

# Characterization and luminescence properties of ZnAl<sub>2</sub>O<sub>4</sub>:Tb<sup>3+</sup> (2.5%) phosphor

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ZnAl<sub>2</sub>O<sub>4</sub>:Tb<sup>3+</sup> (2.5%) phosphor was synthesized by coprecipitation method and then annealed at 1000°C for 3h. The sample was investigated by means of X-ray diffraction to analyze the crystal structure. It was found that a single spinel phase is present and the average crystallite size was found to be around 32 nm. Atomic force microscopy measurements confirmed the nano-size of the particles. The purity of the sample was confirmed, also, by EDX and FT-IR analysis. Optical properties of Tb (2.5%) doped ZnAl<sub>2</sub>O<sub>4</sub> phosphor was analyzed by means of UV/VIS/NIR and photoluminescence (PL) analysis. The band gap of the sample was found to be 4.27 eV. The excitation spectrum showed a broad band centered at 234 nm which correspond to 4f-5d transition and some sharp lines beyond 300 nm which correspond to f-f transitions. The emission spectrum presented an intense peak centered at 545 nm which correspond to the <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub> transition. Also, peaks corresponding to <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>4</sub> (586 nm) and <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>3</sub> (624 nm) transitions were found. The emission colour of terbium doped ZnAl<sub>2</sub>O<sub>4</sub> was found to be green.

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**Keywords:** Zinc Aluminate, Phosphors, Terbium, Luminescence

## 1. Introduction

Spinel type materials are used as catalyst supports due to their high resistance to acids and alkalis and have high melting points [1]. Oxide spinels represent a large group of structurally related compounds many of them having high technological significance [2]. Among oxide spinels, zinc aluminate ZnAl<sub>2</sub>O<sub>4</sub> with a spinel structure presents a high interest. Zinc aluminate spinel has the normal spinel structure with the spatial group Fd3m and consists of a cubic unit cell in which Zn<sup>2+</sup> ions occupy tetrahedral sites and Al<sup>3+</sup> ions the octahedral sites. Because of its high thermal stability, high mechanical resistance, low surface acidity and excellent optical properties ZnAl<sub>2</sub>O<sub>4</sub> spinel is used as catalyst, ceramic and electro-conductive materials [3-5]. Furthermore, zinc aluminate spinel can be used in ultraviolet photoelectronic devices because its optical band gap (3.8 eV) indicates that zinc aluminate spinel is transparent to light with wavelengths higher than 320 nm [5-7]. Zinc aluminate spinel doped with rare earth ions has been investigated, lately, due to its unique luminescent properties which results from its stability and high emission quantum yields [8,9]. This kind of material produces efficient visible emissions in a 4f shell, which, it is insensitive to the influence of its surroundings [10]. Among rare earth ions used for ZnAl<sub>2</sub>O<sub>4</sub> spinel doping, Eu<sup>3+</sup> and Tb<sup>3+</sup> ions are the most used. Tb<sup>3+</sup> ions, because of their large ionic radius (1 Å) may substitute both, Al<sup>3+</sup> (0.53 Å) ions and Zn<sup>2+</sup> (0.74 Å) ions [5] inducing this way a distortion of a crystal structure. Many methods have been reported for rare earth ions (Eu<sup>3+</sup>, Tb<sup>3+</sup>) doped

ZnAl<sub>2</sub>O<sub>4</sub> spinel: solid state [11], hydrothermal [12,13], sol-gel [14] and most used combustion method [10,15].

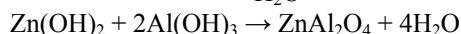
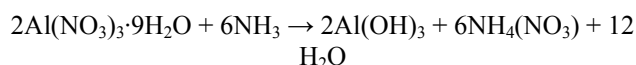
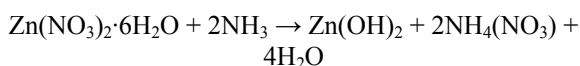
The aim of this paper is to investigate the structural and luminescence properties of Tb<sup>3+</sup> (2.5%) doped ZnAl<sub>2</sub>O<sub>4</sub> phosphor prepared by coprecipitation method using zinc nitrate hexahydrate, aluminium nitrate nonahydrate and terbium chloride as precursors and ammonia solution as precipitating agent.

