Synthesis and photoluminescence characterization of Ce^{3+} and Dy^{3+} activated $ALa(WO_4)_2$(A = Na and Li) novel phosphors

PARAG NIMISHE and S J DHOBLE[*]

Department of Physics, RTM Nagpur University, Nagpur 440 033, India

Abstract. In this paper, we report the synthesis of Ce^{3+} and Dy^{3+} activated alkali lanthanide tungstates, $ALa(WO_4)_2$(where A = Na and Li), prepared by solid state reaction method. The prepared phosphors were characterized by X-ray diffraction and photoluminescence techniques. The $NaLa(WO_4)_2$:Dy^{3+} and $LiLa(WO_4)_2$:Dy^{3+} phosphors show two emission peaks at around 574 and 486 nm (λ_{exc} = 354 nm). $NaLa(WO_4)_2$:Ce^{3+} and $LiLa(WO_4)_2$:Ce^{3+} show two emission peaks at around 378 and 425 nm (λ_{exc} = 350 nm). Excitation wavelengths of Ce^{3+} and Dy^{3+} activated alkali lanthanide tungstates are in near UV region i.e. Hg free excitation. These characterizations of phosphors are applicable for solid state lighting. Accordingly, Ce^{3+} and Dy^{3+} activated $NaLa(WO_4)_2$ and $LiLa(WO_4)_2$ may be the promising materials for solid state lighting applications.

Keywords. XRD; photoluminescence; NUV excitation; novel phosphor; solid state lighting.

1. Introduction

The light emitting diode (LED) has attracted great attention for use as an illuminator for solid-state lighting (Feldmann *et al* 2003; Schubert and Kim 2005). There are several approaches for a white light source using LEDs. Among them the phosphor-based white light source is the most promising. In this system, three red, green and blue phosphors absorb near-UV light from the UV-LED, generating white light. Even though many phosphors for white LEDs are currently available, blue, yellow, green and red phosphors still have problems associated with low brightness and chemical instability (Neeraj *et al* 2004; Schubert and Kim 2005). Therefore, demand for new blue, yellow, green and red phosphors applicable to white LEDs has increased. Most phosphors show a tendency toward strong energy absorption in the region of wavelengths <300 nm due to the charge transfer and $4f_{n-4}f_{n-1}5d$ transition of lanthanide ions (Blasse and Grabmaier 1994). However, the LED used in solid-state lighting provides near-UV light in the range 380–410 nm, which necessitates the new blue, yellow, green and red phosphors to be excited by these wavelengths in the range and to produce high brightness.

The tungstates show a distinctive polymorphic structure (Mokhosoev *et al* 1978; Tzunov *et al* 1986). There are several tungstates like $MgWO_4$, $AlWO_4$ and others which are monoclinic, whereas $CaWO_4$, $SrWO_4$, $BaWO_4$ are tetragonal. The polymorphism is observed in alkai double tungstates too. Among the compounds being reported herein, $KLa(WO_4)_2$ shows monoclinic structure. In $CaWO_4$(Scheelite), the Ca^{2+} ion can be replaced alternately by a monovalent A^+ ion and a trivalent lanthanide ion, Ln^{3+} and can then be written as $ALn(WO_4)_2$.

Excellent mechanical (Dieke 1968), thermal and chemical (Shao *et al* 2009) stabilities of $ALn(WO_4)_2$ are of prime importance from the point of view of their technological and commercial applications. We have chosen La^{3+} cation to represent the lanthanide cations, Ln^{3+}, in $ALn(WO_4)_2$ materials. In tungstate compounds, W^{6+} is coordinated by four oxygen atoms in a tetrahedral site, and the rare-earth/sodium (or lithium) ions occupy eight-coordinated sites.

The alkali rare earth tungstates have been studied so far mostly from the view point of their laser applications. Luminescence characterization of these materials has not been studied much for their lighting applications. Moreover, the luminescent properties of all the potential activators such as Ce^{3+} and Dy^{3+} activated ions have not been adequately studied. Only a few ions like Nd^{3+}, Sm^{3+}, Tm^{3+}, Yb^{3+} (Güell *et al* 2007), Ho^{3+} (Kasprowicz *et al* 2007), Er^{3+} (Mateos *et al* 2002) etc are reported as good activators in tungstate hosts for laser applications. This is probably because of the fact that Ce^{3+} and Dy^{3+} ions doped systems are not promising laser materials as other rare earth based systems. However, they can be excellent phosphor materials. Recently, Gu *et al* (2010) reported results of the morphological and luminescent studies of $NaLa(WO_4)_2$:Eu synthesized by hydrothermal process. Tang and Wang (2004) synthesized the $KLa(WO_4)_2$:Yb^{3+} crystals and Huang *et al* (2004) synthesized $LiLa(WO_4)_2$:Nd^{3+} crystals by CZ method and investigated the absorbance and emission spectra for laser applications. The family of alkali lanthanide tungstate compounds,

