Some physical properties of ZnAl$_2$O$_4$: Cr$^{3+}$ (Co$^{2+}$) powders prepared by hydrothermal method

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Abstract. ZnAl$_2$O$_4$: Cr$^{3+}$ (Co$^{2+}$) nanopowders were prepared by hydrothermal method and annealed at various temperatures. The samples were characterized by X-ray diffraction, transmission electron microscopy, photoluminescence and photoluminescence excitation spectra. The results show that crystal structure and optical properties of the samples were affected by heat treatment regime. When annealing temperature increased, crystal structure of the samples became better. Optical spectra of the ions Cr$^{3+}$ are sensitive to crystal structure of the host lattice. Electron transitions difference in absorption and radiation processes between the samples ZnAl$_2$O$_4$: Co$^{2+}$ unannealed and annealed at high temperature was investigated.

Keywords: ZnAl$_2$O$_4$: Cr$^{3+}$ (Co$^{2+}$), nanopowders, hydrothermal.

1. Introduction
Spinels have attracted interest because of their properties such as high chemical and thermal stability, high mechanical resistance, low sintering temperature and high quantum yields [1]. They are widely used as a phosphor host material for applications in mechano-optical stress sensors, optical coating, thin film electroluminescence displays, stress imaging devices, catalysts and catalysts supports [2, 3]. There are many methods to prepare spinels with nanostructures, such as solid state reaction [4], wet chemical routes: co-precipitation [5], sol-gel [6], hydrothermal method [7].

In this work, we have succeeded in synthesizing nanopowders ZnAl$_2$O$_4$: Cr$^{3+}$ (Co$^{2+}$) with single phase and controlled particle size and morphology by the hydrothermal techniques. We also studied structural, optical properties of Cr$^{3+}$ (Co$^{2+}$) ions doped samples ZnAl$_2$O$_4$ unannealed and annealed at various temperature in the range of 200 - 1200$^\circ$C.

2. Experiment
In this experiment, AlCl$_3$·6H$_2$O, ZnCl$_2$ and Co(NH$_2$)$_2$ were used as source materials. At first, the source materials were dissolved in distilled water and the products were stirred at room temperature. Chromium (cobalt) nitrate was added to above solution with the molar ratio Cr$^{3+}$ (Co$^{2+}$)/ZnAl$_2$O$_4$ varying up 5:1000. After that, an amount of NaOH and then C$_2$H$_5$OH were supplemented to the solution. Next the solution was put into Teflon-lined stainless steel autoclave and kept at the reaction temperature of 200$^\circ$C for 96 hours. Thereafter, the solid material was filtered off, washed with distilled water and then air-dried at 100$^\circ$C.

All the synthesized samples were characterized for their crystallinity phase by power X-ray diffraction (XRD) on a SIMENS D5005 diffractometer using Cu-K$_\alpha$ radiation ($\lambda = 1.54056$ Å). The
morphology and nanostructures of particles were examined by TEM using a JEOL JEM 1010 transmission electron microscope. The optical properties were investigated by photoluminescence (PL) and photoluminescence excitation (PLE) spectra at room temperature on a spectrofluorometer Fluorolog FL3 -22 Jobin Yvon Spex USA.

3. Results and discussion

3.1. Cr$^{3+}$ doped ZnAl$_2$O$_4$ spinel nanopowders

The XRD patterns of nanopowders Cr$^{3+}$ (Co$^{2+}$) doped ZnAl$_2$O$_4$ annealed at various temperatures: 700, 900, 1200°C are shown in figure 1. As seen from the XRD patterns, all the samples are single - spinel phase and no characteristic peaks associated with impurity phase are observed. The peaks can be indexed as (220), (311), (400), (331), (422), (511) and (440) diffraction planes of spinel. With the increase of heat treatment temperature, the intensity of the diffraction peaks increases and their full - width at half- maximum (FWHM) decreases. All of these are associated with the increase of crystallinity and grain sizes. The average grain sizes of the powders sintered at different temperatures were determined by means of the Scherrer's formula and shown in the table 1. It can be noticed that the grain sizes of powders increase with the annealing temperature. The unannealed spinel ZnAl$_2$O$_4$: Cr$^{3+}$ grains have an average size of 5 nm and those calcined at 1200°C have an average size of 18.3 nm. The unit - cell parameters and the grain sizes of all samples were also calculated from the XRD patterns and are shown in table 1.

