

Synthesis and Photoluminescence study of Gd³⁺ doped YP₃O₉ phosphor prepared by Citric sol-gel method

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ABSTRACT

Gd³⁺ doped YP₃O₉ phosphor was synthesized by Citric sol-gel method. The phosphor was characterized by X-ray diffraction (XRD), Photoluminescence (PL). The Phase purity and crystallinity of phosphor is confirmed by X-ray diffraction (XRD) analysis while surface morphology studied by scanning electron microscopy (SEM). The photoluminescence properties of the Y_{0.99}P₃O₉:0.01Gd³⁺ sample was investigated by excitation and emission spectra. The PL excitation spectra of Y_{0.99}P₃O₉:0.01Gd³⁺ phosphor exhibits broad spectra having high intense peak at 275 nm. Under UV excitation (275 nm), Y_{0.99}P₃O₉:0.01Gd³⁺ shows emission peak at 312 nm. The obtained results show that the prepared phosphor is suitable for Phototherapy application.

Keyword : XRD, Photoluminescence, SEM, UV excitation

I. INTRODUCTION

The use of ultraviolet radiation for treatment of various skin diseases is well recognized for long time by the mean of phototherapy. It was an effective treatment for many skin disorders, such as Psoriasis [1], Vitiligo [2], Ofujis disease [3], Erythropoetic Protoporphyrria [4], Pityriasis rosea [5], Uremic pruitus [6] Lichen Sclerosus et Atrophicus [7], Morphea [8], Scleroderma [9], Cutaneous T-cell lymphoma, Lupus Erythematosus [10]. In that method we use artificial ultraviolet radiation ranging from 220 nm to 400 nm delivered by fluorescent lamps to cure skin diseases.

According to the biological and optical properties UV radiation was divided into three categories i.e. UV-C from 220 to 280 nm; UV-B from 280 to 320 nm and UV-A from 320 to 400 nm. UV-A is further divided into two categories UVA1 (340–400 nm) and UV-A2 (320–340 nm).

The inorganic compounds with general formula Ln(PO₃)₃ (Ln = La to Lu and Y) belong to the broader class of phosphate materials which have been extensively investigated because of a suitable absorption in the VUV region, a wide band gap together with a high chemical stability and the relative simplicity of powder synthesis [11–15].

II. EXPERIMENTAL

These materials are potential good phosphors, scintillators and detectors for ionizing radiation. Serra and Giesbrecht were the first to describe three rare-earth salts of general formula $TP_3O_9 \cdot 3H_2O$ with [T = La, Ce and Nd] [16]. Later on, Birke and Kempe described chemical preparations and thermal behavior for $PrP_3O_9 \cdot 4H_2O$, $LaP_3O_9 \cdot 4H_2O$ and $ErP_3O_9 \cdot 4H_2O$ [17-19]. Jouini *et. al.*, studied the scintillator properties of $Pr(PO_3)_3$ phosphor [20]. The first investigation of Nd^{3+} luminescence in $La(PO_3)_3$ was reported by Jouini and co-authors in the framework of laser materials research [21]. The luminescence properties of Eu^{3+} and Tb^{3+} in $La(PO_3)_3$ and $Y(PO_3)_3$ as potential phosphors under VUV excitation have been discussed [22, 23]. Much attention has been paid to the energy migration and transfer processes in Ln-based phosphate compounds [24-26].

Practically, the rare-earth polyphosphates $Ln(PO_3)_3$ can adopt two different crystal structures, depending on the ionic radius of the RE ions. The polyphosphates with large RE^{3+} ions (La-Eu) have an orthorhombic structure with C2221 space group, while those with small RE^{3+} ions (Gd-Lu, Y) have a monoclinic structure with P21/c space group [27, 28]. X. Zhang *et al.*, reported Eu^{3+} doped $Y(PO_3)_3$ phosphor successfully prepared by a conventional solid-state reaction and it shows intense orange-red emission under near-UV excitation. The result also reflects that the phase transformation from monoclinic to orthorhombic when Y^{3+} is totally replaced by Eu^{3+} [29].

