Photoluminescence properties of an efficient colour tunable microcrystalline $Sr_3WO_6:Na^+,RE^{3+}$ (RE = Eu, Dy and Sm) phosphors

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The microcrystalline samples of double perovskite tungstate $Sr_3WO_6:Na^+,RE^{3+}$ (Eu, Dy and Sm) phosphor were synthesized by modified solid state reaction method. The XRD and SEM results reveal the formation of phase pure microcrystalline phosphor samples. Noteworthy appearance of characteristic broad CT band of $(WO_6)^{6-}$ complex is observed in excitation spectra of Dy^{3+} and Sm^{3+} ion doped phosphors. PL emission spectra of Eu^{3+}, Dy^{3+} and Sm^{3+} ions doped phosphors show characteristic emission of rare earth activator. The rare earth ions are doped at non-centrosymmetric 'A' site of the double perovskite tungstate and show no concentration quenching up to 2mol% concentration of rare earth ions.

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1. Introduction

In the present world, our routine practices became more energy dependable. Hence, its demand has enormously increased which exerts pressure on our traditional energy resources and causing the natural imbalance. Lighting consumes around 15 to 20% of producing electricity at worldwide level [1]. To ease the pressures on energy structure, we can reduce the energy consumption in lighting either by modifying the lighting technology or by improving the energy efficiency of the sources. Presently, the solid state lighting technology is being utilized for various purposes which is not only energy efficient, but also environment friendly [2,3]. The researchers are continuously working to improve luminous efficiency of the phosphor material [which will be utilized in PC-LED (phosphor converted light emitting diode)] together with their quality of light by exploring various materials as there is still a possibility for development.

Rare earth ions play a very crucial role in development of efficient phosphor material. Thus, they are preferred dopant amongst the researchers. Rare earth ions give intense and sharp lines in all parts of the visible spectrum, which allow the tuning the colour of the phosphor: hence, this considerably modifies the luminescence properties of the material [4,5]. The selection of host material has equal importance as the selection of activator ion in the development of phosphor for a particular application. Tungstate is self-activated material also could be act as sensitiser, so it could be an interesting host lattices for rare earth ions [6,7]. The double perovskite tungstate is one of the member of tungstate family, which offers simplicity of crystal structure as well as other important physical properties such as ferroelectricity, dielectricity, photocatalytic, magnetoresistance etc. [8-14] which make it the material of interest since 1950s [15,16].

Initially Eman et al. [17] reported the photoluminescence (PL) properties of $Sr_3WO_6:Eu^{3+}$ phosphor in which the phosphor shows the characteristics luminescence indicating the doping at centrosymmetric site and is consistent with our previous work [18]. Furthermore, they continue their work [19] and report the PL properties of the same along with the UV irradiated thermoluminescence properties. Collaterally, Zhao et al. [7] reported the photoluminescence of $Sr_3WO_6:K^+$, Eu^{3+} and they found that the charge compensation results in the enhancement in PL intensity of the phosphor and is comparable to the commercial red phosphor $Y_2O_2S:Eu^{3+}$. Later on, Lee et al. [20] reported the structural, morphological and PL properties of Sr_3WO_6 doped with Eu^{3+} and Sm^{3+} ions. Zhang et al. [21] explore the up-conversion luminescence properties of Er doped Sr_3WO_6 multiphase phosphors for the optical temperature sensor. The PL properties of various rare earth ions activated Sr_3WO_6 phosphors seldom occurred in the literature. The work reported by Zhao et al. [7] attracts our attention because the PL intensity of the phosphor was found to be comparable to commercial phosphor. Hence, in this work we put an effort to present the PL properties of three different rare earth ions (Eu^{3+}, Dy^{3+} and Sm^{3+}) activated double perovskite tungstate (Sr_3WO_6) with charge compensated by Na^+ ion.