![Figure 1. XRD patterns of samples annealed at various temperatures: a) 1200°C, b) 900°C, c) 700°C, d) unannealed.](image)

Figure 2 shows the TEM micrographs of the powder sample formed at 700°C and the unannealed sample. The spinel particles consist of uniform quasi - spherical crystallites with the diameters of 7 nm (annealed at 700°C) and 5 nm (unannealed), which is consistent with calculated results from the XRD patterns.

To confirm the presence of the octahedral Cr$^{3+}$ ions in the ZnAl$_2$O$_4$ nanocrystals, the room - temperature PLE and PL spectra of the powder samples were studied and the results are displayed in figure 3. It shows that the PL spectra of nanoparticles ZnAl$_2$O$_4$: Cr$^{3+}$ is similar to those of bulk crystals doped with octahedral Cr$^{3+}$ ions [8]. This fact indicates that doped ions Cr$^{3+}$ were in the places of octahedral symmetry of synthesized ZnAl$_2$O$_4$ nanocrystals and the emission peaks were assigned to the $^2$E($^2$G) $\rightarrow$ $^4$A$_2$($^4$F) transition of octahedral Cr$^{3+}$ ions. It is found from figure 3a that the
PL spectra of all samples are similar, but the FWHM of emission lines corresponding to zero-phonon $^2E(2G) \rightarrow ^4A_2(4F)$ transition in the wavelength range of 683 - 693 nm are different.

**Table 1.** The dependence of the unit-cell parameters and the grain sizes on annealing temperatures.

| Annealing temperatures (°C) | Unit-cell parameters (Å) | Average grain sizes (nm) |
|-----------------------------|--------------------------|--------------------------|
| 1200                        | 8.080 ± 0.002            | 18.3                     |
| 900                         | 8.082 ± 0.004            | 14.5                     |
| 700                         | 8.087 ± 0.003            | 7.5                      |
| Unannealing                 | 8.121 ± 0.004            | 5.1                      |

In the unannealed sample the broad emission line resulted from an overlapping of N line (689 nm) associated with disordering of ions Cr$^{3+}$ and R line (686 nm) related to ordering of ions. In this case the ratio of the intensity of these lines is approximately equal to 1. So that, with the increase of annealing temperature this ratio is significantly reduced.

The excitation spectra recorded by monitoring the emission of transition $^2E(2G) \rightarrow ^4A_2(4F)$ corresponding to zero-phonon R line were displayed in the figure 3b. It is seen that the PLE spectrum of Cr$^{3+}$ doped ZnAl$_2$O$_4$ nanoparticles consists of two broad bands. The first belongs to the wavelength range of 360 - 450 nm and the second of 450 - 600 nm. Both of them were associated with absorption transitions of octahedral Cr$^{3+}$ ions from the ground level $^4A_2$ to the excited levels $^4T_1$ and $^4T_2$, respectively. Because of the spin - orbit interaction, the level $^4T_1$ is separated into levels $^4A_2(4T_1)$ and $^4E(4T_1)$, so in the first band it is found two absorption peaks at 390 and 417 nm. Moreover, the difference of peak positions in the second band between the unannealed and annealed samples ($\Delta \lambda = 5$ nm) is related to a change of the unit-cell parameters. It is known, in opposite of the first transition $^4A_2 \rightarrow ^4T_1$, a peak position of the second absorption transitions $^4A_2 \rightarrow ^4T_2$ depends on the distances of Zn$^{2+}$ - O$^{2-}$, Al$^{3+}$ - O$^{2-}$. It is seen from table 1 that the unit-cell parameters were the highest in case of unannealed sample ZnAl$_2$O$_4$: Cr$^{3+}$, therefore the distances were large too. And the crystal-field is smaller in comparison with annealing cases. That is why the peak positions corresponding to above mentioned transitions $^4A_2 \rightarrow ^4T_2$ shifted to longer wavelength bands in the unannealed sample.
Both emission and excitation spectra of the Cr$^{3+}$ doped ZnAl$_2$O$_4$ may give detailed information about the surrounding of Cr$^{3+}$ ions in a lattice. That is why the structural and optical probe is very useful.

