SYNTHESIS, PHOTOLUMINESCENCE AND THERMOLUMINESCENCE OF $YAlO_3:Eu^{3+}$ PHOSPHOR

I.H.Dhadade[1*], Vibha Chopra[2], S.J. Dhoble[3*] and S.V. Moharil[3]
[1]Nabira Mahavidyalaya , Katol, Dist, Nagpur,India
[2]P.G. Department of Physics & Electronics, DAV College, Amritsar, Punjab, India
[3]Department of Physics, R.T.M. Nagpur University, Nagpur, India

ABSTRACT

Yttrium orthoaluminate activated by Eu^{3+} ($YAlO_3:Eu^{3+}$) has been synthesized by using modified combustion method and its luminescent properties were investigated. The modified combustion method route consists of the redox reactions between the respective metal nitrates and mixed fuel (glycine + Urea) in a preheated furnace at 500 ^{0}C. Formation of the compound was confirmed by XRD technique and the FullProf Suite program was employed to perform the Rietvield refinement analysis to study the structure of $YAlO_3:Eu^{3+}$ phosphor. The incorporation of Eu^{3+} activator in this phosphor was studied by Photoluminescence investigation. It was found that under UV excitation of 250 nm wavelength, the phosphors shows reddish orange color. The main peak in the emission spectra was attributed to the $^5D_0$–$^7F_2$ at 615 nm suggesting the possible use of this phosphor in fluorescent lamp. Thermoluminescence response of synthesized phosphor was studied using γ –irradiation in the dose range 1 kGy-8 kGy at a heating rate of 5 $^0Cs^{-1}$ at room temperature. The linear response up to 2 kGy suggested the possible use of the phosphor in dosimetry applications.

Keywords : combustion synthesis; mixed fuel urea; glycine

1. Introduction

Yttrium orthoaluminate($YAlO_3$) phosphors doped with rare earth ions are attractive due to their significant applications in optoelectronic devices from many years [1,2]. $YAlO_3:Eu^{3+}$ has been reported for successful storage and retrieval of 248-bit temporal optical data by accumulated photon echoes, owing to the long storage time of this material [3]. $YAlO_3$ phosphors co-activated with Eu^{3+} and Ce^{3+} are very important phosphors for flat panel display application devices, such as field emission displays and plasma display panels [4]. $YAlO_3$ is an excellent host lattice for the trivalent lanthanides, which can very easily substitute the trivalent yttrium (Y^{3+}) by Ce^{3+} [5] and Eu^{3+} [6]. The emission spectra of Eu^{3+} ions in $YAlO_3$ arise from $^5D\rightarrow{}^7F$ transitions [7]. YAP doped with rare earth or transition metals also demonstrate very attractive properties [8] being promising materials as host matrix for laser [9], scintillators [10], thermoluminescent detector [11, 12], holographic recording medium [13] and pigments [14]. Moreover, the luminescence studies of these compounds are of great interest because of their high effective atomic number (Zeff= 31.4), low cost, easy to prepare and easy handling process. Since $YAlO_3$ is an attractive material for having excellent luminescence properties so work is in progress by the research community to explore this material [15-21].

From the literature review, it has been observed that several soft chemical routes have been explored for synthesis of $YAlO_3$ but most of these methods are complex and of high cost for the industrialization. In the present method, modified combustion method (using metal nitrates as the base materials) has been used for the first time to synthesize $YAlO_3:Eu^{3+}$ phosphor and then their photoluminescence and thermoluminescence properties have been studied.

