



Preparation and Characterization of $Y_3Al_5O_{12}:Cr^{3+}$ Nanophosphor by Electrochemical Technique

M. Hosseini^{a*}, H. Goldooz^b, A. Badi^b, A. Kazemzadeh^a

^a Department of Semiconductors, Materials and Energy Research Center (MERC), Meshkin Dasht, Alborz, Iran

^b School of Chemistry, College of Science, University of Tehran, Tehran, Iran

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ABSTRACT

$Y_3Al_5O_{12}:Cr^{3+}$ nanophosphor was synthesized by cathodic electrodeposition method. During the preparation procedure, hydroxide precursors were deposited on the surface of cathode via electrochemical reaction and then the final product was achieved by heat treatment of obtained powder at 1100 °C for 4 h. The structure and properties of the obtained product were investigated by various analysis methods such as X-Ray Diffraction (XRD), Fourier Transform InfraRed (FTIR) Spectroscopy, Photoluminescence Spectroscopy (PL), Scanning Electron Microscopy (SEM) and N_2 adsorption-desorption analysis. The XRD patterns of the synthesized YAG: Cr product, were in good match with the pure $Y_3Al_5O_{12}$ phase and the absence of any other impurities indicates the transformation of Cr^{3+} ions into the host matrix (YAG). In the emission spectrum of prepared material, a broad emission containing four pronounced bands at 685, 695, 710 and 725 nm was observed that indicates the presence of Cr^{3+} ions in the final product and further confirmed the formation of desired oxide product (YAG: Cr). The results of our studies showed that cathodic electrodeposition is a practical and highly efficient method for preparation of $Y_3Al_5O_{12}:Cr^{3+}$ nanophosphor compound.

1. INTRODUCTION

A phosphor material can absorb the electromagnetic radiation from Light Emitting Diodes (LED) and transform it into visible light. The emitted light can be tuned to form a broad (for lighting) or narrow (for solid state lasers) emission spectrum by engineering the phosphor layer structure, morphology and composition. Rare-earth or metal ions activated Yttrium Aluminum Garnets (YAG phosphors) are important crystal materials due to their good chemical, physical, creep resistance and optical properties, used in solid state lasers, Light-Emitting Diodes (LEDs) and so on [1-6]. For example, the optical properties of YAG pure phase doped with transition metal ions (Cr^{4+} , V^{3+} , Cr^{3+} and Co^{2+}) and lanthanide ions (Ce^{3+} , Eu^{3+} , Sm^{3+} and Tb^{3+}) for application as phosphor materials have been studied in many papers [7-13]. Typically, solid state reactions of oxide materials at high temperature (above 1500 °C) are carried out for synthesis of YAG phosphors and to

obtain nanoscale powder of compounds, mechanical milling is often used.

In recent years, several methods have been employed to prepare pure YAG and YAG phosphor such as sol-gel, co-precipitation, solvothermal, combustion and electrochemical method [13-17,21]. Among these methods, electrochemical methods (e.g. cathodic electrodeposition) are in general, simple, low cost, and suitable technique that can be used as an effective method for the synthesis of YAG nanophosphor due to its powerful control on the structure of the hydroxide deposit which can be easily tuned by controlling the base electrogeneration [18-20]. In this method, the hydroxide ions, electrogenerated on the surface of cathode by reduction of water molecules, are reacted with the cations in the bath solution, containing appropriate chloride salts in required stoichiometric amount, to form the final YAG product and as a consequence a hydroxide gel is deposited on the surface of steel substrate (cathode).

* Corresponding Author Email: m.hosseini@merc.ac.ir (M. Hosseini^a)

Heat-treatment of electrodeposited material results in obtaining desired YAG phosphor product.

In this paper, we report the preparation of YAG: Cr ($Y_3Al_5O_{12}:Cr^{3+}$) nanophosphors by cathodic electrodeposition from a bath solution containing suitable chloride salts, at 25 °C and using a current density of 1 mAcm⁻², followed by heat-treatment of obtained electrodeposited material. There are a few reports for preparation of YAG compounds through cathodic electrodeposition method [18-20] and we have previously employed this method to prepare some YAG samples [22] but as far as we know there is no report in the literature for synthesis of YAG: Cr³⁺ nanophosphor by means of cathodic electrodeposition.

2. EXPERIMENTAL PROCEDURES

2.1. Chemicals

Aluminum chloride anhydrous (AlCl₃) Chromium (III) nitrate nonahydrate (Cr (NO₃)₃ · 9H₂O) as well as Yttrium(III) chloride hexahydrate (YCl₃ · 6H₂O) (Aldrich), and ethanol 96 % (Merck).