In the present work, phosphor YP_3O_9 doped with Gd^{3+} was synthesized via a Citric sol-gel method. The synthesized material was characterized using the powder X-Ray Diffraction. The optical properties of Gd^{3+} in YP_3O_9 was studied in detail using a fluorescence spectrometer.

The powder sample $YP_3O_9:Gd^{3+}$ was synthesized for the first time by the Citric acid sol-gel method. The Stoichiometric amounts of high purity precursors Yttrium Oxide (Y_2O_3)(99.99%AR), Ammonia dihydrogen orthophosphate ($NH_4H_2PO_4$), Citric acid, Gadolinium Oxide (99.90%, AR), Ethylene glycol and Acetic acid were taken for the preparation of phosphor.

The starting chemicals Y_2O_3 (99.99%,AR) and Gd_2O_3 (99.99%,AR) was taken in a china clay basin. A small quantity of double distilled water was added and paste was formed. 10 ml of HNO_3 was added drop by drop and mixture was heated slowly under observation to $80^\circ C$ till the paste dissolved completely. The solution was further heated till the excess of acid was boiled off. Afterward small amount of double distilled water was again added and slowly evaporated to dryness. After that solution of citric acid as well as $NH_4H_2PO_4$ were added drop by drop. Mix it well and place it on hot plate at $70^\circ C$ with continuous stirring for 15 min till the precursors dissolved completely leading to a colorless solution. During stirring add 0.5ml of ethylene glycol & 2-3 drops of acetic acid.

On further heating to $100^\circ C$, bubbles were evolved from the bottom of the china clay basin; solution turned pale yellow at $170^\circ C$, turned red & start boiling. The solution was then allowed to cool. Pale yellow gel was formed on cooling. The dry gel was then slowly heated which burnt slowly into dull red flame with the evolution of thin sized and light weighted carbon flakes at $230^\circ C$. The residue was pyrolysis at $\sim 400^\circ C$ into black charcoal / resin which burnt at $\sim 700^\circ C$ and lastly the powder was sintered at $950^\circ C$ for 1 hr to obtained final crystalline powder of $YP_3O_9: Gd^{3+}$. The Flow chart of synthesis method is shown in Fig.1.