2. Experimental

2.1 Synthesis

Instead of the conventional solution combustion synthesis, the modified procedure has been used which led to the formation of desired compounds in a single step. Combustion synthesis is an energy and time saving process, which is easy, safe and can be employed to produce homogeneous, high-purity, crystalline oxides. The characteristic like crystallite size, surface area, extent and nature of agglomeration of the products are primarily governed by flame temperature generated during combustion, which itself is dependent on nature of the fuel and fuel-to-oxidant ratio [22, 23]. Presently, reagent grade (Indian Rare Earths, Ltd.) rare earth oxides/carbonates were converted to the corresponding nitrates by dissolving in nitric acid. The nitrates were dried by prolonged, gentle warming. Stoichiometric amounts of hydrated nitrates of yttrium, aluminum, and Europium were thoroughly mixed with urea/glycine. The nitrates to fuel ratios were calculated by the method described earlier [24, 25]. Due to the presence of large crystallization water in aluminum nitrate, a thick paste was formed. Eu^{3+} ions doped orthoaluminate with general formula $(Y_{1-x}Eu_x)AlO_3$ (x = 0.005 , 0.01 , 0.02 , 0.03 , 0.04) was prepared by rapidly heating an aqueous concentrated paste containing calculated amount of metal nitrates and Urea + glycine in a preheated furnace maintained at 500 ^{0}C. The material undergoes rapid dehydration and foaming followed by decomposition, generating combustible gases. These volatile combustible gases ignite and burn with a flame yielding voluminous solid. The prepared sample was immediately removed from the furnace and was collected. The solid obtained was then milled to fine powders for further characterizations. In our experiments, when urea was used as a fuel, the combustion products were poorly crystallized. Yttrium nitrate does not have exothermic reaction with urea. Hence mixed (glycine + urea) fuel was tried since glycine has exothermic reaction with yttrium nitrate and urea with aluminum nitrate.

2.2 Characterization

X ray diffraction pattern of synthesized sample was recorded using Rigaku- Miniflex-II diffractometer for Phase identification. Photoluminescence was observed with a RF-5301 Spectrofluorophotometer in the range 220 nm – 700 nm using 1.5 nm spectral width. Synthesized $Y_{1-x}AlO_3$ (x = 0.005 mol of Eu^{3+}) samples were irradiated with gamma rays in the range (1 kGy – 8 kGy) using gamma chamber GC 900 and their thermoluminecence characteristics were studied on Nucleonix (TL 1009 I) TLD Reader.

3. Results and Discussion

3.1 X Ray Diffraction studies

The theoretical equation for the formation of $YAlO_3:Eu^{3+}$ phosphor by combustion from metal nitrate and fuel (Urea+ Glycine) at about 500 ^{0}C, may be written as:

$(1-x)Y(NO_3)_3 + xEu(NO_3)_3 + Al(NO_3)_3 +$ (Urea) +(glycine) $\rightarrow Y_1-xEu_xAlO_3$ (s) + gaseous products

YAP was successfully prepared by one step combustion with mixed (glycine + urea) fuel and its XRD pattern was recorded. The FullProf Suite program was employed to perform the Rietveld refinement analysis of the X-ray Diffraction pattern of $YAlO_3$:Eu phosphor [26]. The refined XRD patterns for $YAlO_3$:Eu phosphor is shown in Fig. 1.

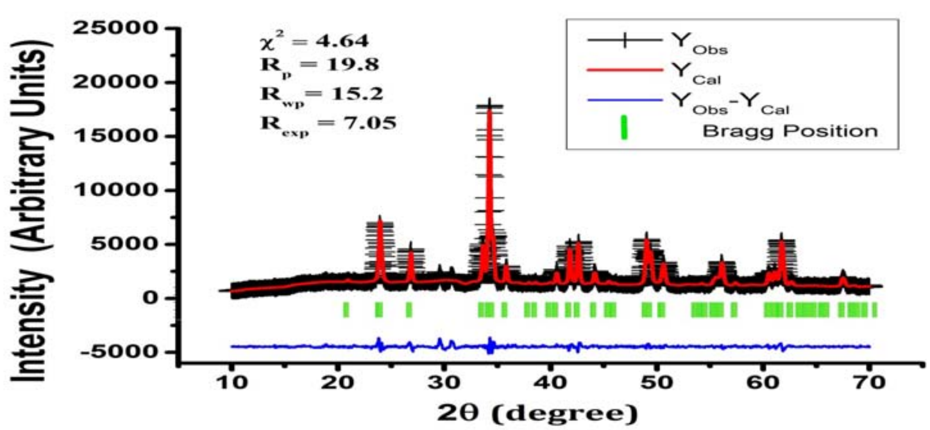

Fig. 1 Rietveld Refinement of X-ray diffraction data of $YAlO_3$:Eu phosphor.

