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Mechanochemical Synthesis of Eu^{3+}-Sm^{3+} co-doped YPO_4 Nanoparticles at Room Temperature and its Photoluminescence Studies

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Abstract—*A series of $Y_{0.95-x}Eu_{0.05}Sm_xPO_4$ (x= 0.01, 0.03, 0.05 and 0.07) and $Y_{0.93-y}Eu_ySm_{0.07}PO_4$ (y=0.01, 0.03, 0.05 and 0.07) phosphors were prepared by mechanochemical method using high energy plenary ball mill followed by annealing the prepared nanoparticles for 4 hours at 1000°C. The structure, morphology, composition and photoluminescence of the samples were characterized by X-ray diffraction (XRD), IR Spectroscopy, Scanning electron microscopy (SEM) and photoluminescence (PL) spectra. The XRD patterns indicate tetragonal phase for all the samples. The SEM image shows rod-like structure which is non-agglomerated and highly dispersible in water. IR study reveals the presence of bending and stretching modes of vibrations of PO_4^{3-} group. The luminescence study of the prepared nanoparticles led to the confirmation that Sm^{3+} can act as the sensitizer of Eu^{3+}.*

Keywords*: plenary, ball mill, photoluminescence, non-agglomerated, bending, stretching and sensitizer.*

1. INTRODUCTION

Nowadays, long afterglow phosphors are attaining quite an interest because of its ability to store the energy from the excitation sources like sunlight, artificial light etc. and release the absorbing energy in the form of visible light even after the removal of the excitation sources [1]. Till now, aluminates based green emitting Dy^{3+} co-doped $SrAl_2O_4$: Eu^{2+}, silicates-based blue emitting Dy^{3+} co-doped $Sr_2MgSi_2O_7$: Eu^{2+} phosphors have been extensively studied [2-5]. In comparision with aluminate based and silicate based long lasting afterglow phosphors, sulfides based red emitting phosphors are chemically unstable with short afterglow duration. Hence, it is necessary to synthesize new red long lasting materials in order to enhance chemical stability and afterglow duration. Due to this, many researchers have paid attention to synthesize long afterglow phosphor by changing host matrix. In 2007, Wang et. al have successfully investigated the optical properties of Eu^{3+}- Sm^{3+} co-doped $Gd_{2-x-y}Eu_xSm_y(MoO_4)_3$[6]. And in 2011, Li et. al have reported the importance of Sm^{3+} ion in the optical properties of Eu^{3+}-Sm^{3+} co-doped $K_2Ba(MoO_4)_2$ red emitting phosphor[7]. Thus in this work, our main target is to prepare Eu^{3+} doped YPO_4 phosphors with improved afterglow duration.

In this present study, we have successfully synthesized a series of $Y_{0.95-x}Eu_{0.05}Sm_xPO_4$ (x= 0.01, 0.03, 0.05 and 0.07) and $Y_{0.93-y}Eu_ySm_{0.07}PO_4$ (y=0.01, 0.03, 0.05 and 0.07) phosphors by a mechanochemical method using high energy plenary ball mill followed by annealing the prepared nanoparticles for 4 hours at 1000°C. In this process, the powder materials are subjected to high energetic impact through different stages which involve repeated mixing, deformation, comminuting, welding and re-welding of the starting materials in a closed vessel of a plenary ball mill [8].The purpose of this process is to produce new reactive surface dangling bonds on the particles from the applied kinetic energy of the moving balls. To obtained particle in nanosize, different parameters like powder to ball mass ratio, rpm of the milling process, milling time, ball size etc. were optimized. The resulted energy transfers from Sm3+ to Eu3+ were interpreted properly and the mechanism of the optical property was also discussed in detail.