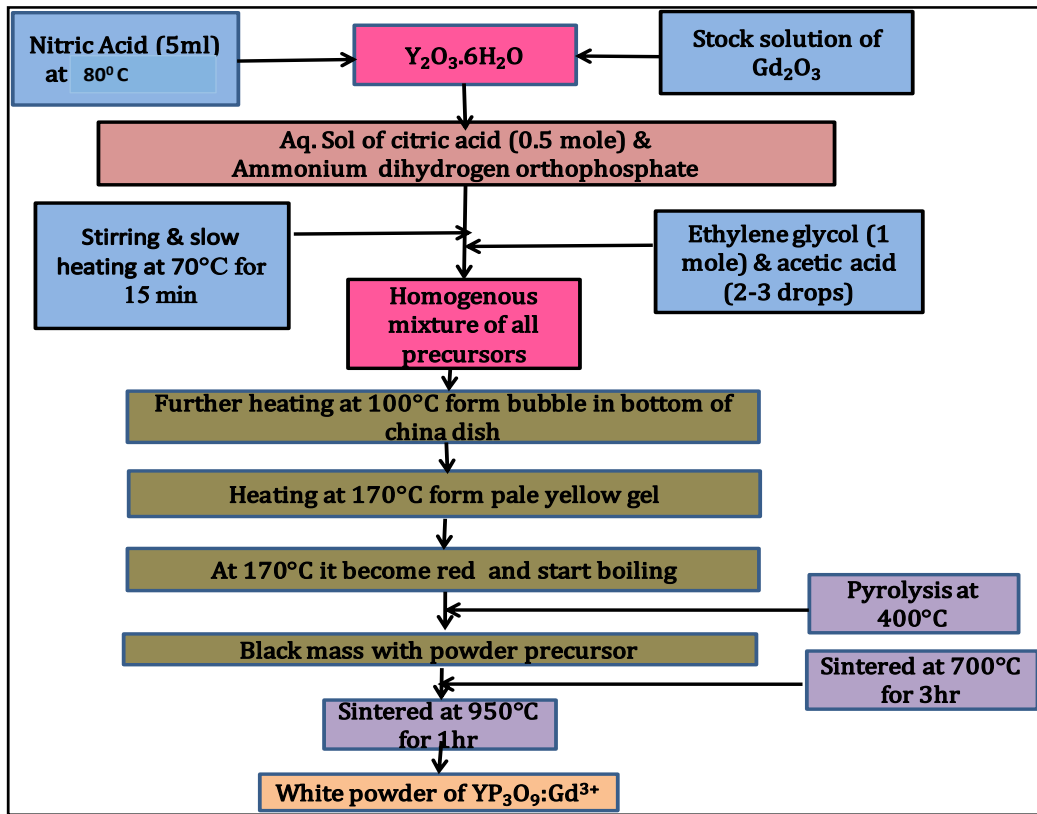


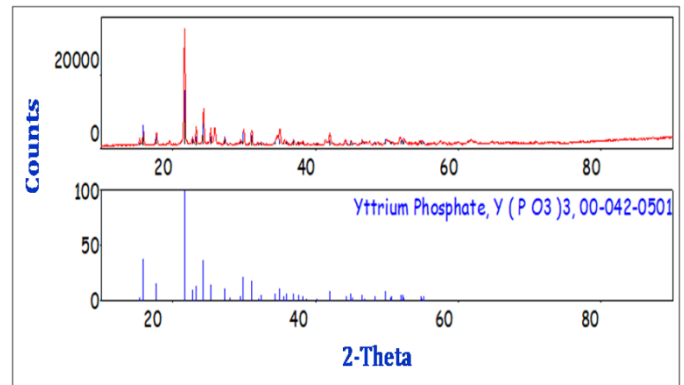
Fig.1. Flow chart citric sol-gel method

III. RESULT AND DISCUSSION

1.1. XRD Analysis

The phase purity and crystal structure of $Y_2P_3O_{13}$ phosphor was confirmed by X-ray diffraction patterns (as shown in Fig.2.). The X-ray pattern of sample indicated a pure phase of the standard $Y_2P_3O_{13}$ and all the peaks were in good agreement with the (ICDD File 00-042-0501). There were no additional peaks found in X-ray pattern.

Also, the XRD shows that the formed material was completely crystalline and was in single phase with Monoclinic structure having lattice parameter with values $a = 14.1520$, $b = 20.1490$, $c = 10.0610$ also $\alpha = 90.00$, $\beta = 127.900$, $\gamma = 90.00$ with volume = 2263.788 & $Z = 1$.

Fig.2. X-ray diffraction of $Y_2P_3O_{13}$ phosphor

1.2. Surface Morphology

It is well known that the morphology is one of the aspects that required for the more efficient luminescence of phosphor materials. Fig.3. represented the SEM image of the host $Y_{0.99}P_3O_{13}:0.01Gd^{3+}$. The phosphor was synthesized by citric sol-gel method by following step by step sintering temperature. The phosphor morphology shows irregular grain with an average size of about $2\mu m$.