2. Experimental

The pure and rare earth doped samples of Sr_3WO_6 phosphors were synthesized by modified high temperature solid state reaction method. The analytically pure starting chemicals [$SrCO_3$, H_2WO_4, Na_2WO_4 and RE_2O_3 (RE = Eu, Dy and Sm)] are used without further purification for the synthesis. The typical chemical reaction for the synthesis of pure host material is given as follows:

$$3SrCO_3 + H_2WO_4 \rightarrow Sr_3WO_6 + 3CO_2 \uparrow + H_2O \uparrow$$

In this synthesis, the stoichiometric amount of the starting chemicals is taken in mortar pestle and pulverized thoroughly for 1 Hr. This reaction mixture was heat treated two times; first at 600˚C for 12 Hrs. and second at 1250˚C for 4 Hrs. followed by slow cooling to room temperature inside the furnace. In between, these two heating steps, the reaction mixture was again reground thoroughly for 1 Hr. after final heat treatment, the highly sintered sample was mildly crushed to fine powder and used as is for further characterization. The RE^{3+} ion doping in various molar concentrations (0-2mol%) were achieved by adding the stoichiometric amount of RE_2O_3 in the reaction mixture and Na_2WO_4 (Na^+ ion) were added in same molar concentration for the charge compensation.

The phase purity and structural analysis of the pure sample was examined by powder X-ray diffraction (XRD) measurement. The XRD patterns were obtain at room temperature from PANalytical X'Pert Pro X-ray diffractometer with Cu K_α radiation (λ = 1.5406A°) operating at 40 kV voltage and 30 mA current. The morphology of the sample surface is analyzed by micrograph of the sample which is recorded on scanning electron microscope (SEM) (JEOL/EO, JSM-6380) operating at the voltage of 10kV. The room temperature PL excitation and emission spectra of as synthesized samples were recorded on the Shimadzu RFPC5301 Spectrofluorophotometer with constant spectral slit width of 1.5nm.

3. Result and discussion

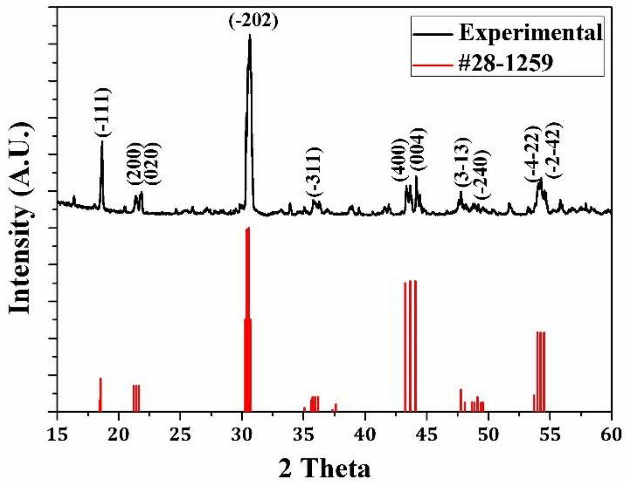

Fig. 1. X-ray diffraction pattern of Sr_3WO_6 compared with JCPDS Standard file #28-1259 (color online)

In order to check the phase purity and crystallinity of as-prepared powder samples of double perovskite tungstate (Sr_3WO_6) were characterized by powder XRD. The XRD patterns of Sr_3WO_6 compared with standard JCPDS file no. 28-1259 are illustrated in Fig. 1. All of the diffraction peaks of as prepared samples are in good agreement with the standard pattern. Few less intense additional peaks are observed in XRD pattern. These additional peaks may correspond to $SrWO_4$ or SrO. As the intensity of these impurity peaks is very less compared to intense peaks of Sr_3WO_6, excluding these peaks, the as synthesized samples are said to be phase pure. Sharp and intense diffraction peaks reveal the well crystallization of the phosphor material.