2. CHARACTERIZATION

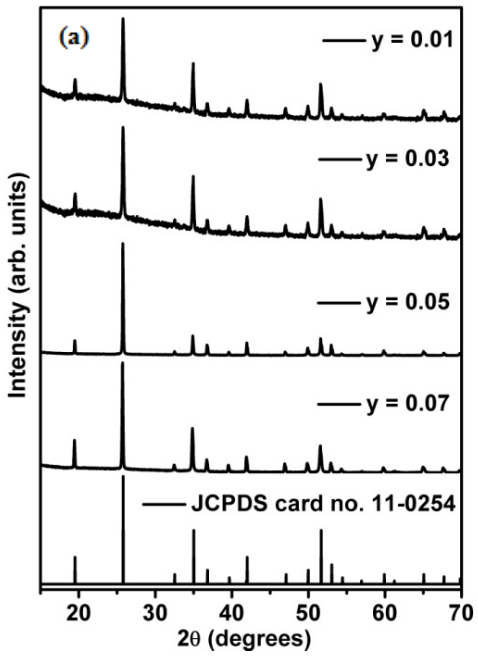
Structural characterization of the samples was carried out by using Bruker diffractometer (eco D8 Advance) with Cu-Kα radiation (λ=0.154nm). Morphology of the sample was characterized by using Scanning Electron Microscope of JEOL (JSM 6490 LV). FT-IR spectra of the samples were studied by Fourier Transform Infra- Red Spectrometer (FTIR) of Perkin Elmer. Luminescence properties of the samples were measured by Hitachi F-7000 Fluorescence Spectrophotometer.

3. RESULTS AND DISCUSSIONS

3.1 XRD Study

Fig. 1(a) and (b) presenting the XRD pattern of $Y_{0.93-y}Eu_ySm_{0.07}PO_4$ (y=0.01, 0.03, 0.05 and 0.07) and of $Y_{0.95-x}Eu_{0.05}Sm_xPO_4$ (x= 0.01, 0.03, 0.05 and 0.07) NPs. All the patterns are found to be well indexed with a tetragonal phase in the space group of 14_1/amd (141) (JCPDS card no. 11-0254). All the crystal phases are found to be similar with no shifting in peak position even though with different doping

concentrations of Eu^{3+} and Sm^{3+} ions indicating that small amount of dopant ions does not influence the crystal structure of the prepared NPs.



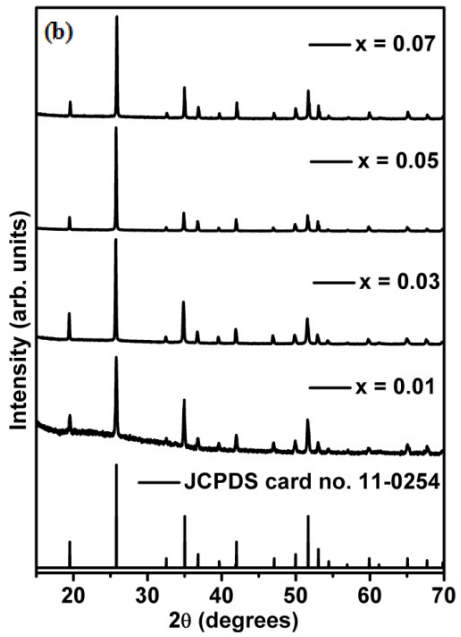


Fig. 1 (a-b). XRD pattern of $Y_{0.93-y}Eu_ySm_{0.07}PO_4$ (y=0.01, 0.03, 0.05 and 0.07) and $Y_{0.95-x}Eu_{0.05}Sm_xPO_4$ (x= 0.01, 0.03, 0.05 and 0.07)

3.2 Microscopy study

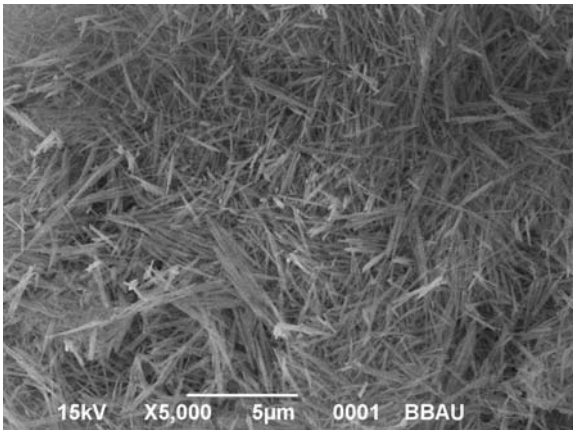


Fig. 2: SEM image of $Y_{0.88}Eu_{0.05}Sm_{0.07}PO_4$

Fig. 2 depicts the morphology of $Y_{0.88}Eu_{0.05}Sm_{0.07}PO_4$ NPs with the structure consists of a rod.