2.2. Synthesis procedure

An electrochemical cell, containing a cathodic steel substrate placed between two parallel graphite anodes, was used to perform cathodic electrodeposition. The required amount of metal salts for preparation of YAG: Cr were dissolved in a 1:3 water-ethanol mixture and served as electrolyte solution in the cell's bath. The steel substrate was electropolished prior to each deposition. [18-20].

A constant current density of 1 mAcm⁻² at 25 °C for 2 h was used to perform deposition experiments. Then, the formed gel-like material on the cathodic steel electrode was scraped and air dried at room temperature for 5 h. At the end, the dried powder of component was heat treated at 1100 °C in air for 4 h in order to conversion of hydroxide precursor into the final oxide product.

2.3. Characterization

A Phillips PW-1800 diffractometer (equipped with a Cu K α radiation source) was employed to evaluate the crystal structure with ranging from 10 to 70 (scanning rate: 5 degrees per minutes). The FT-IR spectra of the YAG and YAG: Cr materials were analyzed on a RAYLEIGH WQF- 510A apparatus. Fluorescence spectra were recorded on Agilent G980A instrument. The surface morphology of the prepared YAG powder was studied using a scanning electron microscope

(TESCAN VEGA3 Model). The specific surface area and pore size distribution of the sample was measured via N₂ adsorption–desorption analysis at 77 K performed by a BELSORP Mini II.

3. RESULTS AND DISCUSSION

3.1. XRD and FT-IR analysis

The XRD patterns of the YAG and Cr³⁺ doped YAG synthesized via the cathodic electrodeposition method at 1100 °C are depicted in Fig.1a-b [18]. All diffraction peaks correspond to the pure Y₃Al₅O₁₂ phase (JCPDS No.082-0575) and no other impurities were observed for YAG: Cr³⁺ (Fig. 1b), indicating that Cr³⁺ ions have been transformed into YAG host framework and the original structure of YAG has remained intact [7-8, 18-20]. The lattice parameter of YAG: Cr is a bit larger than the standard value of cubic YAG, because of a small lattice distortion resulted from the slightly larger radius of Cr³⁺ ions in comparison with Al³⁺ ions [19]. The average sizes of YAG and YAG: Cr particles were determined by means of Scherrer equation [20]. It was found that average grain size of YAG and YAG: Cr nanopowders were around 48 nm and 57 nm respectively.

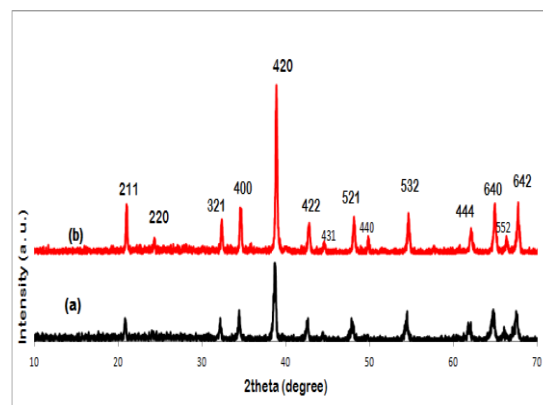


Figure 1. XRD patterns of (a) YAG and (b) YAG:Cr samples

The FTIR spectra of the YAG and YAG: Cr powders are shown in Fig. 2. The characteristic peaks at 722 and 790 cm⁻¹ correspond to the stretching modes of the AlO₆ octahedral in the YAG cubic structure. characteristic peaks at 521, 688 and 570 cm⁻¹ are attributed to the stretching modes of AlO₄ tetrahedral. The bands located below 900 cm⁻¹ are ascribed to M-O vibrations [18-20].

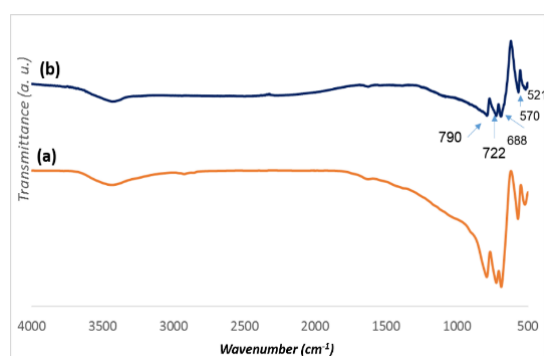


Figure 2. FTIR spectra of (a) YAG and (b) YAG: Cr samples

3.2. Photoluminescence analysis

The emission spectrum of YAG: Cr³⁺ nanophosphor prepared by cathodic electrodeposition method is shown in Fig.3. The spectrum was produced via spin allowed $^4A_2 \rightarrow ^4T_1$ and $^4A_2 \rightarrow ^4T_2$ transition of Cr³⁺ ions with the excitation wavelength at 617nm. Four pronounced bands at 685, 695, 710 and 725 nm were observed in the emission spectrum. The observed bands in the emission spectrum are in good correspondence with the reported results in the literature for YAG: Cr³⁺ nanophosphors that are synthesized via other methods [8]. The line at 695 is result of the Cr³⁺ zero phonon $^2E \rightarrow ^4A_2$ transition, while its associated stokes phonon side bands are near 710 and 725 nm and anti-stokes phonon side band was observed at 685 nm [7-8].