Table 1 Refinement parameters derived from the Rietveld refinement of $YAlO_3$:Eu phosphor.

	$YAlO_3$
Crystal system	Orthorhombic
Space group	*Pnma* (Space group No. 62)
V	203.708 Å^3
Cell parameters	a = 5.1846 Å, b = 5.3268Å, c =7.3761Å, $\alpha = \beta = \gamma = 90^{o}$
R_{wp}	15.2
R_p	19.8
R_{exp}	7.05
χ^2	4.64

The refinement was performed using the Pseudo-Voigt peak profile function and liner interpolation of the background points. The structure crystallized into an orthorhombic crystal with space group *Pnma*. Table 1summarizes the refinement parameters derived from the Rietveld refinement of the XRD pattern of $YAlO_3$:Eu phosphor.

3.2 Photoluminescence Study

Photoluminescence spectra were studied and the PL Intensity of $YAlO_3:Eu^{3+}$ phosphor with varying concentration of Eu^{3+} was noticed that is shown in Fig. 2

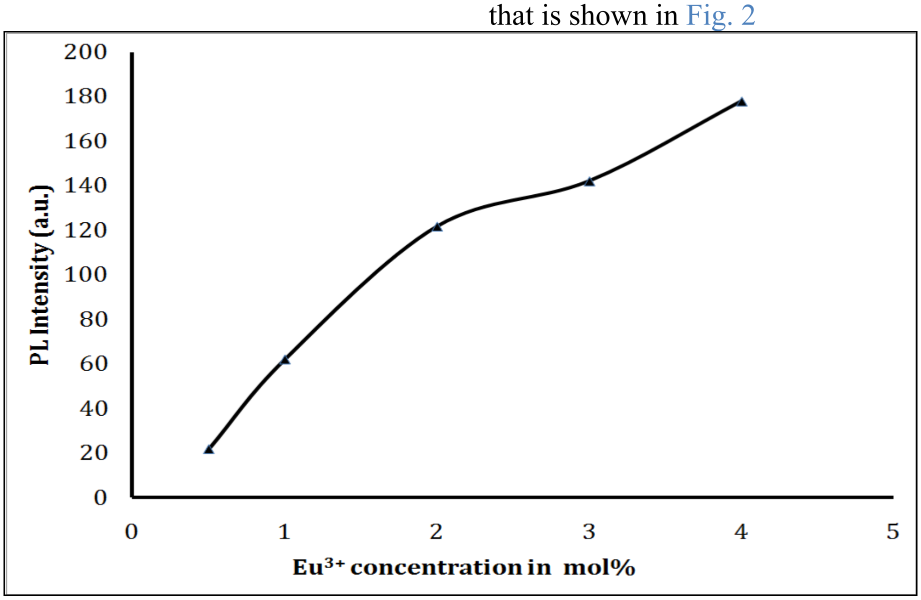

Fig. 2 PL Intensity for varying Eu^{3+} concentration in $YAlO_3:Eu^{3+}$ phosphor

It is observed that $YAlO_3$ shows maximum intensity for 4 mol% of Eu^{3+} concentration. So, the further studies of PL were taken for 4 mol% of Eu^{3+} concentration. The excitation and emission spectra of $YAlO_3:Eu^{3+}$ phosphors are shown in Fig. 3(a) and 3(b) respectively.

