Synthesis and Photoluminescence Properties of Eu^{3+} Doped Double Perovskite Tungstate

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Abstract

The microcrystalline samples of double perovskite tungstates M_3WO_6 (M = Ca, Sr and Ba) doped with Eu^{3+} ion were synthesized by modified solid state reaction method. The phosphor materials were characterized by XRD, SEM and photoluminescence (PL) spectroscopy. The XRD result reveals the formation of well crystallized and phase pure microcrystalline phosphor samples. Both of the PL excitation and emission spectra of M_3WO_6:Eu^{3+} phosphors show very similar nature. The excitation spectra of characteristic yellow emission of Dy^{3+} ion show a broad CT band of $(WO_6)^{6-}$ complex in UV region. The intense host absorption for characteristic yellow emission of Dy^{3+} ion indicates the effective energy transfer from tungstate host to Dy^{3+} ion. The energy transfer from $(WO_6)^{6-}$ complex to Dy^{3+} ion is more efficient in Sr_3WO_6 than Ca_3WO_6 and Ba_3WO_6. The color of Dy^{3+} doped M_3WO_6 phosphors varies from orange to cyan color due to different yellow to blue intensity ratio.

1. Introduction

Tungstate is one of the interesting host materials that have attracted a great deal of interest owing to self-activation, good stability for physical conditions (chemical and thermal) and wider applicability in various fields such as scintillation, solid state laser, electro-optic applications, catalytic etc. Tungstate based phosphors show broad excitation and emission bands due to the ligand to metal charge transfer (CT) transition of $(WO_4)^{2-}$ and $(WO_6)^{6-}$ oxyanion complex. Partially filled deep-lying 4f shells of rare earth ions causes interesting optical properties which make them the favorite activators for doping in various hosts. However, the sharp excitation line of rare earth is less effective and higher concentration leads to quenching of emission. Thus the host sensitization of rare earth ions in tungstate materials is actively studied from last decades **[1-11].** The double perovskite tungstate offer simplicity of crystal structure as well as other important physical properties such as ferroelectricity, dielectricity, photocatalytic, magnetoresistance etc. **[10-15]** which make it the material of interest since 1950s **[2,3]**. M_3WO_6 (M = Ca, Sr and Ba) is another member of double perovskite tungstate family were first discovered in an investigation of the influence of excess of alkaline earth oxide on the luminescence properties of MWO_4 **[16]** and their synthesis and structural properties were studied by Belyaev et al. **[17]**. Recently, King et al. **[18]** studied the structural properties of Sr_3WO_6 and Pang et al.**[20]** reported interesting electrical properties of Ca_3WO_6 and showed that it could be good candidate for microwave application. However, very few attempts were made to study the luminescence properties of Eu^{3+} doped M_3WO_6 (M = Ca and Sr) phosphor **[20-24]**, while the other rarer earth activation and Ba_3WO_6 did not studied so far. Hence,

the investigation of luminescence properties of Eu^{3+} in M_3WO_6 (M = Ca, Sr and Ba) and there correlation between them were considered in this work.

2. Experimental

The pure and Dy^{3+} doped samples of M_3WO_6 were synthesized by modified solid state method. The analytically pure starting chemicals are used without further purification for the synthesis of pure and rare earth doped M_3WO_6. The typical chemical reaction for the synthesis of pure host material is given as follows:

$$3MCO_3 + H_2WO_4 \rightarrow M_3WO_6 + 3CO_2 + H_2O$$

The stoichiometric amount of the starting chemical are taken in mortar pestle and pulverized thoroughly for 1 Hr. Then this reaction mixture was taken in porcelain crucible and heat treated at 600°C for 12 Hrs. followed by slow cooling to room temperature inside the furnace. Then this reaction mixture again reground thoroughly for 1 Hr. and finally sintered at 1250°C for 4 Hrs. and allowed to cool slowly to room temperature inside the furnace. The highly sintered sample was crushed to fine powder and used as is for further characterization.