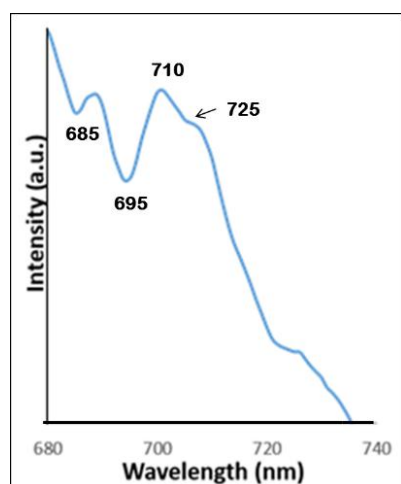


Figure 3. Photoluminescence emission spectrum of YAG: Cr nanophosphor sample

3.3. Surface morphology and EDX analysis

The morphology of the synthesized YAG: Cr nanophosphor was characterized by SEM (Fig. 4a). According to the SEM image, the spherically shaped nanoparticles can be observed in the porous background.

While some particles are agglomerated as clusters but individual particles of about 100 nm are clearly visible. The representative EDX pattern of YAG: Cr nanophosphor is depicted in Fig. 4b. The existence of Al, Y, O and Cr peaks confirms formation of the synthesized YAG: Cr³⁺ component.

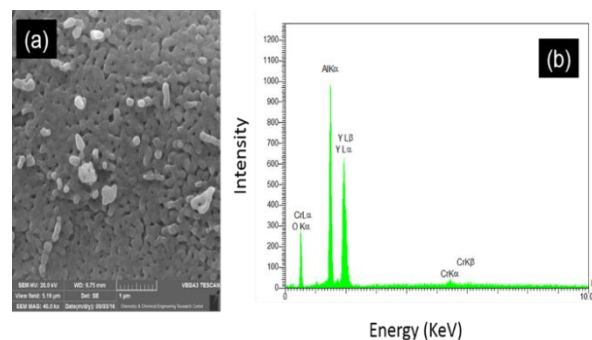


Figure 4. (a) SEM image and (b) EDX spectrum of the synthesized YAG: Cr nanophosphor component

3.4. N₂ adsorption-desorption analysis

The Brunauer, Emmete and Teller (BET) method was used to calculate the SSA of YAG: Cr nanophosphor. The PSD and N₂ isotherm are shown in Fig. 5. The attained isotherm could be classified as the type-III isotherm and the H₂ hysteresis loop based on the IUPAC classification which is characteristic for mesopore structure.

The pore diameter (BJH method) and the surface area of YAG: Cr nanophosphor was determined as 44 nm and 47 m² g⁻¹, respectively [24-25] that are in good agreement with the reported amounts for YAG nanophosphors synthesized via other methods [25].

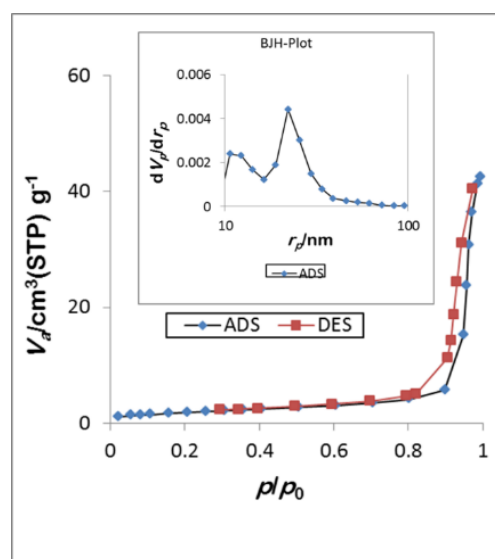


Figure 5. N₂ isotherm of the synthesized YAG: Cr nanophosphor sample (inset: PSD curve of YAG: Cr sample)

4. CONCLUSION

The cathodic electrodeposition method was successfully used to synthesis YAG: Cr nanophosphor and the prepared compound were characterized by various analytical methods. The XRD pattern confirms the incorporation of the Cr³⁺ ions into the YAG framework. The SEM and EDAX analyses show that the prepared material contains spherically shaped nanophosphor particles which are mainly composed of Y, Al, O and Cr elements. Some particles are also observed to be agglomerated as clusters. The PL spectrum confirmed the presence of Cr³⁺ ions in YAG nanomaterial and the N₂ adsorption-desorption analysis revealed the porous structure of YAG: Cr³⁺ with relatively narrow pore size distribution.

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