3.2. Co$^{2+}$ doped ZnAl$_2$O$_4$ spinel nanopowders

According to the computation of Tanabe - Sugano, the tetrahedral symmetry ions 3d$^7$ (Co$^{2+}$) have the same energy level structure as the octahedral symmetry ions 3d$^3$ (Cr$^{3+}$). Due to the investigation of the influence of heat - treatment regime on crystal structure and optical properties of ZnAl$_2$O$_4$: Cr$^{3+}$ samples in the previous section, in this section we study the change of optical properties of ZnAl$_2$O$_4$: Co$^{2+}$.

Up to now there is not unified explanation of the nature of the broad band centered at 660 nm in the emission spectrum. The authors [9, 10] claim that the broad band centered at 660 nm is associated with the $^2E(^2G)\rightarrow^4A_2(^4F)$ transition. Meanwhile, Denisov and his partners [11] assert that this radiation band corresponding to the $^4T_1(^4P)\rightarrow^4A_2(^4F)$ transition. In this work, the experiment results show that the broad band centered at 660 nm isn’t associated with $^2E(^2G)\rightarrow^4A_2(^4F)$ transition, but it may relate to the $^4T_1(^4P)\rightarrow^4A_2(^4F)$ transition. The reasons are as follows:
- Firstly, with the selective excitation wavelength of 390 nm, one can observe a series of narrow lines which is similar to the PL spectrum of Cr$^{3+}$ ion due to the $^2E(^2G)\rightarrow^4A_2(^4F)$ transition in the perfect lattice of spinel.
- Secondly, from the Tanabe - Sugano’s diagram [12], the luminescence peaks which are due to the spin - allowed transition $^2E(^2G)\rightarrow^4A_2(^4F)$ are narrow, while those due to the $^4T_1(^4P)\rightarrow^4A_2(^4F)$ transition depend strongly on host lattice and are usually broad.

Besides, the excitation spectrum of ZnAl$_2$O$_4$: Co$^{2+}$ sample unannealed and annealed at 1200°C were presented in figure 4b. It is found that the excitation spectrum of Co$^{2+}$ doped unannealed sample is similar to the PLE spectrum of Cr$^{3+}$ doped ZnAl$_2$O$_4$ with two broad bands at 393 and 535 nm corresponding to the $^4A_2(^4F)\rightarrow^4T_1(^4F)$ and $^4A_2(^4F)\rightarrow^4T_2(^4F)$ transitions, respectively. Meanwhile, the PLE spectrum of sample sintered at 1200°C is different to unanneled case. The PLE spectrum of sample annealed at 1200°C displays three peaks around 565, 592 and 620 nm which cause the fluorescence $^4T_1(^4P)\rightarrow^4A_2(^4F)$. 

Emission spectra, $\lambda_{ex} = 540$ nm. 

Excitation spectra, $\lambda_{em} = 686$ nm.

**Figure 3.** Emission and excitation spectra of ZnAl$_2$O$_4$: Cr$^{3+}$ sample annealed at various temperatures. 
a) 1200°C, b) 900°C, c) 700°C, d) unannealed.
4. Conclusion

ZnAl₂O₄: Cr³⁺ (Co²⁺) nanopowders were formed by hydrothermal method and subsequently calcined at various temperatures. The ZnAl₂O₄: Cr³⁺ nanopowders annealed in the temperature range of 200 - 1200°C exhibit an increase in the particle sizes from 5 nm (for unannealed sample) to 18 nm (for sample annealed at 1200°C). The PL spectrum of the ZnAl₂O₄: Co²⁺ unannealed nanopowders is similar to the ZnAl₂O₄: Cr³⁺ nanopowders. The PL spectrum of the sample annealed at 1200°C includes one broad band centered at 660 nm when the excitation wavelength is 592 nm. The series of narrow lines in the range of 670 - 710 nm are due to ⁴E(⁴G) → ⁴A₂(⁴F) transition and broad band at 660 nm is due to ⁴T₁(⁴P) → ⁴A₂(⁴F) transition.

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