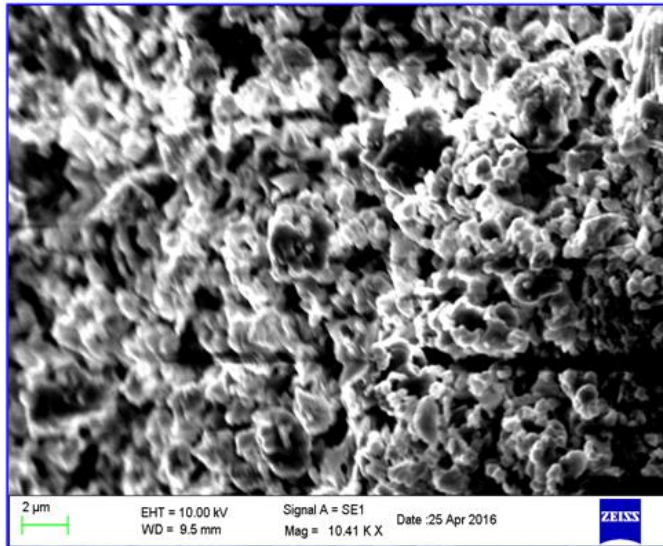


Fig.3. SEM image of $Y_{0.99}P_3O_9:0.01Gd^{3+}$ phosphor

IV. CONCLUSION

The $Y_{0.99}P_3O_9:0.01Gd^{3+}$ powder phosphor was successfully synthesized via the Citric Sol-gel method and their phase purity was confirmed by X-ray diffraction analyses. The SEM images show agglomeration particle because of high sintering temperature. The photoluminescence spectra illustrate that under the excitation of 275 nm phosphor emits sharp and intense emission in Narrowband UVB region (i.e. 312 nm). The obtained result shows that the prepared phosphor i.e. $Y_{0.99}P_3O_9:0.01Gd^{3+}$ could be potential candidate for Phototherapy Application.

1.3. Photoluminescence Analysis

Fig.4. shows the combined emission & excitation spectra of $Y_{0.99}P_3O_9:0.01Gd^{3+}$ phosphor synthesized by Citric sol gel method. The phosphor shows excitation spectra at 275nm having corresponding transition $^8S_{7/2} \rightarrow ^6G_1$. Under the excitation of 275nm the phosphor exhibits emission at 312 nm having corresponding transitions $^6P_{7/2} \rightarrow ^8S_{7/2}$. The emission spectra consist of a weak line at 306 nm followed by a strong one at 312 nm, which correspond to the $^6P_{5/2} \rightarrow ^8S_5$.

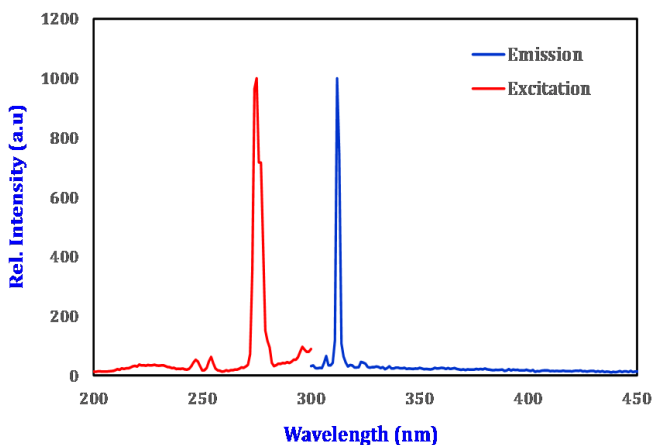


Fig.4. Combined Excitation and Emission spectra of $Y_{0.99}P_3O_9:0.01Gd^{3+}$

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VI. REFERENCES

- [1]. H. Honigsmann, W. Brenner, W. Rauschmeier, Photochemotherapy for cutaneous T cell lymphoma. A follow-up study. *Am. Acad. Dermatol.* 10, 238 (1984)
- [2]. L. Scherschun, J.J. Kim, W.H. Lim, Narrow band ultraviolet B is a useful and well tolerated treatment for vitiligo. *J. Am. Acad. Dermatol.* 44, 999 (2001)
- [3]. T. Ota, Y. Hata, A. Tanikawa, M. Amagai, M. Tanaka, T. Nishikawa, Eosinophilic pustular folliculitis (Ofuji's disease): indomethacin as a first choice of treatment. *Clin. Exp. Dermatol.* 26(2), 179 (2001)