---

*Author for correspondence (sjdhoble@rediffmail.com)

generally represented by the formula, $ALn(WO_4)_2$, where A and Ln are alkali and lanthanide cations, respectively has shown many interesting properties which find their applications in laser host materials (Kaminskii *et al* 1996; Liu *et al* 2005; Garcia-Cortes *et al* 2007), phosphors of LED, X-ray detectors (Kaminskii *et al* 1999; Neeraj *et al* 2004) etc. They are also used as a cooling agent in adiabatic demagnetization for obtaining very low temperatures (Kovács *et al* 2005). Therefore, now a days Ce^{3+} and Dy^{3+} activated novel alkali lanthanide tungstates have become interesting materials in the field of lighting.

As mercury lamps are posing alarming environmental problems, it is the need of the hour to develop technology to produce mercury-free lamps. Under this condition, what is the new lighting system of the near future? White

LEDs and organic ELs are possible candidates. However, both technologies are faced with knotty problems for lighting applications. Recently, luminescence materials doped with Dy^{3+} have drawn much interest for their white emission (Dominiak-Dzik *et al* 2004; Xiu *et al* 2006; Liang *et al* 2008). In general, Dy^{3+} has two dominant bands in the emission spectra in many host matrices. The band located at 571 nm (yellow) corresponds to the hypersensitive transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (DL = 2, DJ = 2), and another band located at 478 nm (blue) is due to the transition $^4F_{9/2} \rightarrow {}^6H_{15/2}$. 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 phosphors are promising white light phosphors and can be used in mercury-free lamps. For
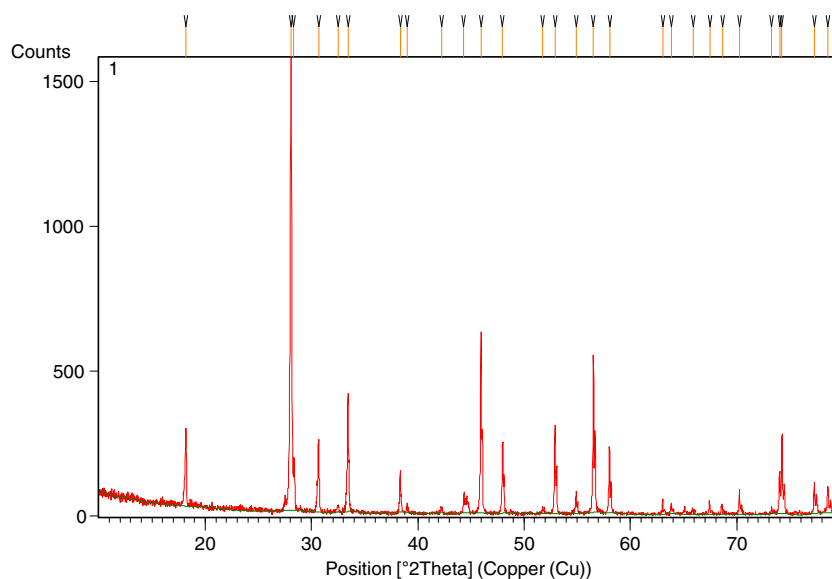


Figure 1. X-ray diffraction pattern of $NaLa(WO_4)_2$.
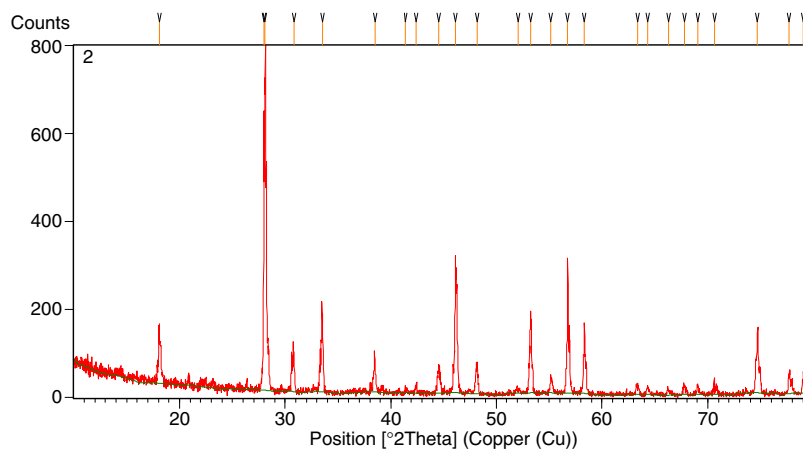
Figure 2. X-ray diffraction pattern of $LiLa(WO_4)_2$.

mercury-free lamps, the excitation energy 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.