The phase purity and structural analysis of the pure sample was examined by 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 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.
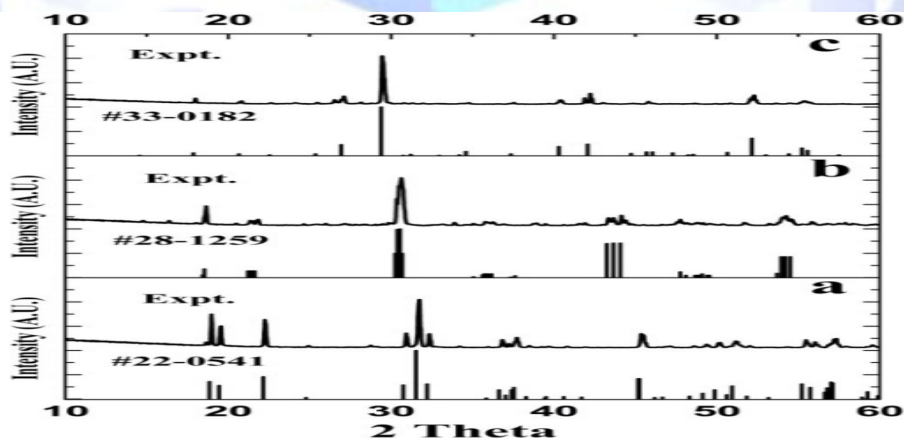
3. Result and Discussion

Fig. 1. X-ray diffraction pattern of (a) Ca₃WO₆, (b) Sr₃WO₆ and (c) Ba₃WO₆.

In order to characterize the phase purity and crystallinity of the as-prepared powder samples of double perovskite tungstate (M_3WO_6; M = Ca, Sr and Ba), the XRD patterns for all samples were examined. The XRD patterns of M_3WO_6 are illustrated in **Fig. 1.** The position of most of the diffraction peaks of diffractograms of samples are in good agreement with the corresponding standard JCPDS files. Few additional peaks were noted in diffractograms; the intensity of these peaks is negligible as compared to intense peak of M_3WO_6, excluding these peaks the as synthesized samples are said to be phase pure. Sharp and intense diffraction peaks reveals the well crystallization of the phosphor material.

The PL excitation spectra of M_3WO_6:Eu^{3+} (2mol%) by monitoring $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} at around 615nm in red spectral region is shown in **Fig. 2a-c.** The PL excitation spectra of Ca_3WO_6:Eu^{3+} (2mol%) consists of a less intense broad band (250-340nm) and some sharp lines at room temperature. The broad excitation band peaking at 305nm is ascribed to the involvement of CT transition from filled 2p orbitals of oxygen to empty 5d orbitals of both tungsten and europium. The sharp characteristic excitation peaks of Eu^{3+} at 364, 384, 397, 417 and 467nm corresponds to the intra f-f transitions within $4f^6$ configuration of Eu^{3+}, which are attributed to $^7F_0 \rightarrow ^5D_4$, $^7F_0 \rightarrow ^5L_7$, $^7F_0 \rightarrow ^5L_6$, $^7F_0 \rightarrow ^5D_3$ and $^7F_0 \rightarrow ^5D_2$ transitions. The nature of excitation spectra of Eu^{3+} doped M_3WO_6 phosphors is very similar except the peak of broad band is at around 310nm. The intensity of broad excitation band in is relatively much lower than characteristic peaks of Eu^{3+} ion, which is in good agreement with earlier report [21-26]. The low intensity of broad band may be the results of overlapping of CT band of W^{6+}-O^{2-} and Eu^{3+}-O^{2-}; 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 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 [4,26]. This result is in good agreement with the other
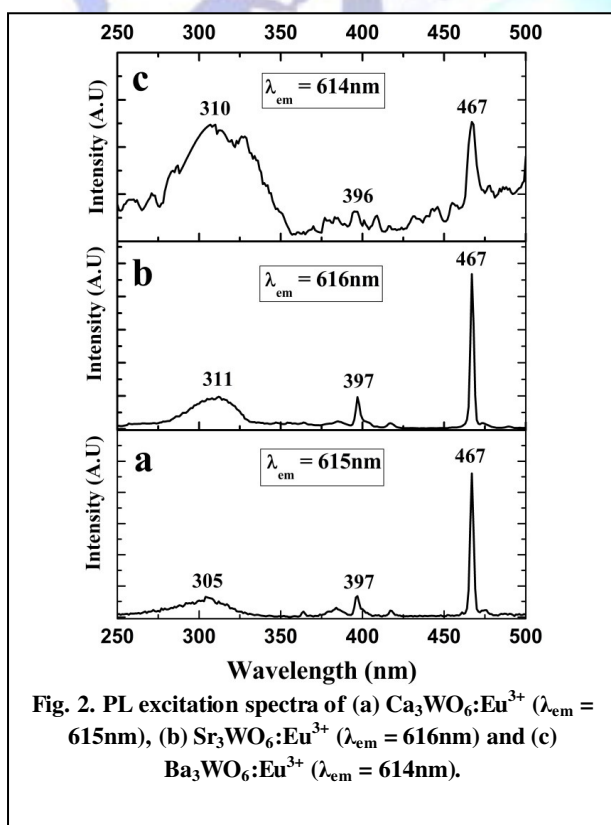