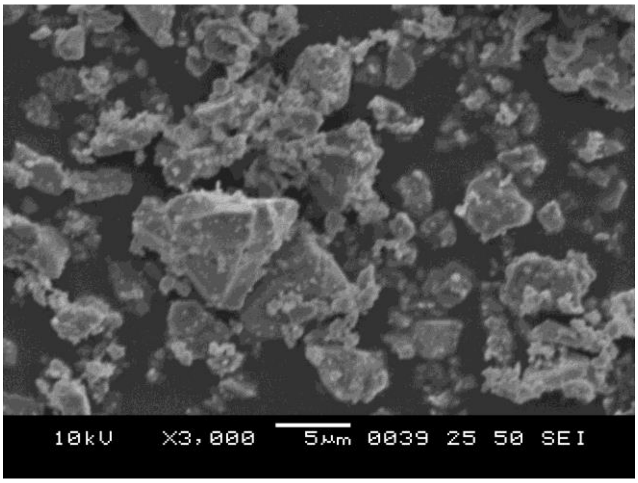

Fig. 2. SEM micrograph of as synthesized Sr_3WO_6 material.

The investigation of the microstructure and morphological properties of Sr_3WO_6 was carried out by SEM micrographs. Typical SEM micrographs of the sample sintered at 1250°C are portrayed in Fig. 2. From the obtained micrographs it is observed that, the grains of Sr_3WO_6 material shows various sizes and shapes that are distributed randomly with loose structure and less pronounced aggregation. The grains are distributed in the size range of 1-6 µm with different shapes. The survey of literature indicates that the phosphor with micrometer grain size is suitable for fabricating the solid-state lighting (SSL) devices. It is noticed that the crystalline powder which exhibits high luminescent intensities in addition to the micro-meter dimensions will find more applications [22,23].

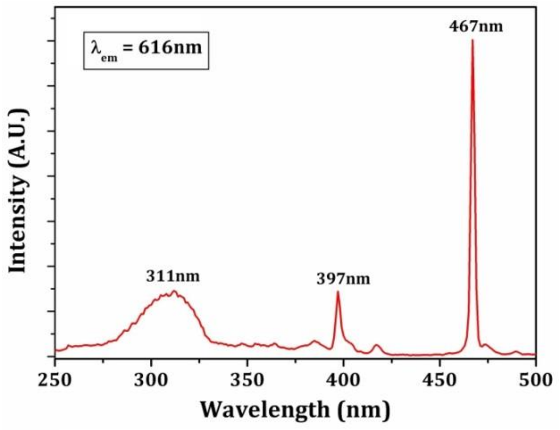

Fig. 3. PL excitation spectra of $Sr_3WO_6:Na^+,Eu^{3+}$ (2mol%) by monitoring emission wavelength at 616nm (color online)

The PL excitation spectrum of $Sr_3WO_6:Na^+,Eu^{3+}$ (2mol%) by monitoring $^5D_0\rightarrow{}^7F_2$ transition of Eu^{3+} at around 616nm in the red spectral region is shown in Fig. 3. The PL excitation spectra of $Sr_3WO_6:Na^+,Eu^{3+}$ (2mol%) consists of a less intense broad band (250-340nm) and some sharp lines at room temperature. The broad excitation band with maximum at 305nm is attributed to the involvement of charge transfer (CT) transition of both W^{6+}-O^{2-} and Eu^{3+}-O^{2-}. The sharp characteristic excitation peaks of Eu^{3+} at 397 and 467nm corresponds to the intra f-f transitions within $4f^6$ configuration of Eu^{3+}, which are attributed to transition from ground state $^7F_0$ to excited states $^5L_6$ and $^5D_2$ respectively. The intensity of a broad excitation band is relatively much lower than narrow peaks of Eu^{3+} ion, which is in good agreement with earlier report [7,17,19,20]. Overlapping of CT band of W^{6+}-O^{2-} and Eu^{3+}-O^{2-} results in the low intensity of broad excitation band which indicates the less efficient energy transfer from $(WO_6)^{6-}$ complex to Eu^{3+} ion. In double perovskite tungstate Eu^{3+} ion substituted at Sr^{2+} (A) site will have W-O-Eu bond close to 90°, so the wavefunction overlaps (using π bonding) and the energy transfer efficiency is reduced [24,25]. This result is in good agreement with the other Eu^{3+} doped tungstate phosphors [26].