Accordingly, mercury-free lamp novel luminescent materials with improved properties are in high demand. In this paper, we report on the preparation and photoluminescence characterization of novel Ce^{3+} and Dy^{3+} activated alkali lanthanide tungstates, $ALa(WO_4)_2$ (where A = Na and Li) phosphors prepared by the solid state diffusion method. To the best of our knowledge, this is for the first time that Ce^{3+} and Dy^{3+} activated $ALa(WO_4)_2$ (where A = Na and Li) phosphors, synthesized through this approach towards their application in the solid state lighting, are reported.
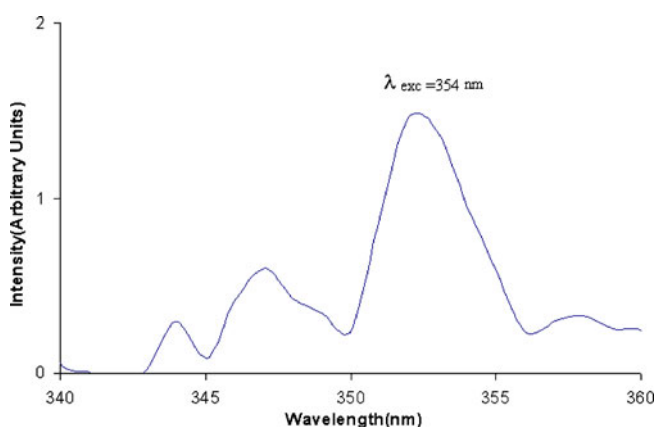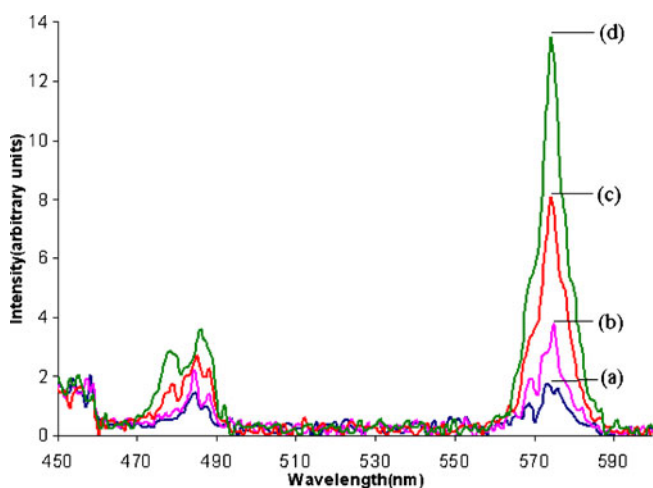
2. Experimental

All the three phosphors, viz. $NaLa(WO_4)_2:Dy^{3+}$ and $LiLa(WO_4)_2:Dy^{3+}$ were prepared by the well known solid state reaction method. The starting chemicals, ANO_3 (where A = Na or Li), La_2O_3, Dy_2O_3/Ce_2O_3 and WO_3 with high purity of 99·9% were used. They were taken in stoichiometric amounts. The Dy^{3+} concentrations were varied from 0·1 to 1 mol%. The starting materials were mixed thoroughly for 1 h using the agate mortar pestle. The crushed samples were placed in a silica crucible and heated at 300°C in muffle furnace for 3 h. Then, they were removed, crushed in the mortar pestle again and heated at 800°C for 24 h. They were mixed intermittently. The stoichiometric reaction of the synthesized compounds is shown below. Finally, the samples in the furnace were allowed to cool down to room temperature.

$$4ANO_3 + 2La_2O_3 + 8WO_3 \rightarrow 4ALa(WO_4)_2 + 2NO_2 + O_2,$$
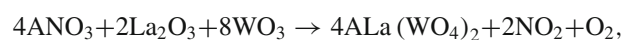
where A = Na or Li.