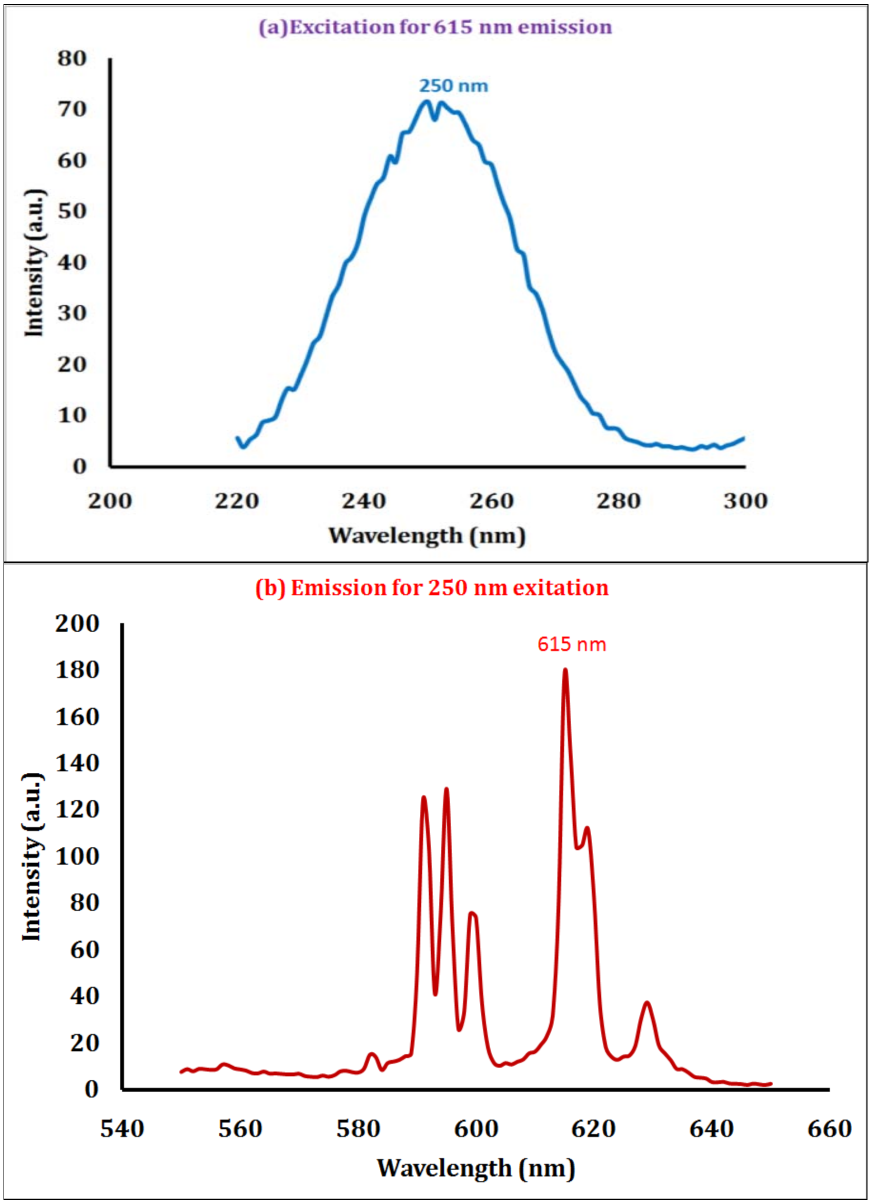

Fig. 3 Photoluminecence spectra (a) Excitation (b) Emission for $YAlO_3:Eu^{3+}$ phosphor

It is observed that under excitation of 250 nm, the strong emission peak of $YAlO_3:Eu^{3+}$ phosphor is due to forced dielectric dipole transition $^5D_0$-$^7F_2$ centered at 615 nm [7]. The emission spectra of this phosphor are composed of emission lines of Eu^{3+} due to magnetic dipole transition and electric dipole transition. In fact, the emission shows two triplets. These transitions are known to contribute color rendering and lumen output. So, these red phosphors can be exploited for fluorescent lamp to get better color rendering index and higher lumen output.