3.3 IR Study

Fig. 3depicts the IR spectra of $Y_{0.86}Eu_{0.07}Sm_{0.07}PO_4$ and $Y_{0.88}Eu_{0.05}Sm_{0.07}PO_4$ NPs, which indicates the presence of bending and stretching mode of vibrations of PO_4^{3-} group. The peaks arise at~ 505 and 620 cm^{-1} are due to $\upsilon_4$vibrations and the strong peaks arise at~ 1003 and 1095 cm^{-1} which are merged together are due to υ_3 vibrations of PO_4^{3-} groups [9-10]. Here the prepared NPs does not exhibit stretching and bending modes of O-H group as the NPs are annealed at 1000^0C for 4 hours after milling for 2 hours.

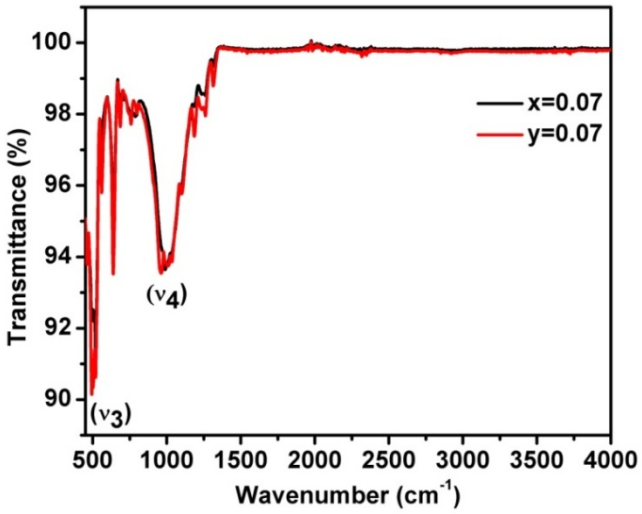


Fig.3: IR spectra of $Y_{0.86}Eu_{0.07}Sm_{0.07}PO_4$ and $Y_{0.88}Eu_{0.05}Sm_{0.07}PO_4$

3.4 Luminescence Study

Excitation spectrum of $Y_{0.93-y}Eu_ySm_{0.07}PO_4$ (y=0.01, 0.03, 0.05 and 0.07)(λ_{em}= 600 nm) and of $Y_{0.95-x}Eu_{0.05}Sm_xPO_4$ (x= 0.01, 0.03, 0.05 and 0.07) (λ_{em}= 615 nm) are shown in fig. 4(a-b). In the UV region of $Y_{0.93-y}Eu_ySm_{0.07}PO_4$ NPs, a broad Eu-O charge-transfer band is observed from 220 nm to 240 nm with a maximum intensity peak at 228 nm. This band is originated from the transition of O^{2-} 2p electron to Eu^{3+} 4f empty orbitals.,And a series of peaks are arise in the excitation spectra due to the intra-configurational 4f-4f transitions of Eu^{3+} ion. Peaks originated at 320 ($^7F_{0,1} \rightarrow {}^5H_{3,6}$), 367 ($^7F_{0,1} \rightarrow {}^5D_0$), 378 ($^7F_{0,1} \rightarrow {}^5G_1$), 394($^7F_0 \rightarrow {}^5L_6$) are from Eu^{3+} ions and the peak at 404 nm ($^6H_{5,2} \rightarrow {}^4K_{11/2}$) is due to the transition of Sm^{3+} ion[11]. But the peak due to Sm^{3+} ion is very weak for $Y_{0.95-x}Eu_{0.05}Sm_xPO_4$(x = 0.01) and the intensity of the peak increases with increase in the value of x, which indicates the transfer of absorption energy from Sm^{3+} ion to Eu^{3+} ion. That is the luminescence intensity of the nanoparticles can be increased by the addition of appropriate amount of Sm^{3+} ion [12].