## 2. Experimental procedure

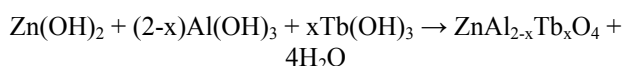
Nanocrystalline Tb (2.5%) doped ZnAl<sub>2</sub>O<sub>4</sub> phosphor was prepared by coprecipitation method and annealed at 1000°C for 3h. As precursors we used zinc nitrate hexahydrate – Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, aluminium nitrate nonahydrate – Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and terbium (III) chloride hexahydrate – TbCl<sub>3</sub>·6H<sub>2</sub>O. As a precipitating agent solution of ammonia (25%) was used.

The precursors were first dissolved in distilled water and then mixed together. The resulting mixture was vigorously stirred on a magnetic stirrer. Ammonia solution was added drop by drop till the final pH of the solution was 9. The mixture was stirred for few hours. Then, the white precipitate was filtered off, washed consecutively with distilled water and dried at 100°C for 6 hours. After drying, the obtained white powder was annealed at 1000°C for 3 hours.

In the coprecipitation process ZnAl<sub>2</sub>O<sub>4</sub> precipitate with spinel structure is formed as a result of the following reactions:



In case of Tb-doped ZnAl<sub>2</sub>O<sub>4</sub> phosphor the reaction became:



Tb-doped ZnAl<sub>2</sub>O<sub>4</sub> phosphor obtained by coprecipitation method was characterized by different methods. Structural characterization was made by means of X-ray diffraction using a X-ray powder diffractometer (PANalytical X'Pert Pro) with monochromatic Cu K $\alpha$  ( $k = 1.5418 \text{ \AA}$ ) incident radiation. To analyze the topography of the surface and to confirm the purity of the sample, atomic force microscope (Nanosurf<sup>®</sup> EasyScan 2 Advanced Research (AFM)) and energy dispersive X-ray analysis (EDX) were used. EDX analysis was performed by a scanning electron microscope SEM+EDX (Model INSPECT S). Infrared spectrum was recorded on a Bruker system Vertex 70 spectrophotometer using KBr pellet method. Optical absorbance spectrum was measured with a UV/VIS/NIR spectrophotometer (Model Lambda 950). The photoluminescence (PL) measurement was carried out using a spectrofluorophotometer at room temperature (Model LS55, Perkin Elmer).

### 3. Results and discussions

As we know, in the ZnAl<sub>2</sub>O<sub>4</sub> normal spinel structure Zn<sup>2+</sup> ions are situated in tetrahedral sites and Al<sup>3+</sup> ions may occupies only the octahedral sites. Because Tb<sup>3+</sup> ions prefer octahedral sites, we prepared Tb (2.5%) doped ZnAl<sub>2</sub>O<sub>4</sub> phosphor assuming that terbium ions would substitute for aluminium ions.

In Fig. 1 X-ray diffraction pattern of pure ZnAl<sub>2</sub>O<sub>4</sub> powder and powder doped with terbium ions is presented.

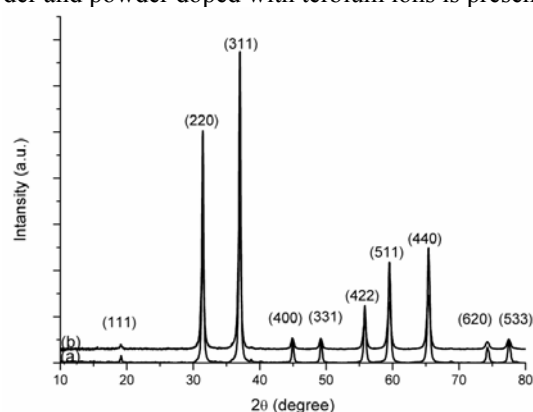


Fig.1. X-ray diffraction pattern of ZnAl<sub>2</sub>O<sub>4</sub> (a) and Tb (2.5%) doped ZnAl<sub>2</sub>O<sub>4</sub> (b) phosphor prepared by coprecipitation method

X-ray diffraction patterns confirmed that the sample obtained by coprecipitation consisted of a single phase ZnAl<sub>2</sub>O<sub>4</sub> spinel (JCPDS no. 05-0669). Impurities from any other residual like zinc oxide, aluminium oxide or terbium oxide was not detected. In the literature usually impurities are observed in the samples obtained by other methods [1,16].