3.3 Thermoluminescence Study

Thermoluminescence of $YAlO_3:Eu^{3+}$ was studied and the TL Intensity of $YAlO_3:Eu^{3+}$ phosphor with varying concentration of Eu^{3+} was noticed that is shown in Fig. 4

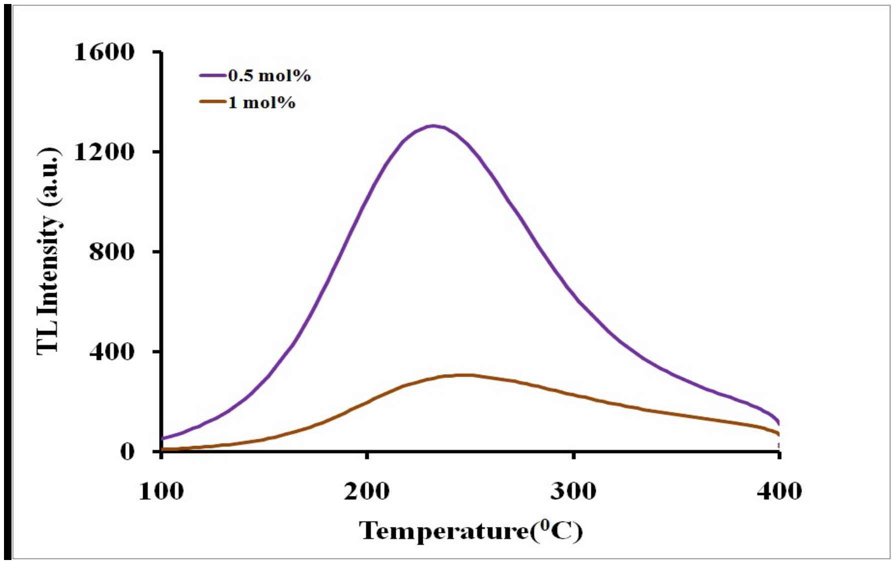

Fig. 4 TL Intensity for varying Eu^{3+} concentration in $YAlO_3:Eu^{3+}$ phosphor

It is revealed that $YAlO_3$ shows maximum TL intensity for 0.5 mol% of Eu^{3+} concentration. So, further, the TL glow curves at different gamma doses were taken for 0.5 mol% of Eu^{3+} concentration in $YAlO_3$ that are shown in Fig. 5.

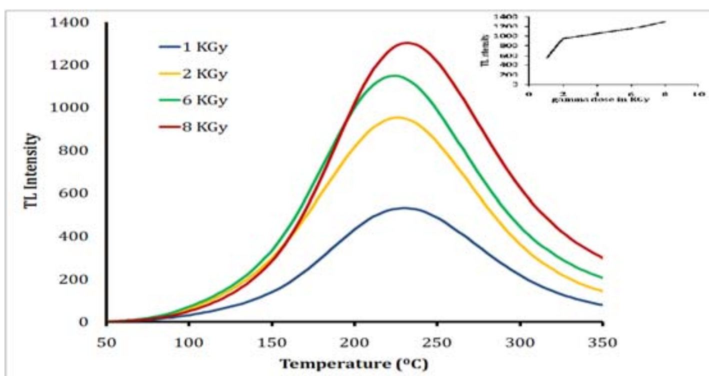

Fig.5: TL glow curves of $YAlO_3:Eu^{3+}$ (0.5%) exposed to gamma irradiation (1 kGy-8 kGy). (Inset: variation of TL intensity with gamma dose)

Gamma irradiation in the dose range 1–8 KGy was done at room temperature. TL of the sample was taken by heating the sample at a heating rate of $5^0C\ s^{-1}$. A single glow peak around 230 ^0C was observed indicating that there is possibly one kind of trapping site/luminescent center generated due to gamma irradiation.. The TL intensity of peak keeps on increasing with increase in dose. Since the low doses of gamma radiation are unable to create enough defect states to produce TL. On increasing the dose the total energy density will overcome the surface barrier to produce more defects states and enhance the TL intensity. So this is the reason for increase in intensity with dose [27] The inset of Fig. 6 shows the TL response curve which shows that response is linear up to 2 KGy then it becomes sublinear that can be explained by Track interaction model [28, 29].

