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Novel phosphors of $ALaLiWO_6:Dy^{3+}$ (A = Sr^{2+} and Ba^{2+}) for white light applications

Parag Nimishe[1], S.J. Dhoble[2]

Department of Physics, RTM Nagpur University, Nagpur 440033, India

*Corresponding author. E-mail: paragnimishe@gmail.com, sjdhoble@rediffmail.com

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ABSTRACT

In this paper we report the synthesis and luminescence of Dy^{3+} activated tungstates of the type $ALaLiWO_6$ (where A = alkaline earth metals Sr and Ba), prepared by solid state diffusion reaction method. These novel luminescent tungstate materials were characterized by X-ray diffraction, scanning electron microscope (SEM) and photoluminescence (PL) techniques. The Dy^{3+} activated $ALaLiWO_6$ (where A = Sr and Ba) phosphors are effectively excited around 350 nm which is mercury free excitation in near UV and give a broad emission band peaking around 470 nm(blue region) along with a sharp characteristic peak at 577 nm (yellow region). Thus, the Dy^{3+} activated $ALaLiWO_6$ phosphors may be used in white light applications. Copyright © 2011 VBRI press.

Keywords: Phosphors; white lighting; photoluminescence; XRD, SEM.

Parag Nimishe did his M. Sc. in Physics from Pt. Ravishankar Shukla University,Raipur in the year 1987. Subsequently, he joined K.D.K. College of Engineering, Nagpur, as a lecturer. After working there for nearly 12 years, he was appointed the Principal of Bhalerao Science College, Saoner, Distt. Nagpur, MS, India. Presently, along with his regular administrative and teaching responsibilities he is engaged in the research in the area of luminescence and has a good number of publications in national and international journals. Recently, he presented a paper in the International congress on advanced materials, held at University of Jinan, China.

S.J. Dhoble obtained M.Sc. degree in Physics from Rani Durgavati University, Jabalpur, India in 1988. He obtained his Ph.D. degree in 1992 on Solid State Physics from Nagpur University, Nagpur. Dr.S.J. Dhoble is presently working as an Associate Professor in Department of Physics, R.T.M. Nagpur University, Nagpur, India. During his research carrier, he is involved in the synthesis and characterization of solid state lighting nanomaterials as well as development of radiation dosimetry phosphors using thermoluminescence, mechanoluminescence and lyoluminescence techniques. Dr. Dhoble published several research papers in International reviewed journals on solid-state lighting, LEDs, radiation dosimetry and laser materials. He is an executive member of Luminescence Society of India.

Introduction

Recently, interest in mixed tungstates i.e. having more than one cations, with their structure related to the $CaWO_4$ scheelite-type, has considerably increased because they have been recognized as the important optical materials [**1**]. The introduction of rare earth ions into these tungstates as activators has gone a long way in improving their luminescence properties [**2-5**]. Therefore, the scope of the applications of rare earth activated tungstate compounds have also widened greatly. More recently, double tungstate (with two cations) single crystals have become very attractive materials as laser hosts due to their large rare-earth ion admittance [**6-7**]. However, the studies on rare earth activated double tungstates are mostly confined to their LASER applications [**8-11**]. Their application in Light Emitting Diodes (LEDs) and White Light Emitting Diodes (WLEDs) have not been investigated adequately. White light-emitting diodes (W-LEDs) offer benefits such as high luminous efficiency, low energy consumption, long lifetime, and environment friendly and so on. They are tipped to be the next generation solid state lighting [**12**]

The preparation and general properties of this type of tungstates were reported by Brixner [**13**] and Singh et al.[**14**]. However, to the best of our knowledge, the luminescent properties of the lanthanum activated mixed tungstates and their possible applications in other fields like scintillation and solid state Lighting (SSL), have not been investigated and reported adequately so far. Here, we are reporting the synthesis of a family of tungstate compounds with formula $ALaLiWO_6:Dy^{3+}$ (where A = Sr, Ba),

alongwith their characterization and possible Solid State Lighting (SSL) applications in generation of white light.