Fig. 2. PL excitation spectra of (a) Ca_3WO_6:Eu^{3+} (λ_{em} = 615nm), (b) Sr_3WO_6:Eu^{3+} (λ_{em} = 616nm) and (c) Ba_3WO_6:Eu^{3+} (λ_{em} = 614nm).
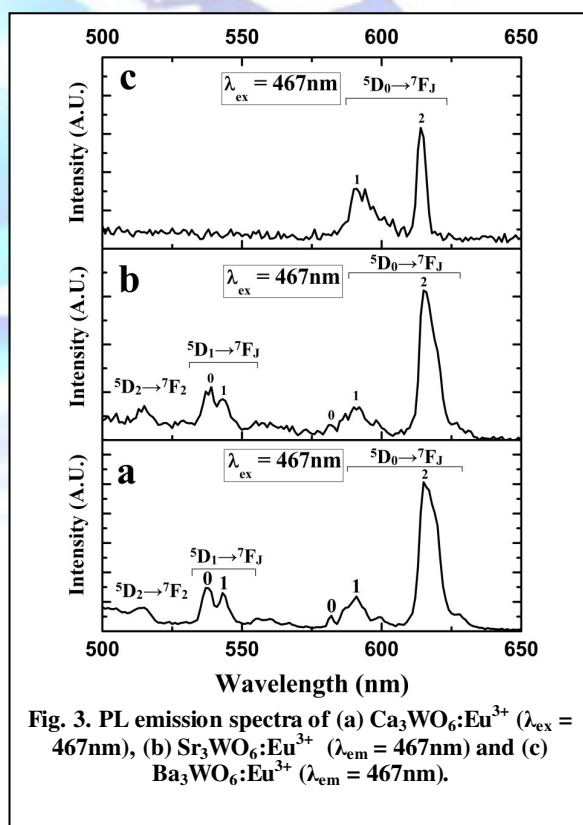
Fig. 3. PL emission spectra of (a) Ca_3WO_6:Eu^{3+} (λ_{ex} = 467nm), (b) Sr_3WO_6:Eu^{3+} (λ_{em} = 467nm) and (c) Ba_3WO_6:Eu^{3+} (λ_{em} = 467nm).

tungstate based phosphors [26,27].

The room temperature PL emission spectra of M_3WO_6:Eu^{3+} (2mol%) (M =Ca, Sr and Ba) under the blue light excitation of 467nm is shown in **Fig. 3a-c**. The emission spectrum of Eu^{3+} doped Ca_3WO_6 phosphor consists of intense and sharp characteristic peaks at 514, 537, 543, 582, 591 and 615nm which are attributed to $^5D_I \rightarrow ^7F_J$ (I, J = 0, 1 and 2) transitions of Eu^{3+} ion. It is seen that the nature of emission spectrum of Eu^{3+} doped Sr_3WO_6 phosphor is same as that of Eu^{3+} doped

Ca_3WO_6 phosphor; however, the emission spectrum of Eu^{3+} doped Ba_3WO_6 phosphor shows only two peaks at 590nm and 614nm which are attributed to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions respectively, and the emission related to transition from higher states ($^5D_{1,2}$) is not observed. It is worthwhile to note that in all three emission spectra show most intense emission peak at around 615nm in red region which is attributed to $^5D_0 \rightarrow {}^7F_2$ transition. This red emission from Eu^{3+} luminescence center has better perception to human eye. This red emission is attributed to ED ($^5D_0 \rightarrow {}^7F_2$) transition of Eu^{3+} which is forbidden electric dipole transition. However, admixture of odd-parity electronic configuration to the pure 4f one (like a non-centrosymmetric crystal field component) can allow the ED transitions partially and their probability is much higher than the probability of parity-allowed MD ($^5D_0 \rightarrow {}^7F_1$) transition. The site symmetry of Eu^{3+} ion in the host lattice can be predicted by asymmetry ratio which can be defined as,

$$asymmetry\ ratio = \frac{I(^5D_0 \rightarrow {}^7F_2)}{I(^5D_0 \rightarrow {}^7F_1)}$$