Several complementary methods were used to characterize the prepared phosphor. The prepared host lattice was characterized for their phase purity and crystallinity by X-ray powder diffraction (XRD) using PAN-analytical diffractometer (Cu-Kα radiation) at a scanning step of 0·01°, continue time 20 s, in the range of 2θ from 10° to 120°; the average crystallite size was calculated from the broadening of the X-ray line (311) using Scherrer's equation. The surface morphology and particle size of the rare earth doped tungstate phosphors prepared in the present investigation were studied using scanning electron microscope. The photoluminescence measurement of excitation and emission were recorded on a Shimadzu RF5301PC Spectrofluorophotometer. The same amount of sample, 2 g, was used for each measurement. Emission and excitation spectra were recorded using a spectral slit width of 1·5 nm.
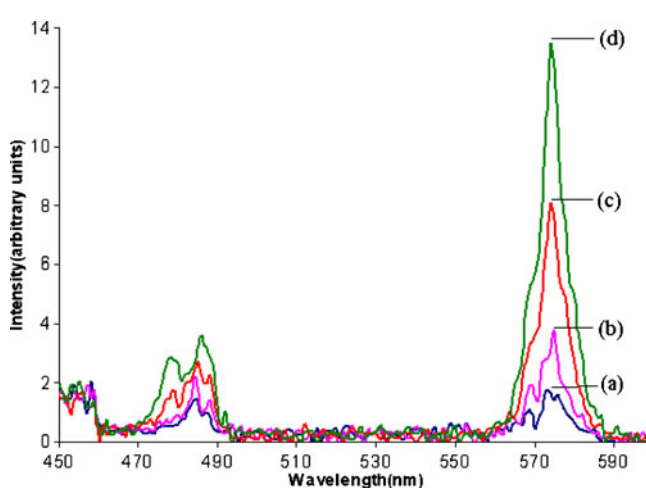

Figure 3. Excitation spectra of $NaLa(WO_4)_2:Dy^{3+}$ and $LiLa(WO_4)_2:Dy^{3+}$, monitored at 574 nm.

Figure 4. Emission spectra of $NaLa(WO_4)_2:Dy^{3+}$ at λ_{exc} = 356 nm, corresponding to Dy^{3+} concentrations: (a) 0·1 m%, (b) 0·2 m%, (c) 0·5 m% and (d) 1 m%.

Figure 5. Emission spectra of $LiLa(WO_4)_2:Dy^{3+}$ at λ_{exc} = 354 nm, corresponding to Dy^{3+} concentrations: (a) 0·1 m%, (b) 0·2 m%, (c) 0·5 m% and (d) 1 m%.

3. Results and discussion

3.1 *X-ray diffraction pattern*

Figures 1 and 2 show the X-ray diffraction (XRD) pattern of $NaLa(WO_4)_2$ and $LiLa(WO_4)_2$. Both the XRD patterns match well with the standard JCPDS file nos 79-1118 and 25-0829, respectively. The XRD patterns of these compounds do not indicate the presence or traces of reactants which is an indirect evidence of formation of desired compounds. The patterns also indicate that the final products i.e. $NaLa(WO_4)_2$ and $LiLa(WO_4)_2$, are formed in homogeneous form. Their calculated lattice parameters are in accordance with those of the JCPDS cards.

It is worth noting that no change is seen in the structures of the above compounds after doping of Dy^{3+} or Ce^{3+} ions.

3.2 *Photoluminescence characterization*

The excitation spectra of $NaLa(WO_4)_2$:Dy^{3+} and $LiLa(WO_4)_2$:Dy^{3+} phosphors are observed at 354 nm in both the phosphors (monitored at 574 nm). Therefore, only the excitation spectrum of $LiLa(WO_4)_2$:Dy^{3+} is shown here in figure 3. The emission spectra of $NaLa(WO_4)_2$:Dy^{3+} and $LiLa(WO_4)_2$:Dy^{3+} compounds, observed in the range of 400–650 nm while keeping excitation wavelength at 354, are shown in figures 4 and 5.

The PL emission is observed at 486 and 574 nm to have strikingly similar nature in both the phosphors, differing only in their relative PL peak intensity values. The PL emission peaks are observed at 574 nm in the yellow and 486 and 426 nm in the blue regions of visible spectrum, respectively. The peak at 574 nm is due to $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition of electric dipole moment whereas that at 486 nm is due to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition of magnetic dipole due to Dy^{3+}