Experimental

The undoped and Dy^{3+} doped $ALaLiWO_6$ compounds were prepared by the Solid State diffusion reaction technique. The analar grade 99.9% pure chemicals $A(NO_3)_2$, La_2O_3, $LiNO_3$, Dy_2O_3 and WO_3 were used as starting materials. The concentration of Dy^{3+} ions was in the range of 0.05- 1mol%. All the chemicals were weighed in stoichiometric proportion, mixed and then crushed in an agate mortar pestle thoroughly. Nitrates being hygroscopic in nature, the mixture therein became wet on crushing. It was dried at 200^0C in an electric oven for one hour and crushed again. The dried mixture in the powder form was put in a resistive furnace to heat it while increasing its temperature gradually at the rate of 5^0C/minute till it reached 800^0C. It was taken out and mixed in mortar pestle again for the reaction to take place efficiently. After that, it was heated at a fixed temperature of 800^0C for 24 hrs. Finally, the phosphors, thus prepared, were allowed to cool down to room temperature slowly.

The prepared phosphors were characterized for their phase purity and crystallinity by X-ray powder diffraction (XRD) using PAN-analytical analytical XPert PRO X-ray diffractometer with Cu-K*á* radiation of wavelength 1.54 AU, at a scanning step of 0.01^0, for continue time of 20s, in the range of $2\theta = 10^0$ to 80^0. The surface morphology and particle size of the rare earth doped tungstate phosphors prepared in the present investigation were studied using an FEI Philips-XL-30 model of scanning electron microscope (SEM). The photoluminescence measurement of excitation and emission were recorded on the Shimadzu RF5301PC Spectrofluorophotometer. The same amount of sample (2g) was used for each measurement. Emission and excitation spectra were recorded using spectral slit width of 1.5 nm.

Results and discussion

XRD pattern

Fig. 1 and **2** show the X-ray diffraction (XRD) patterns of $SrLaLiWO_6$ and $BaLaLiWO_6$ respectively. To the best of our knowledge, there are no standard JCPDS files for these compounds. However, The XRD patterns of $BaLaLiWO_6$ compound is well in line with the XRD pattern of $BaLaLiWO_6$:Nd^{3+} reported by Dan Zhao et al [**15**]. It was observed that, the doping of $Dy3^+$ion in these compounds does not change the XRD patterns significantly. Because the small amount of doped rare earth ions has virtually no effect on the phase structures [**16**].

The obtained patterns do not indicate the presence or traces of reactants which is an indirect evidence of formation of desired compounds. This also indicates the completion of the reaction. The patterns indicate that the final products are formed in homogeneous form.

Morphophological characterizations

The scanning electron microscopic images of $BaLaLiWO_6$ and $SrLaLiWO_6$ are shown in **Fig. 3** (**a**) and (**b**) respectively. The morphological studies performed using the scanning electron microscope (SEM) techniques show that all the compounds are in fluffy and porous form. This may be due to the agglomeration of the material. The individual particles are scarcely seen in **Fig. 3** (**a**) of $BaLaLiWO_6$ and **Fig. 3** (**b**) of $SrLaLiWO_6$.

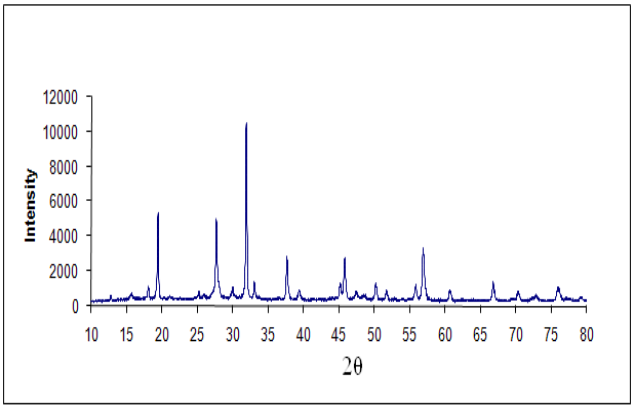

Fig. 1. XRD of $SrLaLiWO_6$.

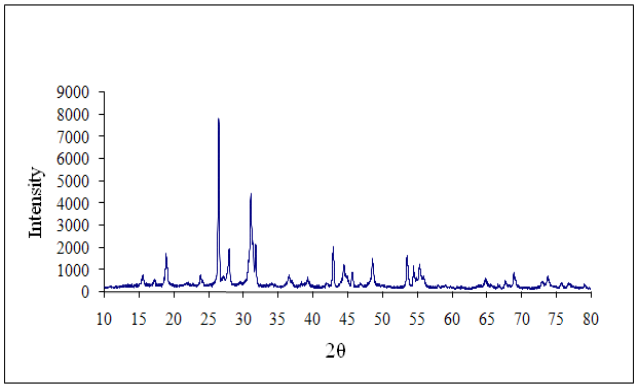

Fig. 2. XRD of $BaLaLiWO_6$.