The diffraction peaks present in X-ray diffraction pattern can be indexed as (111), (220), (311) (400), (331), (422), (511), (440), (620) and (533). The diffraction peaks are indexed to spinel (space group Fd3m) phases. One can see that the most intensive peak is the one indexed as (311) plane. This plane indicates the standard powder diffraction pattern of ZnAl<sub>2</sub>O<sub>4</sub> phase and the (220) plane indicates the preferred orientation of powder.

From Fig. 1 we can observe a small shift of diffraction peaks for ZnAl<sub>2</sub>O<sub>4</sub> (a) and Tb-doped ZnAl<sub>2</sub>O<sub>4</sub> (b) powders. This shift appears due to terbium ions presence. The presence of terbium ions in ZnAl<sub>2</sub>O<sub>4</sub> induces distortions of its crystal structure due to the large differences in their ionic radius (1 Å for Tb<sup>3+</sup> and 0.53 Å for Al<sup>3+</sup> ions) as was reported before in other works [10]. Furthermore, it can be seen that the intensity of some diffraction peaks changes as well. In Table 1 are presented the position of diffraction peaks and their relative intensity for both, pure ZnAl<sub>2</sub>O<sub>4</sub> and terbium doped ZnAl<sub>2</sub>O<sub>4</sub> powder.

Table 1.

No.	hkl	ZnAl <sub>2</sub> O <sub>4</sub>		Tb (2.5%) doped ZnAl <sub>2</sub> O <sub>4</sub>	
		2 Theta (deg)	Relative Intensity (%)	2 Theta (deg)	Relative Intensity (%)
1	111	19.1984	2.03	19.1529	2.19
2	220	31.4321	74.74	31.4514	70.86
3	311	37.0053	100	36.9923	100
4	400	44.9758	6.99	44.9040	7.33
5	331	49.2256	7.41	49.2064	7.01
6	422	55.7787	17.66	55.7972	17.97
7	511	59.4884	31.66	59.4975	31.87
8	440	65.3634	36.34	65.3322	36.42
9	620	74.2290	4.91	74.2318	4.67
10	533	77.4367	6.49	77.4250	6.13

Using Scherrer's equation [17] the average crystallite size ( $d$ ) was calculated from X-ray line broadening ( $d_{311}$ ). The average crystallite size was found to be around 67 nm for undoped powder and 32 nm for the doped one. Thus, it can be observed that the average crystallite size decreases when the powder is doped with terbium ions.

To confirm the results achieved from X-ray diffraction analysis and to analyze the topography of the surface, atomic force microscopy analysis was performed. The topography of the surface of Tb (2.5%) doped ZnAl<sub>2</sub>O<sub>4</sub> prepared by coprecipitation method and annealed at 1000°C for 3h achieved by atomic force microscopy is presented in Fig. 2.

Atomic force microscopy (AFM) was performed using contact mode cantilever. The scanning size was

$1\mu\text{m} \times 1\mu\text{m}$ . The AFM image shows that the particles tend to agglomerate due to their small sizes. AFM measurements data showed that the average particle size (d) for Tb (2.5%) doped  $\text{ZnAl}_2\text{O}_4$  prepared by coprecipitation method is around 34 nm. This result confirmed the results achieved from X-ray diffraction analysis.

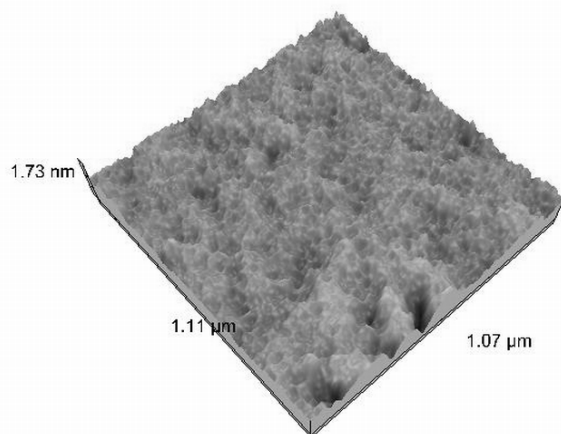


Fig. 2. AFM image for Tb (2.5%) doped  $\text{ZnAl}_2\text{O}_4$  prepared by coprecipitation method.