ion. The 426 nm peak is observed due to the splitting of magnetic dipole moment. The peak intensities at wavelengths 574 and 486 nm are seen to be in increasing order with increasing concentration of Dy^{3+} ions and maximum intensity is observed in both phosphors at 1 mol% of ions. The PL intensity of $LiLa(WO_4)_2$:Dy^{3+} phosphor is higher than that of $NaLa(WO_4)_2$:Dy^{3+} phosphor.
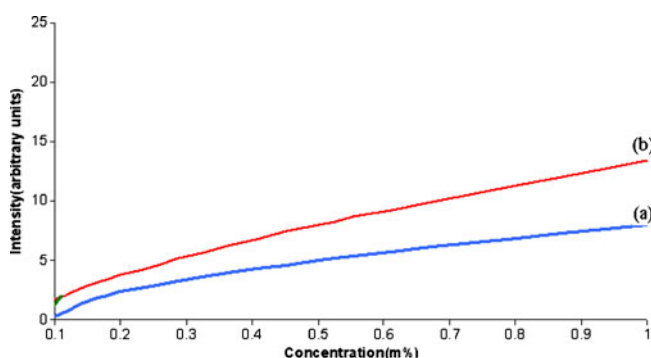
The PL emission increases with the concentration of activator ion, Dy^{3+} (1 mol%). In the present case, the Dy^{3+} ion may enter into the host lattice to substitute La^{2+} or Na^+/Li^+ or it may be located on surfaces of the crystals. The ionic radii of Dy^{3+} (91·2 pm) is much larger than Li^+ (76 pm) and smaller than La^{2+} (103·2 pm) and Na^+ (102 pm). The first possibility is more feasible. Most of the Dy^{3+} ions are entering into the lattice $LiLa(WO_4)_2$ as compared to $NaLa(WO_4)_2$ phosphor and few of them are located at the surface. Its substitution at Li^+ site in $NaLa(WO_4)_2$ will lead to more distortion in the host in comparison to its substitution in $NaLa(WO_4)_2$ phosphor. Monovalent cations are charge compensates to divalent and trivalent ions, developed the symmetry in host lattice. The charge compensating defects in the immediate vicinity is likely to influence the local site symmetry of activator in the host lattics. This is reflected in the emission spectra, wherein asymmetry factor is higher in $LiLa(WO_4)_2$ sample compared to $NaLa(WO_4)_2$ phosphor. As Dy^{3+} ions progressively replace the Li^+ ions, an increase in PL emission intensity is observed and asymmetry factor progressively reduced. The low-symmetry location of Dy^{3+} results in predominant emission of $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition. Hence, $LiLa(WO_4)_2$ phosphors show strong PL emission intensity as compared to $NaLa(WO_4)_2$ phosphor when Dy is doped as shown in figure 5. Usually, a low doping gives weak luminescence, but excess doping perhaps causes quenching of luminescence. The maximum intensity of Dy^{3+} is observed at 1 mol% as shown in table 1.

Table 1. PL intensity comparison table.

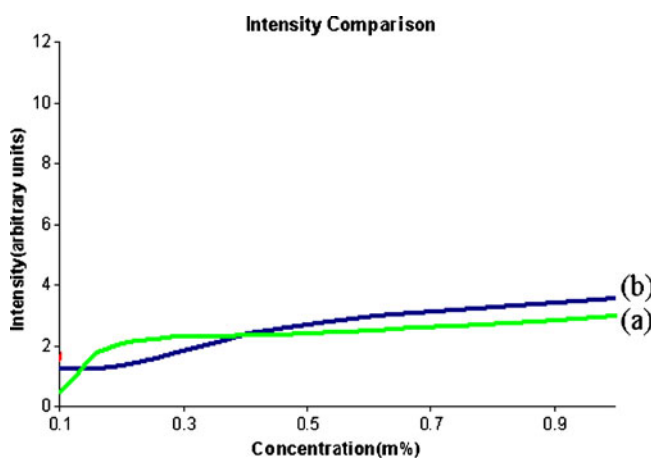| Compound	Wavelength (nm)	PL intensity (arb. units)
$NaLa(WO_4)_2$:$Dy_{0.1}$	573·9699, 485·07	8·0492, 0·4422
$NaLa(WO_4)_2$:$Dy_{0.2}$	573·9699, 485·07	4·9599, 2·0796
$NaLa(WO_4)_2$:$Dy_{0.5}$	573·9699, 485·07	2·3549, 2·392
$NaLa(WO_4)_2$:Dy_1	573·9699, 485·07	0·2796, 2·9586
$LiLa(WO_4)_2$:$Dy_{0.1}$	573·9699, 485·07	13·3872, 1·255
$LiLa(WO_4)_2$:$Dy_{0.2}$	573·9699, 485·07	08·0286, 1·37
$LiLa(WO_4)_2$:$Dy_{0.5}$	573·9699, 485·07	03·8095, 2·7208
$LiLa(WO_4)_2$:Dy_1	573·9699, 485·07	01·6591, 3·5788
$Nala(WO_4)_2$:Ce_1	379·0700, 425	39·3708, 5·2552
$NaLa(WO_4)_2$:Ce_2	378·0700, 425	25·1024, 4·2118
$NaLa(WO_4)_2$:Ce_5	378·0700, 425	25·5030, 4·2809
$NaLa(WO_4)_2$:Ce_{10}	378·0700, 426	28·5447, 3·07
$LiLa(WO_4)_2$:Ce_1	378, 423·9299	35·8330, 4·7918
$LiLa(WO_4)_2$:Ce_2	379, 425·0000	34·4780, 5·5437
$LiLa(WO_4)_2$:Ce_5	378, 423·9299	32·0117, 5·1754
$LiLa(WO_4)_2$:Ce_{10}	378, 423·9299	21·4725, 3·9379