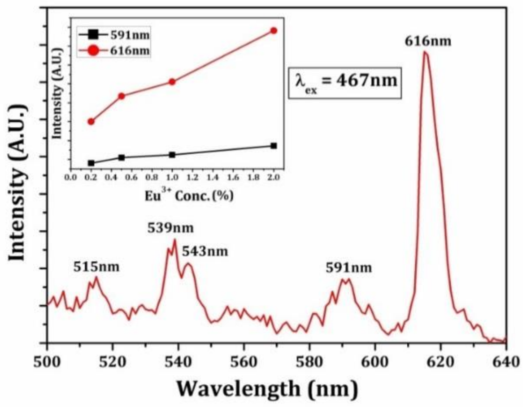

Fig. 4. PL emission spectra of $Sr_3WO_6:Na^+,Eu^{3+}$ (2mol%) excited at wavelength 467nm (In inset shows the variation of intensity of 591 and 616nm peaks with Eu^{3+} concentration) (color online)

The room temperature PL emission spectra of $Sr_3WO_6:Na^+,Eu^{3+}$ (2mol%) under the excitation of blue light (467nm) is shown in Fig. 4. The typical emission spectrum of Eu^{3+} activated Sr_3WO_6 phosphor consists of intense and sharp characteristic peaks of Eu^{3+} ion at 515 ($^5D_2\rightarrow{}^7F_2$), 539 ($^5D_1\rightarrow{}^7F_0$), 543 ($^5D_1\rightarrow{}^7F_1$), 591 ($^5D_0\rightarrow{}^7F_1$) and 616nm ($^5D_0\rightarrow{}^7F_2$). Emission related to transition from higher states ($^5D_{1,2}$) are also observed in addition to the usual orange-red emission from lowest excited state ($^5D_0$) [7,17,19,20]. The effects of Eu^{3+} concentration on the intensity of orange-red emission peaks at 591 and 616nm, respectively were also carried out and the results of which are displayed in inset of Fig. 4. It is seen that, orange-red emission peaks the intensity rises with Eu^{3+} concentration without quenching up to 2mol%.

Remarkable spectroscopic property of Eu^{3+} is a well-known probe to investigate the symmetry of the site in the host lattice by comparing the emission intensities of hypersensitive electric dipole (ED) transition with magnetic dipole (MD) transition. The ratio of intensities of the emission peaks due to ED ($^5D_0\rightarrow{}^7F_2$) transition to MD ($^5D_0\rightarrow{}^7F_1$) transition is helpful to predict the symmetry of the doped site. Eu^{3+} ion is substituted at non-centrosymmetric site if the ratio is greater than 1 otherwise at centrosymmetric site in the host lattice [6,7].

In the present case the ratio is found to be 4.54 for 2mol% Eu^{3+} doped phosphor sample which indicates that Eu^{3+} is lodged at A site in the double perovskite host lattice and this is in good agreement with the earlier reports [6,7,17,19,27]. This could be understood that the substitution of Eu^{3+} at Sr^{2+} (A) site in Sr_3WO_6 is accompanied by Sr^{2+} ion vacancy (V_M) (due to charge imbalance) and lattice strain (due to the different ionic radius). These defects in the lattice lowers the local site symmetry at Eu^{3+} substituted site and act as a luminescence quenching center. Na^+ ion replaces the Sr^{2+} ion vacancy (V_M) site, thereby reducing the lattice strain and act as charge compensator which could improve the emission intensity [7].

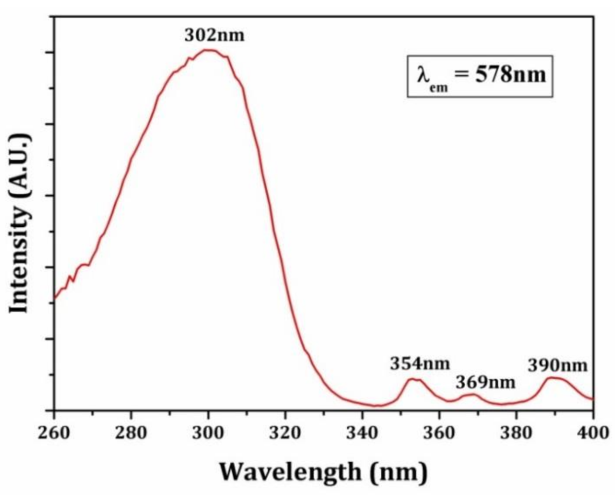

Fig. 5. PL excitation spectra of $Sr_3WO_6:Na^+,Dy^{3+}$ (2mol%) by monitoring emission wavelength at 578nm (color online)