Chemical composition and purity of the terbium doped  $\text{ZnAl}_2\text{O}_4$  was analyzed by means of energy dispersive X-ray analysis (EDX). The EDX spectrum for Tb (2.5%) doped  $\text{ZnAl}_2\text{O}_4$  phosphor prepared by coprecipitation method is presented in Fig. 3.

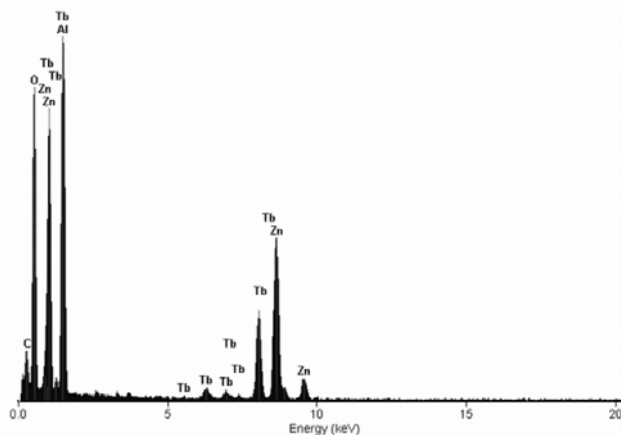


Fig. 3. EDX analysis for Tb (2.5%) doped  $\text{ZnAl}_2\text{O}_4$  prepared by coprecipitation method

EDX analysis confirmed the purity of the sample, only Zn, Al and Tb elements and no impurity trace was found.

FT-IR analysis was performed to confirm the results obtained by X-ray diffraction and EDX analysis. In Fig. 4 a typical transmittance FT-IR spectrum of Tb (2.5%) doped  $\text{ZnAl}_2\text{O}_4$  phosphor prepared by coprecipitation method and annealed at  $1000^\circ\text{C}$  for 3h is shown. The FT-IR spectrum was recorded using KBr pellets. FT-IR spectrum was recorded between  $400$  and  $4000\text{ cm}^{-1}$  at room temperature.

As we can see three strong bands below  $1000\text{ cm}^{-1}$  and few bands between  $1000$  and  $4000\text{ cm}^{-1}$  appears. Those three bands that appear below  $1000\text{ cm}^{-1}$  are related to the stretching mode (bands centered at  $667$  and  $563\text{ cm}^{-1}$ ) and to the bending mode (band centered at  $503\text{ cm}^{-1}$ ) of Al-O and O-Al-O in octahedral coordination state ( $\text{AlO}_6$ ) [18,19]. These bands are characteristic for zinc aluminate spinel [20]. Further, the bands which appear between  $1000$  and  $4000\text{ cm}^{-1}$ , centered at  $1046$ ,  $1633$  and  $3235\text{ cm}^{-1}$  may be attributed to the vibration mode of hydroxyl groups (OH) and to the deformation vibration of water molecule [13,20]. The results achieved by FT-IR analysis confirmed the purity of Tb (2.5%) doped  $\text{ZnAl}_2\text{O}_4$  phosphor. Also, these results are in agreement with data achieved by X-ray diffraction analysis.

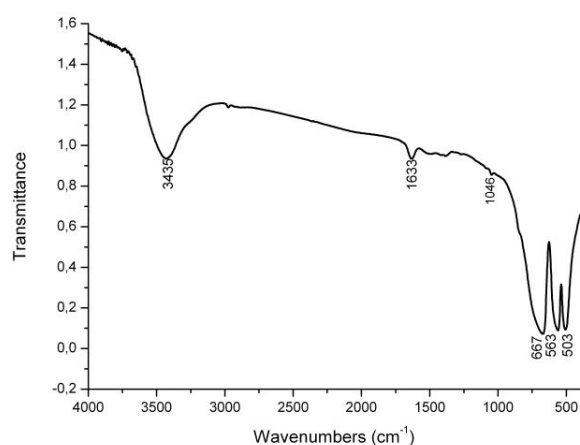


Fig. 4. FT-IR spectrum of Tb (2.5%) doped  $\text{ZnAl}_2\text{O}_4$  prepared by coprecipitation method and annealed at  $1000^\circ\text{C}$  for 3h

UV/VIS/NIR and PL analysis were performed to analyze the optical properties of terbium doped zinc aluminate phosphor prepared by coprecipitation method.