4. Conclusion

$YAlO_3:Eu^{3+}$ powder phosphors have been synthesized using modified combustion method employing mixed (Urea + Glycine) as fuel for the first time. The process involves a low temperature self-propagating ignition route which is safe, simple and rapid for the production of fine and homogeneous powders. A single phase YAP was obtained and confirmed by XRD studies. Also, FullProf Suite program was employed to perform the Rietvield refinement analysis of the XRD pattern. The main peak in the emission spectra is assigned to the characteristic transitions of Eu^{3+} ($^5D_0$–$^7F_2$) displaying bright luminescent reddish orange color These phosphors can be exploited for fluorescent lamp to get better color rendering index and higher lumen output. Thermoluminescence study reveals appearance of single TL glow peak indicating that there is possibly one kind of trapping site/luminescent center generated due to gamma irradiation. Up to 2 kGy TL glow peak intensities show linear behavior with γ-dose. Therefore, $YAlO_3:Eu^3$ phosphor prepared by modified combustion method may be useful in high dose radiation dosimetry.

References

[1] S. Geller, E.A. Wood, Crystallographic studies of perovskite-like compounds. I. Rare earth orthoferrites and $YFeO_3$, $YCrO_3$, $YAlO_3$, Acta Crystallogr. 9 (1956) 563-568.

[2] T. Takeda, T. Miyata, F. Muramatsu, T. Tomiki, Fast decay UV phosphor-$YAlO_3$-Ce, J. Electrochem. Soc.127 (1980) 438-444.

[3] M. Mitsunaga, N. Uesugi, 248-Bit optical data storage in $Eu^{3+}:YAlO_3$ by accumulated photon echoes, Opt. Lett. 15 (3) (1990) 195-197.

[4] G.C. Kim, S.I. Mho, H.L. Park, Observation of energy transfer between Ce^{3+} and Eu^{3+} in $YAlO_3$: Ce, Eu, J. Mater. Sci. Lett. 14 (1995) 805-806.

[5] J.A. Mares, M. Nikl, C. Pedrini, B. Moine, K. Blezek, A study of fluorescence emission of Ce^{3+} ions in $YAlO_3$crystals by the influence of doping concentration and codoping with Nd^{3+} and Cr^{3+}, Mater. Chem.Phys. 32 (1992) 342-348.

[6] J. Garcia-Moreno, W.A. Sibley, C.A. Hunt, J.M. Spaeth, Optical properties of Eu^{2+}, Eu^{3+} and Mn^{2+} in cubic perovskite crystals, J Lumin. 42 (1988) 35-42.

[7] M. Mitsunaga, N. Uesugi, Linear and nonlinear spectroscopy of Eu^{3+} in crystals, J. Lumin. 48-49 (1991) 459-462.

[8] H.Bromberger, K.J Yang , D .Heinecke , T. Dekorsy, L.H Zheng, J.Xu, and G.J.Zhao, Comparative Investigations on Continuous Wave Operation of a Cut and b Cut Tm,Ho:$YAlO_3$ Lasers at Room Temperature, Opt. Express, 19 (2011) 06505.

[9] H .Gao and Y. Wang, Photoluminescence of Eu^{3+} Activated $YAlO_3$ under UV–VUV Excitation, Mater Res Bull. 42 (2007) 921.

[10] M. Nikl, A .Yoshikawa, A.Vedda and T. Fukuda, Development of Novel Scintillator Crystals, J Cryst Growth. 292 (2006) 416.

[11] Y. Zhydachevskii , A Suchocki., M.Berkowski, D. Sugak, P.Bilski and S.Warchol, Characterization of $YAlO_3:Mn^{2+}$ Thermoluminescent Detectors, Radiat Meas. 45 (2010) 516.

[12] Y. Zhydachevskii, , M Berkowski., S. Warchol, and A. Suchocki, , Dosimetric Properties of the 570 K Thermoluminescence Peak of $YAlO_3$:Mn Crystals, Radiat Meas. 46 (2011) 494.