- [4]. L.J. Warren, S. George, Erythropoietic protoporphyria treated with narrow-band (TL-01) UVB phototherapy. *J. Dermatol.* 39,179 (1998)
- [5]. V. Leenutaphng, S. Jiamton. UVB phototherapy for pityriasis rosea: a bilateral comparison study. *J. Am. Acad. Dermatol.* 33(6), 996 (1995)
- [6]. J.D. Blachley, D.M. Blankenship, A. Menter, T.F. Parker, J.P. Knochelam, Uremic pruritus: skin divalent ion content and response to ultraviolet phototherapy. *Am. J. Kidney Dis.* 5(5), 237 (1985)
- [7]. A. Kreuler, T. Jansen, M. Stucker, M. Herde, K. Hoffmann, P. Altmeyer, G. Vonkobyletzki, Low-dose ultraviolet-A1 phototherapy for lichen sclerosus et atrophicus. *Clin. Exp. Dermatol.* 26,30 (2001)
- [8]. J.L.M. Hawk, *Sunbeds. Radiat. Prot. Dosim.* 91, 143 (2000)
- [9]. A. Morita, K. Kobayashi, I. Isomura, T. Tsuji, J. Krutmann, Ultraviolet A1 (340–400 nm) phototherapy for Scleroderma in systemic sclerosis. *J. Am. Acad. Dermatol.* 43, 670 (2000)
- [10]. T.P. Millard, J.L.M. Hawk, Ultraviolet therapy in lupus. *Lupus* 10,185 (2001)
- [11]. S. Hachani, B. Moine, A. El-akrmi, M. Ferid, *J. Lumin.* 130 (2010) 1774.
- [12]. Yu. Wang, D. Wang, *J. Sol. State Chem.* 180 (2007) 3450.
- [13]. L.N. Zorina, Zh.A. Ezhova, I.V. Tananaev, N.P. Soshchin, V.P. Orlovskii, A.V. Lavrov, *Izv. AN USSR Inorg. Mater.* 20 (1984) 2014.
- [14]. Riadh Ternanea, Mokhtar Ferid, Gerard Panczer, Malika Trabelsi-Ayadi, Georges Boulon, *Opt. Mater.* 27 (2005) 1832.
- [15]. S. Briche, D. Zambon, D. Boyer, G. Chadeyron, R. Mahiou, *Opt. Mater.* 28 (2006) 615.
- [16]. O.A. Serra and E. Giesbrecht, *J. Inorg. Nucl. Chem.*, 30 (1968) 793.
- [17]. P. Birke and G. Kempe, *Z Chem.*, 13 (1973) 151.
- [18]. P. Birke and G. Kempe, *Z Chem.*, 13 (1973) 65.
- [19]. P. Birke and G. Kempe, *Z Chem.*, 13 (1973) 110.
- [20]. A. Jouini, J.C. Gâcon, M. Ferid, M. Trabelsi-Ayadi, *Opt. Mater.* 24 (2003) 175.
- [21]. A. Jouini, J.C. Gâcona, A. Brenier, M. Ferid, M. Trabelsi-Ayadi, *J. Lumin.* 99 (2002) 365.
- [22]. D. Wang, Y. Wang, Y. Shi, *J. Lumin.* 131 (2011) 1154.
- [23]. R. Ternanea, M. Ferid, G. Panczer, M. Trabelsi-Ayadi, G. Boulon, *Opt. Mater.* 27 (2005) 1832.
- [24]. H. S. Kiliaan, F. P. van Herwijnen, G. Blasse, *J. Solid State Chem.* 74 (1988) 39.
- [25]. M. Buijs, G. Blasse, *J. Lumin.* 39 (1988) 323.
- [26]. S. Hachani, B. Moine, A. El-akrmi, M. Ferid, *J. Lumin.* 130 (2010) 1774.
- [27]. H.Y.P. Hong, The crystal structure of ytterbium metaphosphate, YbP_3O_9 , *Acta Cryst. B* 30 (1974) 1857e1861.
- [28]. J. Matuszewski, J. Kropiwnicka, T. Znamierowska, The crystal structure of lanthanum metaphosphate LaP_3O_9 , *J. Solid State Chem.* 75 (1988) 285e290.
- [29]. Xinguo Zhang, Peican Chen, Zizhou Wang, Liya Zhou, Fangxiang Zhou, *Solid State Sciences* 58 (2016) 80-85