The optical absorbance spectrum of Tb (2.5%) doped  $\text{ZnAl}_2\text{O}_4$  phosphor was obtained from diffuse reflectance spectrum recorded in the region  $230 - 480\text{ nm}$  at room temperature.

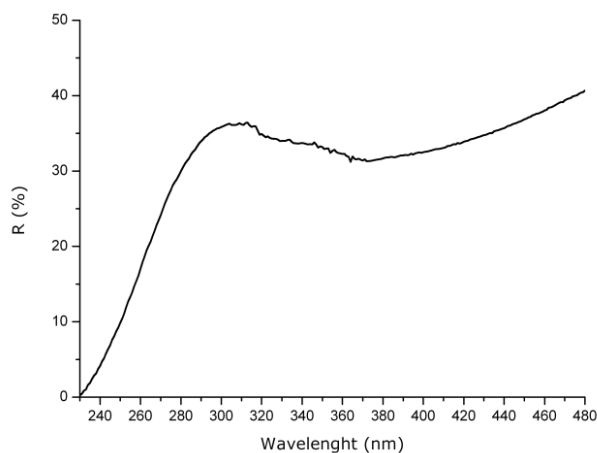


Fig. 5. Diffuse reflectance spectrum for Tb (2.5%) doped  $\text{ZnAl}_2\text{O}_4$  prepared by coprecipitation method

In Fig. 6 absorbance spectrum of Tb (2.5%) doped  $\text{ZnAl}_2\text{O}_4$  phosphor obtained from diffuse reflectance spectrum is shown.

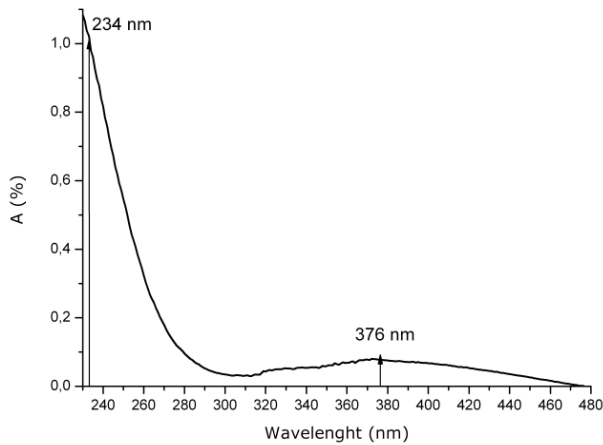


Fig. 6. Absorbance spectrum of Tb (2.5%) doped  $\text{ZnAl}_2\text{O}_4$  prepared by coprecipitation method

As we can see, the absorbance spectrum shows a broad band under 300 nm centered at 234 nm. This band is attributed to 4f-5d transitions. Also, we can see some sharp lines of low intensity beyond 300 nm. These lines are attributed to f-f transitions [10,15]. All these transitions are specific for terbium ions.

Using Kubelka-Munk equation [21,22] the band gap value of the prepared sample was determined. From the absorbance spectrum, we plotted  $\{(k/s)(h\nu)\}^2$  ( $\text{eV}^2$ ) vs.  $h\nu$  (Fig. 7), where  $k$  denotes the absorption coefficient,  $s$  is the scattering coefficient, and  $h\nu$  is the photon energy.