[13]G.B Loutts, M .Warren, L.Taylor, R.R. Rakhimov, H.R Ries, G .Miller,
Manganese Doped Yttrium Orthoaluminate: A Potential Material for Holographic Recording and Data Storage, Phys. Rev. B. 57 (1998) 3706 .

[14] M. Shirpour, M Faghihi Sani, and A .Mirhabibi, Synthesis and Study of a New Class of Red Pigments Based on Perovskite $YAlO_3$ Structure, Ceram Ind. 33 (2007) 1427.

[15] P.Gnutek, C.Rudowicz, Extracting structural information from low symmetry crystal field parameters-case study: Er^{3+} and Nd^{3+} ions in $YAlO_3$, j. rare earths. 27 (2009) 619-623

[16] L.W.Golacki, N.V.Gaponenko, L.S.Khoroshko, A.M.Asharif, J.Misiewicz, A.Podhorodecki, Thermal Tb emission quenching in $YAlO_3$ matrix embedded in porous anodic alumina, Opt. mater. 37 (2014) 200-203

[17] Chunxiao Lu, Yang Chen, Yun Li, Chunhong Ma, Yuwei Guo, Ying Li, Jun Wang, The effect of different co-catalysts (CuO, MoS_2 and Pt) on hydrogen production of Er^{3+}:$YAlO_3/NaTaO_3$ by visible-light-induced methanol splitting, Energy. 93 (2015) 749-757

[18] Ya Zhydachevskii, A.Morgun, S.Dubinski, YanYu, M.Glowacki, S.Ubizskii, V.Chumak, M.Berkowski, A.Suchocki, Energy response of the TL detectors based on $YAlO_3$:Mn crystals, Rad. Measur. 90 (2016) 262-264.

[19] Huma Nazli Baig, Jagjeet Kaur Saluja, D. HaranathInvestigation of luminescence properties of Dy3+ doped YAlO3 phosphors synthesized through solid state method, Optik – Inter. J.Light Electron Optics. 127 (2016) 9178-9195

[20] Yuhei Shimizu, Kazushige Ueda, Yoshiyuki Inaguma, Photoluminescence excitation spectra of lanthanide doped YAlO3 in vacuum ultraviolet region, Opt. Mater. 66 (2017) 327-331

[21] M. Malinowski, M. Kaczkan, S. Turczyński, Energy transfer and upconversion of Sm3+ ions in YAlO3. Opt. Mater. 63 (2017) 128-133.

[22] J. Huang, H. Zhuang, W.L. Li, Synthesis and characterization of nano crystalline $BaFe_{12}O_{19}$ powders by low temperature combustionMater Res Bull. 38 (2003) 149-159

[23] J.J. Kingsley, L.R. Pederson, Energetic materials in ceramic synthesis, J. Mater. Res. Soc. Synt. Proc. 296 (1992) 361

[24] J.J Kingsley K. Suresh, K.C Patil, Combustion Synthesis of Fine Particle Metal Aluminates, J. Mater. Sci. 25 (1990) 1305.

[25] J.J Kingsley, N Manickam, K.C Patil, Combustion Synthesis and Properties of Fine Particle Fluorescent Aluminous Oxides, B Mater. Sci. 13 (1990) 179.

[26] J. Rodríguez-Carvajal, Recent advances in magnetic structure determination by neutron powder diffraction, Phys. B Condens. Matter. 192 (1993) 55–69.

[27] V.Chopra, P. Singh, L.Singh, Thermoluminescence study of gamma irradiated BCNO nanophosphor, Radiat. Phy. Chem. 81 (2012) 771–775

[28] S. Mahajna, Y.S. Horowtz, The unified interaction model applied to the gamma ray induced supralinearity and sensitization of peak 5 in LiF:Mg,Ti (TLD-100), J. Phys. D: Appl. Phys. 30 (1997) 2603.

[29] Y.S. Horowitz, O. Avila, M. Rodrigues, Theory of heavy charged particle response (efficiency and supralinearity) in TL materials, Nucl. Instrum. Methods Phys. Res. B 184 (2001) 85.