The PL emission intensity comparison is shown in table 1 which gives the values of concentrations and corresponding peak intensities for all the three Dy^{3+} activated phosphors. For a better comparison, figures 6 and 7 are given which correspond to the peaks at 576 and 486 nm, respectively. It can be seen that amongst the three Dy^{3+} activated alkali double tungstate reported here, LiLa(WO$_4$)$_2$:Dy^{3+} shows the maximum intensities for all emission peaks.

Figure 8 shows schematic energy level diagram of Dy^{3+} ion. In general, Dy^{3+} has two dominant bands in the emission spectra in many host matrices. The blue emission band located at 486 nm due to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition and the band located at 576 nm (yellow) corresponds to the hypersensitive $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition. 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 phosphors are promising white light phosphors and can be used in mercury-free lamps.
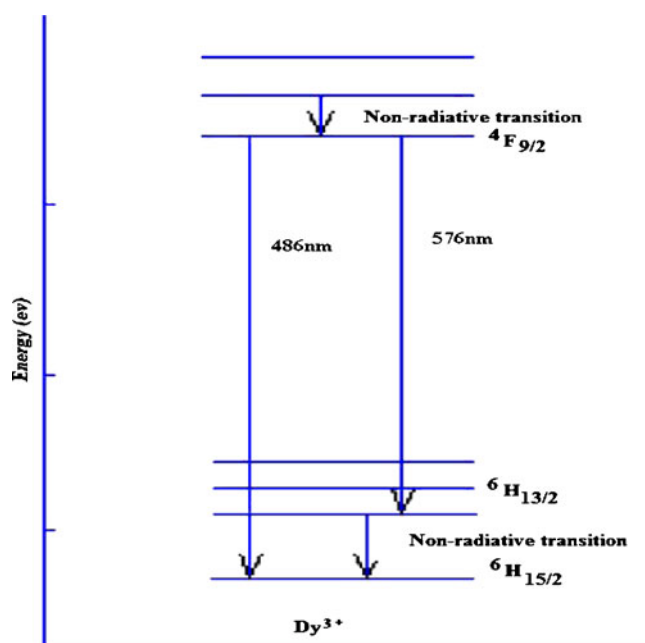
Ce^{3+} is a very good candidate for studying the behaviour of 5d electrons. Ce^{3+} has only one outer electron and only two spin-orbital splitting 4f states ($^2F_{5/2,\ 7/2}$). Thus, its excited state energy structure is simpler than that of the other trivalent rare-earth ions. The excitation spectra of the NaLa(WO$_4$)$_2$:Ce^{3+} and LiLa(WO$_4$)$_2$:Ce^{3+} are shown in figure 9, The excitation peak are observed in both the phosphors at 350 nm. The emission spectra of these phosphors, taken while keeping excitation wavelength at 350 nm, are shown in figures 10 and 11, respectively. In both the phosphors of NaLa(WO$_4$)$_2$:Ce^{3+} and LiLa(WO$_4$)$_2$:Ce^{3+}, the peaks are