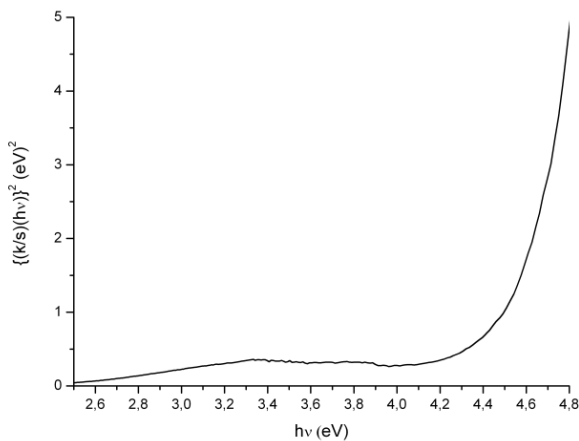


Fig. 7. Plot of  $\{(k/s)(h\nu)\}^2$  ( $\text{eV}^2$ ) vs.  $h\nu$  (energy) for Tb (2.5%) doped  $\text{ZnAl}_2\text{O}_4$  prepared by coprecipitation method

The band gap of Tb (2.5%) doped  $\text{ZnAl}_2\text{O}_4$  phosphor is determined from the plot of  $\{(k/s)(h\nu)\}^2$  ( $\text{eV}^2$ ) vs.  $h\nu$ . The band gap was calculated by extrapolating the linear portion of the curve to  $h\nu$  equal to zero (Fig. 7).

The band gap value was found to be around 4.27 eV. According to the literature, the band gap of pure zinc

aluminate spinel is around 3.8 eV [5,7]. Thus, by doping  $\text{ZnAl}_2\text{O}_4$  spinel with terbium ions, we increased its band gap value, which makes this material a good candidate for photoelectronic device applications.

The photoluminescent behavior of Tb (2.5%) doped  $\text{ZnAl}_2\text{O}_4$  phosphor was analyzed at room temperature. In Fig. 8 the excitation spectrum of the prepared sample can be seen.

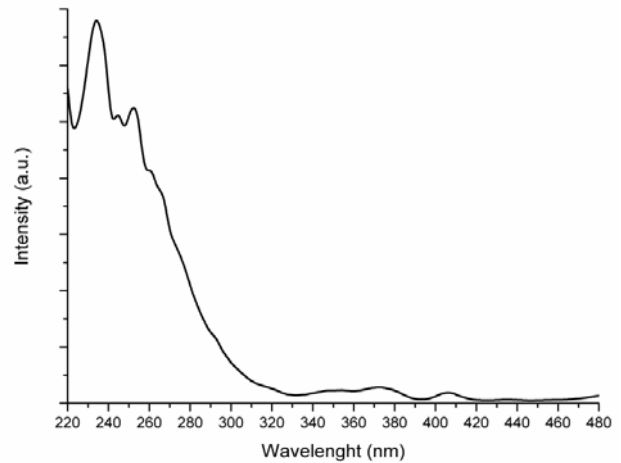


Fig. 8. Excitation spectrum of Tb (2.5%) doped  $\text{ZnAl}_2\text{O}_4$  ( $\lambda_{em}=545$  nm) prepared by coprecipitation method

The excitation spectrum was monitored at 545 nm in the range 220 – 480 nm. As we can see, the excitation spectrum is similar to the absorbance spectrum. The broad band centered at 234 nm is the most intense, and the sharp lines beyond 300 nm are present also. The broad band centered at 234 nm corresponds to the 4f→5d transition, specific for  $\text{Tb}^{3+}$  ions [15].

In Fig. 9 the typical emission spectrum of Tb (2.5%) doped  $\text{ZnAl}_2\text{O}_4$  phosphor is shown.

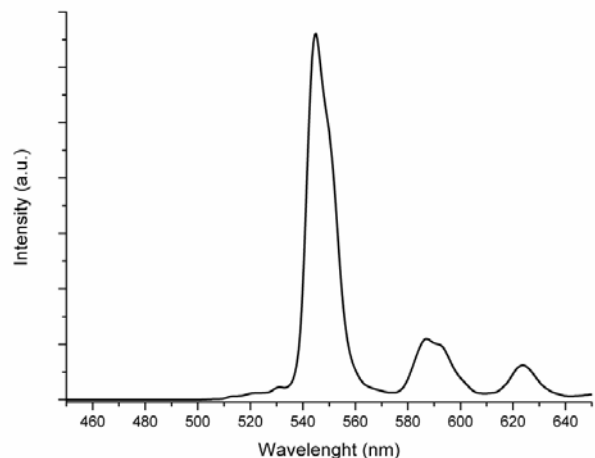


Fig. 9. Emission spectrum of Tb (2.5%) doped  $\text{ZnAl}_2\text{O}_4$  ( $\lambda_{ex}=234$  nm) prepared by coprecipitation method

