Pink $ZnAl_2O_4:Cr^{3+}$ pigment was prepared by hydrothermal synthesis and annealed at 1000ºC. The prepared sample was characterized by X-ray diffraction, atomic force microscopy and UV/VIS/NIR measurements. The results showed a single – spinel phase for $ZnAl_2O_4:Cr^{3+}$ pigment. The average crystallite size was found to be around 31 nm. The optical absorbance spectrum exhibits two broad bands in the range 300 – 450 nm and 450 – 600 nm. These bands were associated with absorption transition of octahedral Cr^{3+} ions from the ground level $^4A_2$ to the excited levels $^4T_1$ and $^4T_2$.

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1. Introduction

In the last year many studies has been dedicated to synthesis and characterization of traditional and glass ceramic pigments. These studies have the main aim to increase the number of colored materials useful for industrial applications [1]. One of the most intensively studied host material is zinc aluminate spinel ($ZnAl_2O_4$). Aluminate-based spinels are used as catalyst materials, catalyst support and have applications as the best wide band gap semiconductor material for photoelectric devices [2-4]. $ZnAl_2O_4$ have the chemical formula AB_2O_4, where A is Zn ion that occupies a tetrahedral site and B represents Al ion which occupies the octahedral sites of a cubic crystal. Zinc aluminate spinel has the normal spinel structure with the spatial group Fd3m. Many synthesis for $ZnAl_2O_4$ preparation, such as: coprecipitation [5], hydrothermal method [6,7], sol–gel [8,9], combustion synthesis [10] were reported. This host material can be doped with various ions but the most interesting are the transition ions. Between them, Cr^{3+} ion is the responsible for the pink colored pigments. Pink Cr^{3+}-doped spinels are investigated mainly due to their chromatic and technological properties. In low crystal field, the cromophore Cr^{3+} is responsible of green colour, but in high crystal field it induces a pink colour [11]. Cr^{3+} doped spinles are stable at high temperatures thus they can be used in ceramic applications [12].
In this work, we report the hydrothermal synthesis of pink Cr^{3+}- doped zinc aluminate pigment annealed at 1000ºC using zinc nitrate hexahydrate, aluminium nitrate nonahydrate and chromium nitrate hexahydrate as precursors.

2. Experimental procedure

Pink Cr^{3+}-doped $ZnAl_2O_4$ was prepared by hydrothermal method and then treated thermally at 1000ºC. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) and chromium nitrate hexahydrate ($Cr(NO_3)_3 \cdot 9H_2O$) were used as precursors. As a precipitating agent water solution of ammonia (25%) was used. The precursors were dissolved in distilled water and the mixture was stirred on a magnetic stirrer for few hours. The appropriate amount of ammonia was added drop by drop till pH value became 9. The resulting suspension was transferred into a Teflon-lined stainless steel autoclave and sealed tightly then was introduced in an oven at 220ºC for 16 h. The resulted precipitate was then filtrated and washed many times with distilled water and ethylic alcohol, then dried in an oven at 100°C for 6 hours. After drying, the resulting powder was treated thermally at 1000°C for 3h. The fine pink powder was then characterized by different methods.

The characterization of the prepared sample was achieved by X-ray powder diffractometer (PANalytical X'Pert Pro) with monochromatic Cu Kα (k = 1.5418 Å) incident radiation. The topography of the surface was achieved by atomic force microscopy (Nanosurf® EasyScan 2 Advanced Research (AFM)). UV/VIS/NIR measurement was carried out using a UV/VIS/NIR spectrophotometer (Model Lambda 950).

3. Results and discussions

The crystallinity and purity of the sample prepared by hydrothermal method were determined by means of X-ray diffraction.

To reveal the structural properties in Fig. 1 and 2 the X-ray diffraction pattern of pink $ZnAl_{2-x}Cr_xO_4$ (x=0.01) pigment for both, as prepared sample and the one treated thermally in comparison with the undoped $ZnAl_2O_4$ sample are presented. The undoped and doped samples were prepared in the same conditions.

As seen from the Fig. 1 the as prepared sample presents specific spinel phase peaks which can be indexed as (111), (220), (311) (422), (511), (440) and (533). In comparison with this, the samples heated at 1000ºC for 3h

(Fig. 2) presents higher crystallinity degree and the presence of (400), (331), (620) diffraction peaks can be observed. The diffraction peaks were indexed using diffraction planes specific for cubic zinc aluminate spinel (JCPDS no. 05-0669). Also, it can be observed that diffraction pattern for doped sample presents a small shift in comparison with undoped sample because of the presence of Cr^{3+} ions.