Figure 6. PL intensity of 574 nm peak corresponding to Dy^{3+} concentrations for phosphors (a) NaLa(WO$_4$)$_2$:Dy^{3+} and (b) LiLa(WO$_4$)$_2$:Dy^{3+}.
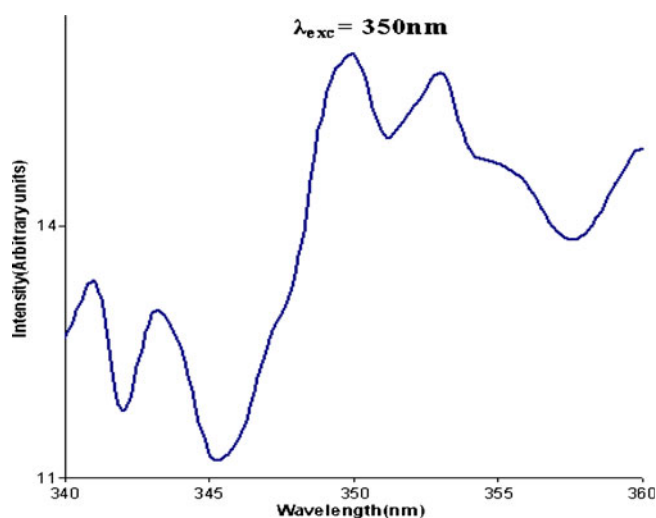

Figure 8. Schematic energy level diagram of Dy^{3+} ion.

Figure 7. PL intensity of 485 nm peak corresponding to Dy^{3+} concentrations for phosphors (a) NaLa(WO$_4$)$_2$:Dy^{3+} and (b) LiLa(WO$_4$)$_2$:Dy^{3+}.
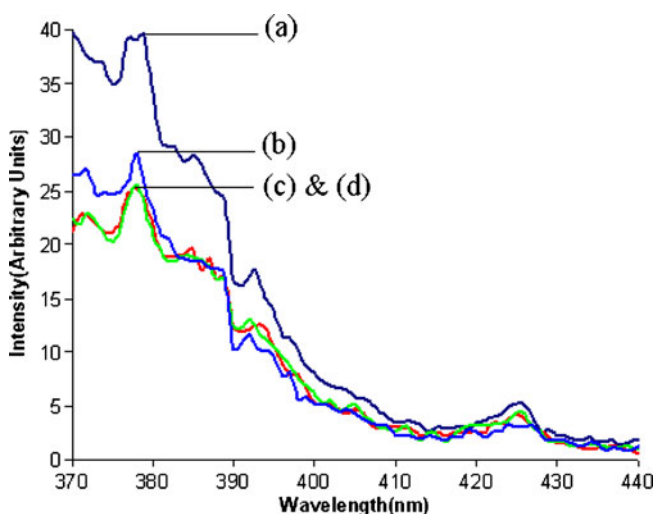

Figure 9. Excitation spectra of LiLa(WO$_4$)$_2$:Ce^{3+} monitored at nm.
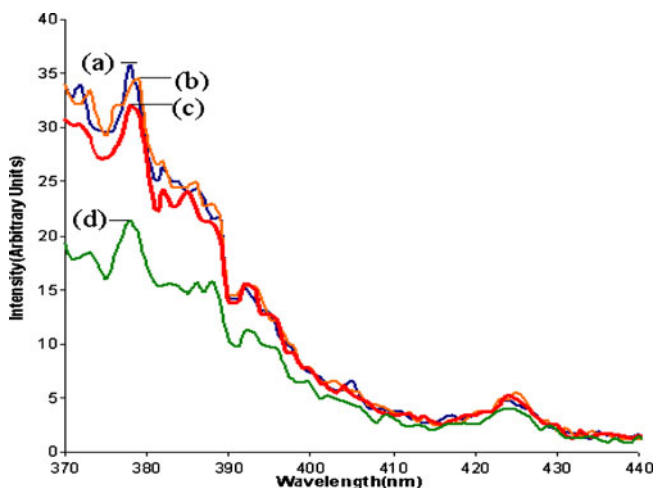
observed around 378 and 425 indicating UV and blue emissions, respectively. A shoulder around 393 nm is also seen. The UV emission around 380 nm is most intense. The maximum intensity of Ce^{3+} ion are observed at 1 and 2 mol% of Ce^{3+} ion among all the concentrations range from 01 to 10 mol% in $NaLa(WO_4)_2$:Ce^{3+} and $LiLa(WO_4)_2$:Ce^{3+} phosphors, respectively.

It is interesting to note, from figures 10 and 11 also, that the emission in both $NaLa(WO_4)_2$:Ce^{3+} and $LiLa(WO_4)_2$:Ce^{3+} has strikingly similar nature and differs only in their relative PL peak intensity values. From table 1, and figures 10 and 11, it is observed that the intensity of $LiLa(WO_4)_2$:Ce^{3+} is around similar intensity than that of $NaLa(WO_4)_2$:Ce^{3+} for all corresponding peaks.

4. Conclusions

The solid state diffusion method for synthesis of alkali rare earth double tungstates phosphors was found to be a suitable method for solid state lighting materials. It produced the desired phosphors in the homogeneous form; free from the traces of constituent reactants, which is confirmed from their XRD and photoluminescence characterization.