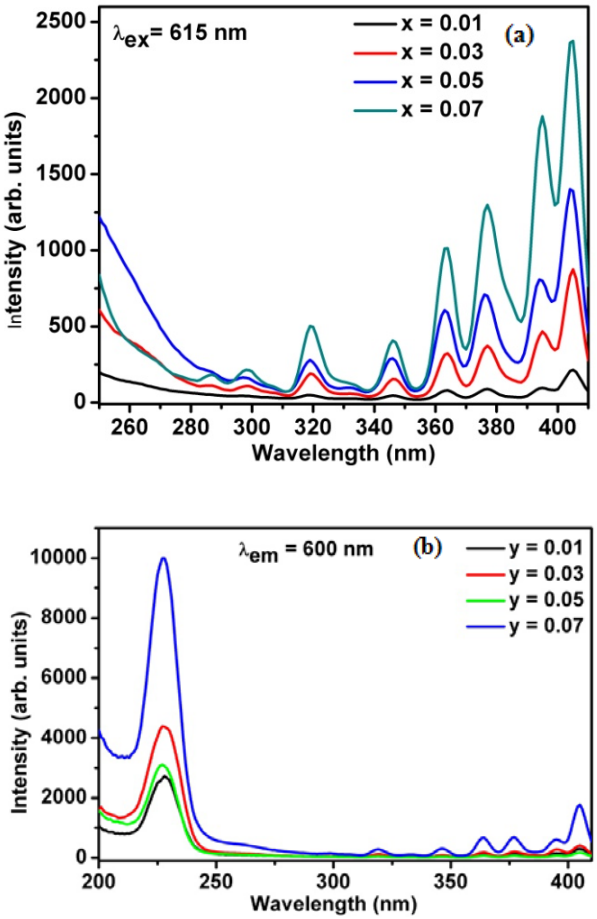
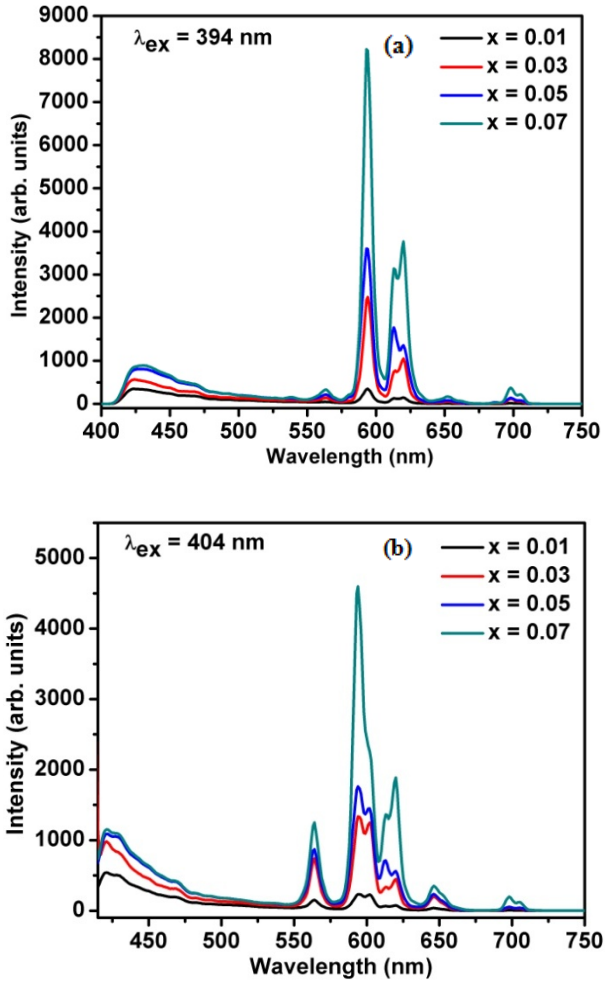


Fig. 4 (a-b) Excitation spectra of $Y_{0.95-x}Eu_{0.05}Sm_xPO_4$ (x= 0.01, 0.03, 0.05 and 0.07) and $Y_{0.93-y}Eu_ySm_{0.07}PO_4$ (y=0.01, 0.03, 0.05 and 0.07) NPs.