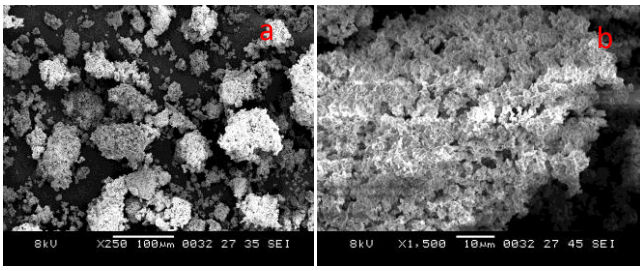

Fig. 3. SEM image of (**a**) $BaLaLiWO_6$ (**b**) $SrLaLiWO_6$.

PL properties of $SrLaLiWO_6$:Dy^{3+} and $BaLaLiWO_6$:Dy^{3+}

The excitation spectra of $SrLaLiWO_6$:Dy^{3+} and $BaLaLiWO_6$:Dy^{3+} phosphors were observed at 350 and 352 nm respectively. Thus, the excitation wavelengths of all the three phosphors fall in the near ultraviolet (NUV) region of the electromagnetic spectrum. They are shown here in **Fig. 4** and **6**, respectively. Under these excitations, the as prepared compounds $SrLaLiWO_6$:Dy^{3+} and $BaLaLiWO_6$:Dy^{3+} show a very broad emission spectra over the region of 370-550 nm, as seen in **Fig. 5** and **7**. The characteristic intrinsic luminescence of the hosts, due

to the WO_6^{-6} ion, lies in this region. In all the compounds, this major emission broad band is peaking around 470 nm. In addition, another sharp characteristic peak around 570 nm is also observed in the emission spectra.

The band located at 570 nm (yellow) corresponds to the hypersensitive transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$ ($D_L = 2$, $D_J = 2$), and another band located at 470 nm (blue) is due to the transition $^4F_{9/2} \rightarrow {}^6H_{15/2}$. Thus, it can be seen that the characteristic peak of Dy^{3+} ion at 470 nm falls in the region of characteristic broad band (370-550 nm) of the hosts $ALaLiWO_6$ as mentioned above. The results of analysis indicate that the hosts absorb excitation energy, then transfers part of the energy to rare-earth ions Dy^{3+}, and this is followed by luminescence of Dy^{3+}. The resonant transfer of energy is preferable.

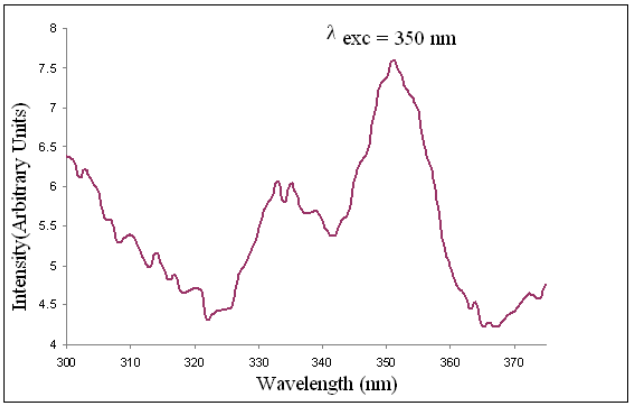

Fig. 4. The Excitation spectra of $SrLaLiWO_6:Dy^{3+}$.

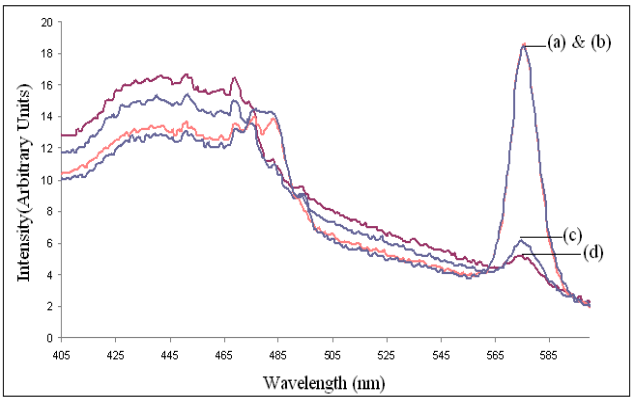

Fig. 5. The Pl emission spectra of $SrLaLiWO_6:Dy^{3+}$ showing peak intensities of emission at 577 nm (**a**) 0.5mol % (**b**)18.419mol % (**c**)0.05mol% and (**d**) 0.1mol%.