Emission spectrum was monitored at  $\lambda_{ex} = 234$  nm in the range 450–650 nm at room temperature. The most intense emission peak is centered at 545 nm. This is a

specific peak for green emission. Also, low intensity peaks at 586 and 624 nm are observed. The observed peaks are attributed to  $^5D_4 \rightarrow ^7F_5$  (545 nm),  $^5D_4 \rightarrow ^7F_4$  (586 nm) and  $^5D_4 \rightarrow ^7F_3$  (624 nm), respectively [23,24]. All those transitions are specific transition of terbium ions. Also, we can observe that in the range 450-510 nm emission spectrum of Tb (2.5%) doped  $ZnAl_2O_4$  phosphor does not present any specific emission peak for the host lattice  $ZnAl_2O_4$ , which appears between 420 and 490nm as was reported in the other works [10,15].

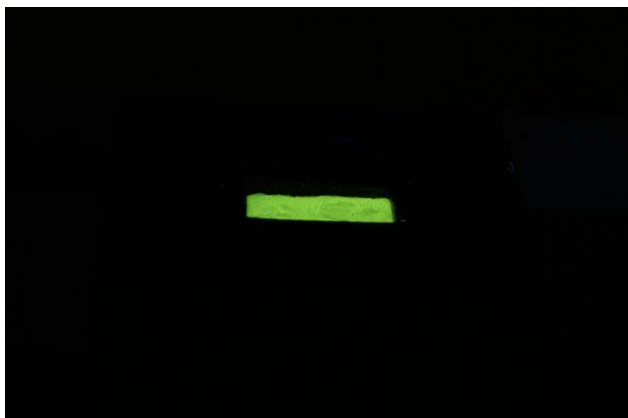


Fig. 10. Image of Tb (2.5%) doped  $ZnAl_2O_4$  prepared by coprecipitation method.

Furthermore, to view the colour of emission, before performed photoluminescence measurements we did analyzed the sample by using a ultraviolet (UV) lamp. The sample was irradiated with UV light for few seconds. As we can see in Fig. 10 the colour of emission is green which is in agreement with the most intensive peak of emission (545 nm) because this value is situated in the green region.

These results show that Tb (2.5%) doped  $ZnAl_2O_4$  phosphor prepared by coprecipitation method has high luminescent properties.

#### 4. Conclusions

In this paper we demonstrate that coprecipitation method may be used to achieve Tb (2.5%) doped  $ZnAl_2O_4$  phosphor. X-ray diffraction analysis demonstrated that a single spinel phase is present and no impurity trace was found and that the average crystallite size was found to be around 32 nm which means that we can achieve nanomaterials using coprecipitation method. Energy dispersive X-ray and FT-IR analysis confirmed the the Tb (2.5%) doped  $ZnAl_2O_4$  phosphor was pure and no impurity trace was found.

The obtained results indicate that Tb (2.5%) doped  $ZnAl_2O_4$  phosphor can be used as a source for new photoelectronic devices, because we achieved an increment of the band gap value of Tb (2.5%) doped  $ZnAl_2O_4$  phosphor. Moreover, photoluminescence measurements showed high luminescence properties of the

Tb (2.5%) doped  $ZnAl_2O_4$  phosphor obtained by coprecipitation method. The emission spectrum of Tb (2.5%) doped  $ZnAl_2O_4$  phosphor does not present any specific emission peak for the host lattice  $ZnAl_2O_4$  like was reported in other work. The most intense emission was the green emission which corresponds to the  $^5D_4 \rightarrow ^7F_5$  transition. In the future work, we propose to increase the optical properties of Tb doped  $ZnAl_2O_4$  phosphor by increasing the concentration of  $Tb^{3+}$  ions.

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