- The XRD characteristic shows the XRD data of prepared phosphors well match with standard XRD data.
- The photoluminescence studies of prepared phosphors, $NaLa(WO_4)_2$:Dy^{3+} and $LiLa(WO_4)_2$:Dy^{3+}, show the two emission peaks at around 574 and 486 nm ($\lambda_{exc} = 356$ nm).
- $NaLa(WO_4)_2$:Ce^{3+} and $LiLa(WO_4)_2$:Ce^{3+} phosphors PL characteristics show the two emission peaks at around 378 and 425 nm ($\lambda_{exc} = 350$ nm).
- Excitation wavelength of Ce^{3+} and Dy^{3+} activated alkali lanthanide tungstates in near UV region i.e. Hg free excitation, these characterization of phosphors is applicable for solid state lighting.
- Therefore, prepared Ce^{3+} and Dy^{3+} activated alkali lanthanide tungstates phosphors may be applicable for Hg free excited solid state low energy consumption lighting.

Figure 10. Emission spectra of $NaLa(WO_4)_2$:Ce^{3+}. Peaks at 378 nm correspond to concentrations of Ce^{3+} ions at (a) 1 m%, (b) 2 m%, (c) 5 m% and (d) 10 m%. Peaks at 25 nm for all concentrations almost overlap each other.

Figure 11. Emission spectra of $LiLa(WO_4)_2$:Ce^{3+}. Peaks at 378 nm correspond to concentrations of Ce^{3+} ions at (a) 1 m%, (b) 2 m%, (c) 5 m% and (d) 10 m%. Peaks at 425 nm for all concentrations almost overlap each other.

References

Blasse G and Grabmaier B C 1994 *Luminescent materials* (Berlin, Heidelberg; Springer) p. 42

Dieke G H 1968 *Spectra and energy levels of rare earth ions in crystals* (New York: Interscience Publishers)

Dominiak-Dzik G, Ryba-Romanowski W, Kovács L and Beregi E 2004 *Radiat. Meas.* **38** 557

Feldmann C, Jüstel T, Ronda C R and Schmidt P J 2003 *Adv. Funct. Mater.* **13** 511

García-Cortés A *et al* 2007 *IEEE J. Quantum Elect.* **43** 157

Gu J *et al* 2010 *Solid State Sci.* (in press)

Güell F, Massons J, Gavaldà Jna., Pujol M C, Aguiló M and Díaz F 2007 *Spain J. Appl. Phys.* **101** 033108

Huang X, Lin Z, Hu Z, Zhang L, Huang J and Wang G 2004 *J. Cryst. Growth* **269** 401

Kaminskii A A, Bagaev S N, Grebe D, Eichler H J, Pavlyuk A A and Macdonald R 1996 *Quantum Electron.* **26** 193

Kaminskii A A *et al* 1999 *Appl. Opt.* **38** 4533

Kasprowicz D, Mielcarek S, Trzaskowska A, Majchrowski A, Michalski E and Drozdowski M 2007 *Cryst. Res. Technol.* **42** 1370

Kovács L, Borowiec M T, Majchrowski A, Baraldi A and Capelletti R 2005 *Cryst. Res. Technol.* **40** 444

Liang X, Zhu C, Yang Y, Yuan S and Chen G 2008 *J. Lumin.* **128** 1162

Liu J *et al* 2005 *Phys. Status Solidi (a)* **4** R29

Mateos X, Pujol M C, Güell F, Solé R, Gavaldà Jna., Aguiló M, Díaz F and Massons J 2002 *Phys. Rev.* **B66** 214104

Mokhosoev M V, Alexeev F P and Lutsyk V I 1978 *Phase diagrams of molybdate and tungstate systems* (Nauka) p. 320 (in Russian)

Neeraj S, Kijima N and Cheetham A K 2004 *Chem. Phys. Lett.* **387** 2

Shao Q, Li H, Wu K, Dong Y and Jiang J 2009 *J. Lumin.* **129** 879

Schubert E F and Kim J K 2005 *Science* **308** 1274

Tang L and Wang G 2004 *J. Cryst. Growth* **274** 100033

Tzunov V K, Efremov V A and Velihkodnyi Yu A 1986 *Crystal-lochemistry and properties of double molybdates and tungstates* (Leningrad: Nauka) (in Russian)

Xiu Z L, Yang Z S, Lü M K, Liu S W, Zhang H P and Zhou G J 2006 *Opt. Mater.* **29** 431