On the comparison of intensities it is seen that the characteristic emission at 470 nm of $SrLaLiWO_6:Dy^{3+}$ is more intense than $BaLaLiWO_6:Dy^{3+}$. These phosphors also show very weak concentration quenching at 5mol% of Dy^{3+}ion which gives the liberty to enhance the intensity of emission by increasing the concentration of the dopant. Also, as the emission spectra show the emission of blue and yellow colors, it is possible to obtain near-white emission with only Dy^{3+}-activated luminescence materials, by adjusting the yellow-to-blue intensity ratio (Y/B) value appropriately. Therefore, the Dy^{3+} activated $ALaLiWO_6$ phosphors are promising white light phosphors and can be used in mercury-free lamps. For mercury-free lamps, the excitation energy is mainly composed of VUV radiation but VUV energy is mostly absorbed by the host crystal, if the energy can be transferred from host to rare-earth (RE) ions then the rare earth ions can emit visible light. So the host absorption intensity is very important for VUV-excited phosphors applied in mercury-free lamp.

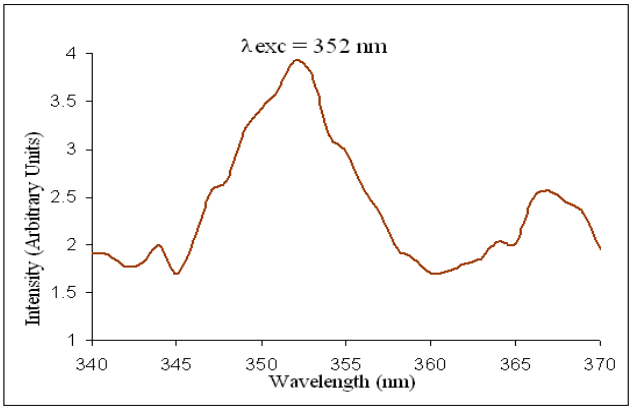

Fig. 6. The excitation spectra of $BaLaLiWO_6 : Dy^{3+}$.

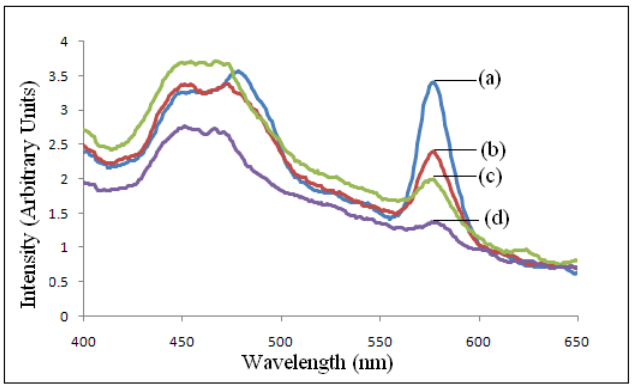

Fig. 7. The Pl emission spectra of $BaLaLiWO_6:Dy^{3+}$ showing peak intensities of emission at 577 nm corresponding to (**a**) 0.05mol% (**b**) 0.1 mol% (**c**) 0.2mol% and (**d**) 0.5mol%.

Conclusion

The Dy^{3+} activated $ALaLi(WO_4)_2$ (where A = Sr and Ba) phosphors synthesized by the solid state diffusion reaction method. They were found to be in homogeneous form and free from the traces of constituent reactants. This was confirmed from their XRD and photoluminescence characterizations. The morphological studies performed using the scanning electron microscope (SEM) techniques show that the all the compounds are in a fluffy and porous form. The individual particles are scarcely seen and are observed to have dimensions of the order of 100 nm. In the Dy^{3+} activated $ALaLiWO_6$ (where A = Sr and Ba) phosphors there are two emission bands located at 570 nm (yellow) and 470 nm(blue) when they are excited by the radiation of wavelength around 350 nm. By adjusting the yellow-to-blue intensity ratio (Y/B) value appropriately, it is possible to obtain near-white emission with only Dy^{3+}-activated luminescence materials. Therefore, the Dy^{3+} activated $ALaLiWO_6$ (where A = Sr and Ba) compounds

are promising white light phosphors and can be used in mercury-free lamps.

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