Where, $I(^5D_0 \rightarrow {}^7F_2)$ and $I(^5D_0 \rightarrow {}^7F_1)$ are the intensities of ED and MD transitions respectively. The asymmetry ratio is greater than 1 when Eu^{3+} substituted at non-centrosymmetric site and the ratio is less than 1 when Eu^{3+} substituted at centrosymmetric site in the host lattice. In present case the asymmetric ratio is found to be 4.39 ($Ca_3WO_6:Eu^{3+}$), 4.54 ($Sr_3WO_6:Eu^{3+}$) and 2.01 ($Ba_3WO_6:Eu^{3+}$) which indicates that Eu^{3+} is substituted at A site in the host lattice and this is in good agreement with the earlier report [21-25]. This could be understood that the substitution of Eu^{3+} at M^{2+} site in M_3WO_6 is accompanied by M^{2+} ion vacancy (V_M) (due to charge imbalance) and lattice strain (due to different ionic radius). These defects in lattice reduce the local site symmetry at Eu^{3+} site and also act as luminescence quenching center. The improvement in emission intensity could be achieved by introducing Na^+ ion which will act as charge compensator and reduces lattice strain [24]. The effects of Eu^{3+} concentration on the intensity of red emission peak were also performed and the results of which are displayed in **Fig. 4a-c**. It is seen that the intensity of red emission peak increases with increase in Eu^{3+} concentration without quenching up to 2mol%.
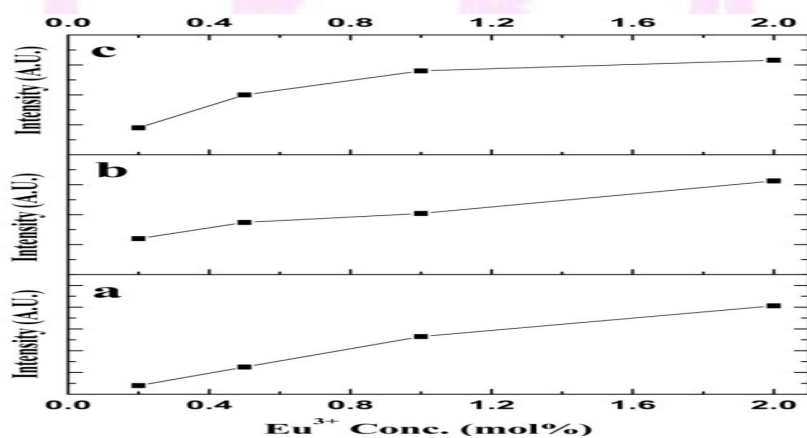

Fig. 4. Variation of emission intensity of (a) $Ca_3WO_6:Eu^{3+}$ (615nm), (b) $Sr_3WO_6:Eu^{3+}$ (616nm) and (c) $Ba_3WO_6:Eu^{3+}$ (614nm) with molar concentration of Eu^{3+}.

4. Conclusion

The Eu^{3+} doped microcrystalline samples of M_3WO_6 (M = Ca, Sr and Ba) phosphor were successfully synthesized via modified solid state reaction method. The XRD patterns reveal the formation of well crystallized and phase pure samples. The nature of excitation spectra of Eu^{3+} activated M_3WO_6 phosphors is very similar for M = Ca, Sr and Ba. The characteristic intense red emission of Eu^{3+} ion in M_3WO_6 shows occupation of non-centrosymmetric site by Eu^{3+} ion in the host lattice. The Eu^{3+} activated M_3WO_6 phosphors did not show concentration quenching up to 2mol% concentration of Eu^{3+} ion in the host lattice. The energy transfer from $(WO_6)^{6-}$ complex to Eu^{3+} ion is the matter of interest for the development of the phosphor for SSL application but future work has to be done in order to improve the absorption in near UV region.

6.References

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