The average crystallite size (d) was calculated from X-ray line broadening (d_{311}) using Schererr's equation [13]. It was found that in the case of pink $ZnAl_2O_4:Cr^{3+}$ (x=0.01) pigments the average crystallite size increases with temperature from 15 nm to 31 nm.

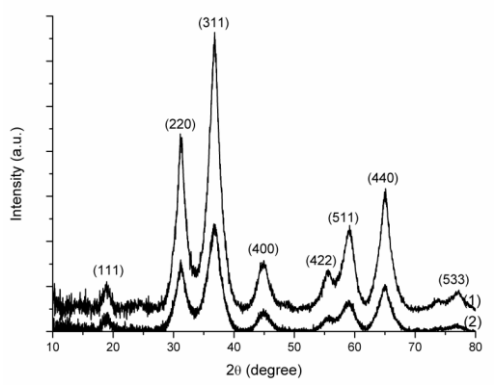

Fig. 1. X-ray diffraction pattern for pink $ZnAl_2O_4:Cr^{3+}$ pigment: 1) as prepared and 2) annealed at 1000ºC.

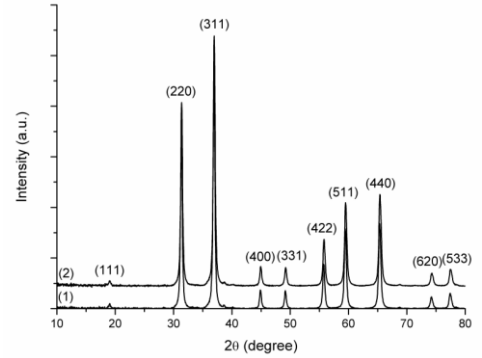

Fig. 2. X-ray diffraction pattern for pink $ZnAl_2O_4:Cr^{3+}$ pigment: 1) as prepared and 2) annealed at 1000ºC.

The volume and parameter of the unit cell was calculated using X'Pert HighScore Plus program. These values are presented in Table 1.

Table 1.

Sample	V (Å^3)	a (Å)
$ZnAl_2O_4$ as prepared	532.20	8.104±4
$ZnAl_2O_4$ annealed at 1000ºC	523.41	8.059±2
$ZnAl_{2-x}Cr_xO_4$ (x=0.01) as prepared	533.94	8.113±3
$ZnAl_{2-x}Cr_xO_4$ (x=0.01) annealed at 1000ºC	524.97	8.067±2

As we can see, the volume and parameter of the unit cell is higher for $ZnAl_{2-x}Cr_xO_4$ (x=0.01) which means that the Cr^{3+} ions are presence in our structure and its due to the fact that ionic radius of Cr^{3+} ions (0.63 Å) it is higher then that of Al^{3+} ions (0.53 Å) [14,15]. Also, it can be seen that this parameters depends on heating temperatures. The volume and parameter of the unit cell decreases when temperature increases [16].

Because of its higher crystallinity degree and because the aim of this work is to reveal the optical properties of prepared sample, further we will refer only to the sample $ZnAl_2O_4:Cr^{3+}$ obtained after annealing at 1000ºC.

Energy dispersive X-ray analysis (EDX) was performed to analyze the chemical composition of the prepared sample. A typical EDX spectrum for $ZnAl_{2-x}Cr_xO_4$ (x=0.01) annealed at 1000ºC for 3h is presented in Fig. 3.

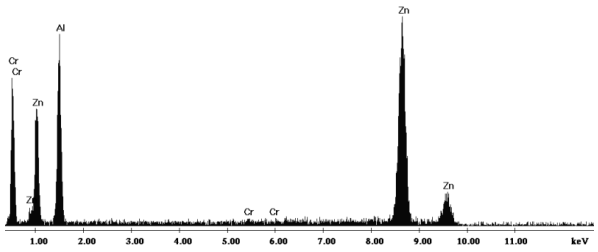

Fig. 3. The qualitative EDX analysis of $ZnAl_2O_4:Cr^{3+}$ annealed at 1000ºC.