The room temperature PL excitation spectra of Dy^{3+} (2mol%) activated Sr_3WO_6 phosphor by monitoring $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition in the yellow region (at 578nm) is shown in Fig 5. The excitation spectrum consists of an intense broad band in the UV spectral region and some weak characteristic peaks in the near UV region. The intense broad band in UV region having maximum at 302nm is mainly attributed to the CT transition of $(WO_6)^{6-}$ complex. The sharp characteristic peaks at around 354, 369 and 390nm is are assigned to forbidden intra 4f transition of Dy^{3+} ion and are attributed to transition from ground state $^6H_{15/2}$ to excited states $^4M_{15/2}+{}^6P_{7/2}$ (354nm), $^4I_{11/2}+{}^6P_{3/2}$ (369nm) and $^4M_{21/2}+{}^4I_{13/2}+{}^4K_{17/2}+{}^4F_{7/2}$ (389nm) [28]. The intensity of the CT band of $(WO_6)^{6-}$ complex is found to be nearly 11.95 times higher than characteristic peaks of Dy^{3+} ion. The intense host absorption for characteristic yellow emission of Dy^{3+} ion indicates the effective energy transfer from tungstate host to Dy^{3+} ion.

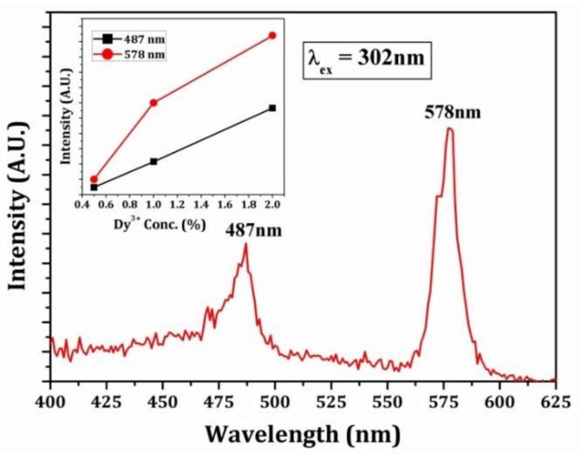

Fig. 6. PL emission spectra of $Sr_3WO_6:Na^+,Dy^{3+}$ (2mol%) excited at wavelength 302nm (In inset shows the variation of intensity of 487 and 578nm peaks with Dy^{3+} concentration) (color online)

Fig. 6 shows the emission spectra of Dy^{3+} (2mol%) activated Sr_3WO_6 phosphor under the CT excitation of 302nm. The emission spectrum of Dy^{3+} activated Sr_3WO_6 phosphor shows two narrow blue (487nm) and yellow (578nm) emission bands which are characteristic of Dy^{3+} ion; the blue emission peak is attributed to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition and yellow emission peak is attributed to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition of Dy^{3+} ion [28]. The intensity of yellow peak is higher than blue one, also the emission related to $(WO_6)^{6-}$ complex has not observed this shows that the most efficient energy transfer from $(WO_6)^{6-}$ complex to Dy^{3+} ion. Alike Eu^{3+} ion Dy^{3+} ion is also used as spectroscopic probe for investigation of site symmetry. In case of Dy^{3+} ion the ratio of hypersensitive ED transition ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) to parity allowed MD transition ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) is found to be 1.84 which confirms the substitution of rare earth ion at non-centrosymmetric site in host lattice. The influence of Dy^{3+} ion concentration in the host lattice on blue (487nm) and yellow (578nm) emission peaks was also investigated and shown in inset of Fig. 6. It is seen that the intensity of the yellow peak is increased with increase in Dy^{3+} concentration up to 2mol% without quenching.