Fig.5 (a-d) shows the emission spectra of $Y_{0.95-x}Eu_{0.05}Sm_xPO_4$ (x= 0.01, 0.03, 0.05 and 0.07) and $Y_{0.93-y}Eu_ySm_{0.07}PO_4$ (y=0.01, 0.03, 0.05 and 0.07) at the excitation wavelength of 394 nm and 404 nm respectively. From the spectrum, it can be seen that the major emission peaks are located at around 593 nm and 615 nm, which arise from the magnetic dipole transition ($^5D_0 \rightarrow {}^7F_1$), and the electric dipole transition ($^5D_0 \rightarrow {}^7F_2$) respectively. Moreover, magnetic dipole transition is more intense than electric dipole transition indicating that Eu^{3+} ion occupies an asymmetric site. The emission peaks from Sm^{3+} ion transitions at around 565 nm ($^4G_{5/2} \rightarrow {}^6H_{5/2}$) and 646 nm ($^4G_{5/2} \rightarrow {}^6H_{9/2}$) are also observed. With increase in doping concentration of Sm^{3+} ion, the intensity of the emission peaks is also enhanced. The excitation peaks of Eu^{3+} ion at 394 nm are also involved in the excitation peaks of Sm^{3+} at 404 nm ($^6H_{5/2} \rightarrow {}^4K_{11/2}$) transition. Hence the optical properties of Eu^{3+} ion can be enhanced by adding an appropriate amount of Sm^{3+} ion which indicates that Sm^{3+} ion can act as a sensitizer of Eu^{3+} ion.



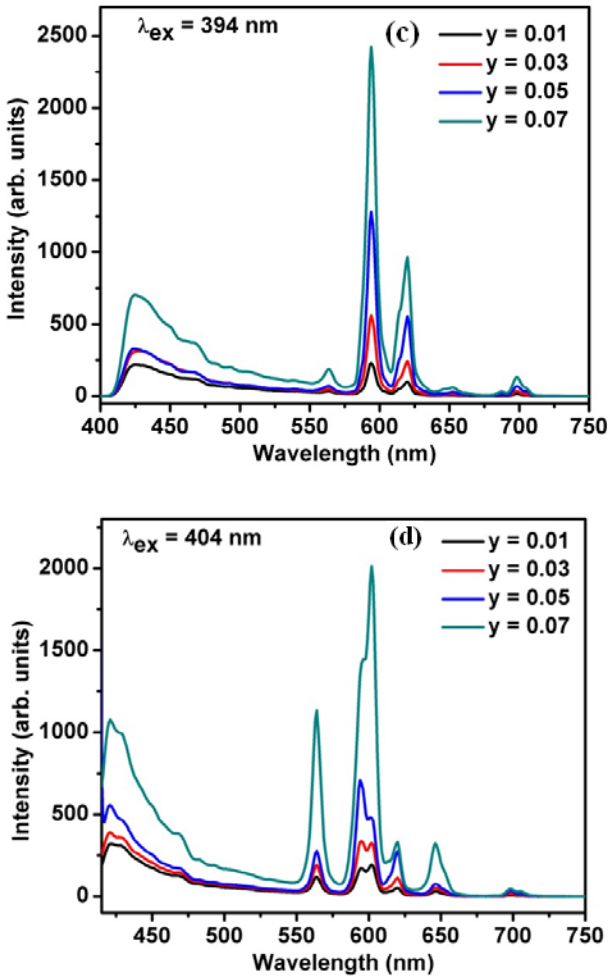


Fig. 5 (a-d): Emission spectra of $Y_{0.95-x}Eu_{0.05}Sm_xPO_4$ (x= 0.01, 0.03, 0.05 and 0.07) and $Y_{0.93-y}Eu_ySm_{0.07}PO_4$ (y=0.01, 0.03, 0.05 and 0.07) NPs at the excitation wavelength of 395 nm and 404 nm respectively.

3.5 Conclusions

We have successfully synthesized a series of $Y_{0.95-x}Eu_{0.05}Sm_xPO_4$ (x= 0.01, 0.03, 0.05 and 0.07) and $Y_{0.93-y}Eu_ySm_{0.07}PO_4$ (y=0.01, 0.03, 0.05 and 0.07) phosphors by high energy plenary ball mill method followed by annealing the prepared nanoparticles for 4 hours at 1000°C. All the prepared nanoparticles show tetragonal phase with no shifting in peaks position with different doping concentration. From the luminescence spectrum, it is proved that Sm^{3+} ion can act as a sensitizer for Eu^{3+} ion.

4. ACKNOWLEDGEMENTS

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