As we can see from EDX spectrum, no impurity trace was found, only the Zn, Al and Cr elements. This result confirmed the purity of the obtained sample.

To analyze the topography of the surface for the $ZnAl_{2-x}Cr_xO_4$ (x=0.01) atomic force microscopy (AFM) was performed. Scanning size was 1μm × 1μm and was made using the contact mode cantilever.

From the AFM measurements data, the average particle size was found to be approximately 39 nm. These measurements are in agreement with X-ray diffraction data. Because of the small sizes as we can see from AFM images sample present agglomerates.

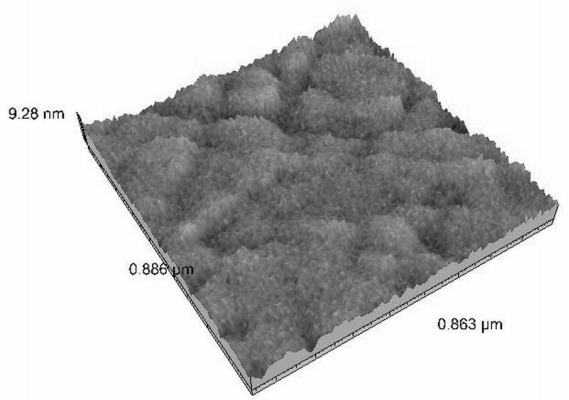

Fig. 4. AFM images of $ZnAl_2O_4:Cr^{3+}$ annealed at 1000ºC.

The optical absorbance spectrum was determined by diffuse reflectance using a UV/VIS/NIR spectrophotometer. The optical absorbance spectrum was detected in the 300-700 nm range at room temperature. In Fig. 5 the absorbance spectrum of $ZnAl_{2-x}Cr_xO_4$ (x=0.01) nanocrystals is presented.

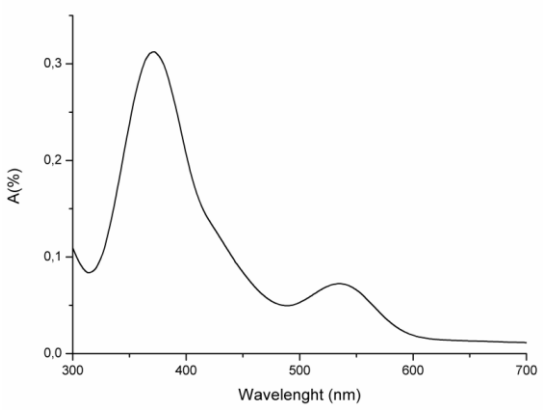

Fig. 5. Absorbance spectra of $ZnAl_2O_4:Cr^{3+}$ annealed at 1000ºC.

The optical absorbance spectrum of $ZnAl_2O_4:Cr^{3+}$ nanocrystals consist of two broad bands. First band appear between 300 – 450 nm centered at 370 nm and the second one between 450 – 600 nm centered at 535 nm. These, two bands, are associated with absorption transition of octahedral Cr^{3+} ions from the ground level $^4A_2$ to the excited levels $^4T_1$ and $^4T_2$ [1].

The absorbance spectrum of $ZnAl_2O_4:Cr^{3+}$ nanocrystals reveals the presence of Cr^{3+} ions in octahedral coordination and no other phases or sites of it. Thus, the pink Cr^{3+}-doped $ZnAl_2O_4$ with a low concentration of Cr^{3+} ions is a good candidate for ceramic pigments applications.

4. Conclusions

It is possible to obtain pink $ZnAl_2O_4:Cr^{3+}$ pigment by hydrothermal method using zinc nitrate hexahydrate, aluminium nitrate nonahydrate and chromium nitrate hexahydrate as precursors and water solution of ammonia (25%) as a precipitating agent. $ZnAl_2O_4:Cr^{3+}$ pink pigment prepared by hydrothermal method and then annealed at 1000ºC showed a single – spinel phase and the average crystallite size was found to be around 31 nm. The optical absorbance spectrum exhibits two broad bands in the range 300 – 450 nm and 450 – 600 nm. These bands were associated with absorption transition of octahedral Cr^{3+} ions from the ground level $^4A_2$ to the excited levels $^4T_1$ and $^4T_2$. Thus, no other phases or sites of Cr^{3+} ions are reveal to be present.

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