Fig. 7 depicts the room temperature excitation spectra of Sm^{3+} activated Sr_3WO_6 phosphor by monitoring orange red emission due to $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition at 600nm of Sm^{3+} ion. The typical excitation spectra consist of a broad band peaking at 303nm and sharp characteristic peaks. The broad excitation bands in UV region observed in the excitation spectra of both Sm^{3+} and Dy^{3+} ion doped phosphor are of similar nature and their origin is same; sharp characteristic peaks located at 410 and 424nm are corresponding to intra f-f transition of $4f^5$ configuration of Sm^{3+} ion and are attributed to transition from ground state $^6H_{5/2}$ to excited state $^4K_{11/2}$ and $(^6P, {}^4P)_{5/2}+{}^4M_{19/2}$ respectively [20.23].

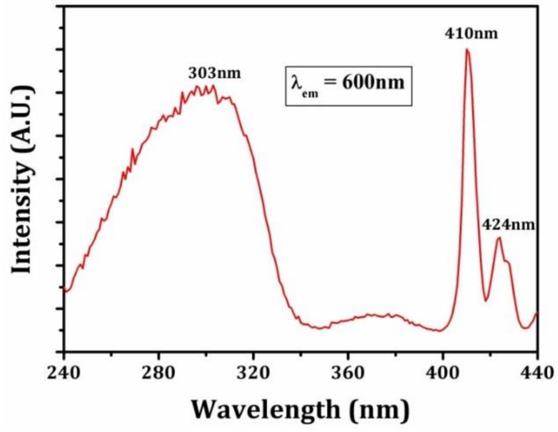

Fig. 7. PL excitation spectra of $Sr_3WO_6:Na^+,Sm^{3+}$ (2mol%) by monitoring emission wavelength at 600nm (color online)

The presence of the CT band of $(WO_6)^{6-}$ complex in the excitation spectra of characteristic orange-red emission of Sm^{3+} ion indicating the phenomenon of energy transfer from $(WO_6)^{6-}$ complex to Sm^{3+} ion similar to the Dy^{3+} ion. However, the transfer of energy is not efficient as Dy^{3+} ion because the intensity of CT band is comparable to the characteristic lines of Sm^{3+} ion.

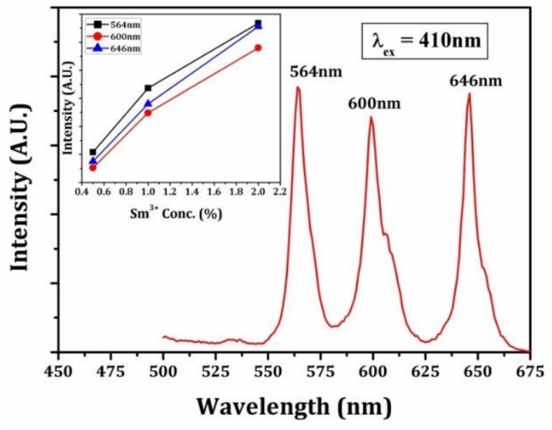

Fig. 8. PL emission spectra of $Sr_3WO_6:Na^+,Sm^{3+}$ (2mol%) excited at wavelength 410nm (In inset shows the variation of intensity of 564, 600 and 646nm peaks with Sm^{3+} concentration) (color online)

The room temperature PL emission spectra of $Sr_3WO_6:Na^+,Sm^{3+}$ (2mol%) phosphor under the violet excitation of 410nm is depicted in Fig. 8. The Sm^{3+} ion activated phosphor exhibits three sharp emission peaks centred in green-yellow (564nm), orange-red (600nm) and red (646nm) spectral region. These three emission peaks are respectively accredited to $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^4G_{5/2}\rightarrow{}^6H_{7/2}$ and $^4G_{5/2}\rightarrow{}^6H_{9/2}$ transitions of $4f^5$ configuration of Sm^{3+} ion [20.23]. It is worthwhile to note that the intensity of peak in green-yellow (564nm) region is relatively more intense than other two in orange-red and red region. These emission peaks show intensity variation with Sm^{3+} ion concentration (inset of Fig. 8). The intensity of these peaks is found to increase with Sm^{3+} ion concentration in the host lattice without concentration quenching up to 2mol% concentration of Sm^{3+} ion in the host lattice.

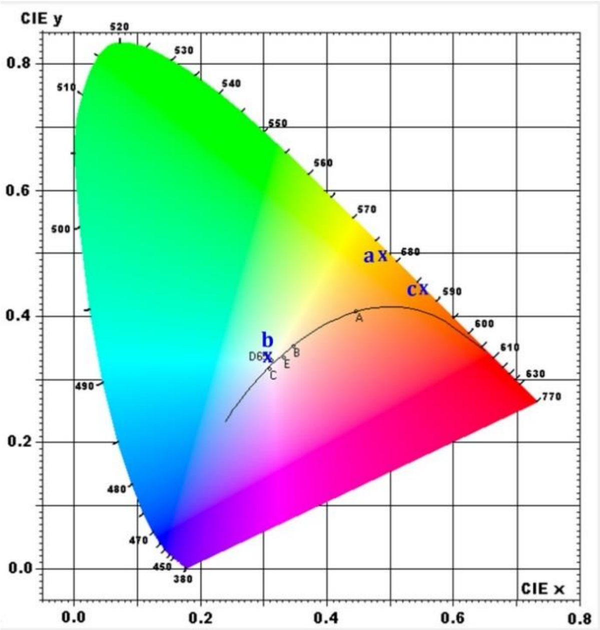

Fig. 9. The CIE colour space chromaticity diagram of $Sr_3WO_6:Na^+,RE^{3+}$ [RE = (a) Eu (0.489,0.495), (b) Dy (0.306,0.337) and (c) Sm (0.554, 0.440)] phosphors (color online)

The performance of phosphor material on colour luminescent emission could be evaluated by Commission Internationale de l'Eclairage (CIE) chromaticity coordinate which is based on the ability of the human eye to match color. The CIE chromaticity coordinates of the phosphor were calculated adopting the standard procedure for the system [29]. The representation of the colours of $Sr_3WO_6:Na^+,RE^{3+}$ (RE = Eu, Dy and Sm) phosphors on 1931 CIE chromaticity diagram is represented on Fig. 9. The chromaticity coordinates of Eu^{3+} activated M_3WO_6 phosphors under the blue (467nm) excitation show different hues of orange colour, $Sr_3WO_6:Na^+,Eu^{3+}$ phosphors mainly show yellowish-orange colour while $Sr_3WO_6:Na^+,Sm^{3+}$ phosphor shows reddish-orange colour. It is worthwhile to note that the $Sr_3WO_6:Na^+,Dy^{3+}$ phosphor shows white emission under the UV (303nm) emission, but the ineffective absorption in the near UV region limits its applicability for white LED.

4. Conclusion

The RE^{3+} (Eu^{3+}, Dy^{3+} and Sm^{3+}) ions activated microcrystalline samples of Sr_3WO_6 phosphor were successfully synthesized via modified solid state reaction method at around 1200ºC. The XRD pattern of as synthesized samples reveals the formation of well crystallized triclinic phase of samples and well matched with the standard JCPDS PDF. The SEM micrographs show the formation of grains with irregular shapes and size in the range 1-6μm. The rare earth ion occupies the non-centrosymmetric ‘A’ site in the double perovskite host lattice. The emission spectrum of $Sr_3WO_6:Na^+,Eu^{3+}$ phosphor consists of series of intense and sharp characteristic peaks in green to red region (515, 539, 543, 591 and 616nm) which gives it a yellowish orange hue. $Sr_3WO_6:Na^+,Dy^{3+}$ phosphor shows only blue (487nm) and yellow (578nm) emission peaks which give the whitish appearance to the phosphor. $Sr_3WO_6:Na^+,Sm^{3+}$ phosphors show three characteristic emission bands in green-yellow (564nm), orange-red (600nm) and red (646nm) spectral region which give the orange-red appearance. The PL intensity did not show concentration quenching up to 2mol% concentration of rare earth ions in the host lattice.

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