The synthesis, characterisation and potential of Eu^{3+} doped molybdate phosphors for white light emitting diodes.

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ABSTRACT

A wide variety of Eu^{3+} doped molybdate phosphors were synthesised using the solid state reaction route and their photoluminescent properties were compared. Their crystal structures were investigated. A relationship between cell size and emission intensity was apparent. The implications of this for phosphor design are discussed.

1. INTRODUCTION

The mass production of the first "white light" light emitting diodes (LEDs) for solid state lighting used a broad band yellow phosphor emitting phosphor YAG:Ce coated on a blue GaN LED chip[1-3]. The white light thus obtained is by the additive-mixing of broad-band yellow light emitted by the phosphor together with some of the blue light from the LED[4-7]. However, the spectral composition of the light produced by the conventional two-band white LED differs from that of natural white light due to a halo effect of blue/yellow colour separation and poor colour rendering caused by the lack of a red component[8]. To improve this a separate red phosphor light source has been and is still the subject of intensive research to compensate for the red deficiency of the output light[9] and this is commercially limited to divalent europium ion activated phosphors[4,9]. Such phosphors include calcium and strontium sulfide[4,6]. These phosphors are chemically unstable and undesirable in efficiency[5,8,9] as are many of the metal nitrides.

There has been/is therefore the need to find suitable chemically stable alternative red emitting phosphors that can be activated by the blue light from LEDs. Although most of the phosphors used for red emission in pc-WLEDs have Eu^{2+} cations as activators there have been suggestions to use Eu^{3+} in certain lattices[10]. R^{3+} (where R = rare earth element) cations manifest spectra with f-f transitions (the electrons in the f orbitals are shielded from their surroundings, and thus largely unaffected by the external bonding though they are sensitive to the symmetry of the bonding). This shielding makes the emission and excitation bands very narrow. Eu^{3+} cations manifest a large energy gap (between the lowest luminescent energy state and the highest non-luminescent energy state) and can give rise to strong luminescence intensity.

In the last ten years a large number of papers have appeared that suggest phosphors based on the general formula AEu(MO$_4$)$_2$ (where A = Li$^+$, Ag$^+$, Na$^+$, K$^+$ or Rb$^+$: M = Mo or W or both and Eu^{3+} may be substituted by Y^{3+} and/or Sm^{3+} and/or the formulae are related but the cations or the ratio of the cations to anions differ) are good red emitters when excited by blue LED light[4,8-14] (this list of references is not comprehensive but in this publication, space is limited). Unfortunately none of these papers gave luminous efficacy measurements (LEMs) up to the time of our work.[15] In that work LEMs on some representative red phosphors of general formula LiEu$_{2-x}$Y$_x$(MoO$_4$)$_2$-$_x$(WO4)$_x$ were reported. We previously described how LEMs are made[6] and compared the values obtained to those of SrS:Eu^{3+}, CaS:Eu^{3+} (discussing the implications therein). The drawbacks of this approach were explained.[6] In addition we discussed how the excitation spectra can be broadened by the addition of a small amount of Sm^{3+} in place of Y^{3+}.

Despite these inherent drawbacks we are still working in this field. In this work, a number of different molybdate phosphors (claimed to be good candidates for red phosphors to convert blue LED light from the literature[4, 8, 9, 11-14]) were studied to examine factors affecting their emission intensity.

2. EXPERIMENTAL

The solid state reaction was employed as the method of syntheses for the various phosphors of formulation as stated in Table 1 below. Materials used were carbonates of barium, calcium, strontium, and zinc, oxides of europium, lanthanum, gadolinium, and molybdenum, and nitrates of magnesium and silver. The appropriate materials were speed mixed for a total time of six minutes at speeds ranging from 1500-3500rpm. Firings were conducted in air for three hours.

X-ray powder diffraction (XRPD) of the samples was performed using a Bruker D8 Advance X-ray powder diffractometer fitted with a CuKα source and LynxEye^{TM} silicon strip detector. The morphology and the particle size of the samples were determined using a Zeiss Supra 35 VP field emission scanning electron

microscope and using a JEOL 2000FX transmission electron microscope. Photoluminescence (PL) measurements were carried out using a Bentham Instruments dual excitation and emission monochromator system.

The luminous efficacies of all the samples were obtained using a bespoke phosphor research spectrometer system (Bentham Instruments Ltd., Reading, UK) which has the ability to measure the phosphor light output at elevated temperatures. The system uses a 215 high voltage power supply, 217 power supply and a display, TMc300 single grating monochromator with internal drive electronics and a xenon light source. The exciting light is introduced into an integrating sphere via a fibre optic cable and focused onto the sample. The power of the exciting light is measured using a $BaSO_4$ sample which is used to calculate the amount of light absorbed by the phosphor sample. All samples were measured at room temperature using 390 nm (or 395 nm) and 460 nm (or 465 nm) light excitation.

3. RESULTS AND DISCUSSION

The unit cell dimensions and cell volumes of some of the materials prepared in this work are presented in the Table. 1. The proportions of Eu^{3+} used were taken from the optimised work in the literature[4, 8, 9, 11-14] except that the Ba compound was not optimised previously[11] so we used the same amount as was used in the Ca[9] and Mg[12] phosphors (i.e. 0.24). In addition we decided to use the 0.24 concentration for the Sr[13] and Zn[14] molybdates (to be more uniform) though papers reported that 0.25 and 0.20 were best. For the two Ag compounds we used the literature values.[4, 8] The main structural type is the scheelite-type tetragonal phase.

Table 1. Cell type lattice parameters and cell volume where the structures are tetragonal.

Phosphor	Structure	Lattice parameters (Å)	Cell volume (Å³)
$Mg_{0.76}Eu_{0.24}MoO_4$	Monoclinic		
$Ca_{0.76}Eu_{0.24}MoO_4$	Tetragonal	a=5.2266(1) c=11.4375	312.44(1)
$Sr_{0.76}Eu_{0.24}MoO_4$	Tetragonal	a=5.3904(1) c=11.9922(3)	348.45(1)
$Ba_{0.76}Eu_{0.24}MoO_4$	Tetragonal	a=5.5778(1) c=12.7971(3)	398.14(1)
$Zn_{0.76}Eu_{0.24}MoO_4$	Triclinic		
$AgGd_{0.70}Eu_{0.30}(MoO_4)_2$	Tetragonal	a=5.2673(1) c=11.5771(3)	321.20(1)
$AgLa_{0.70}Eu_{0.30}(MoO_4)_2$	Tetragonal	a=5.3358(1) c=11.7046(3)	333.24(1)
$LiEu(MoO_4)_2$	Tetragonal	a=5.2014(1) c=11.3309(3)	306.55(1)
$LiEu(MoO_4)(WO_4)$	Tetragonal	a=5.2066(1) c=11.3088(3)	306.56(1)

The excitation spectra were studied between 200nm and 500nm and the emission spectra between 380nm and 800nm. The excitation wavelengths used in this work for the majority of the molybdate phosphors synthesised are 465nm and 395nm and are thus suitable as materials for use with LEDs emitting in the near-UV and blue region. In the excitation spectra, the broad excitation bands between ~230nm and ~355nm can be ascribed to O→Mo, a charge transfer transition[4,8,12,13,16]. However, the charge transfer band of $Eu^{3+} \rightarrow O^{2-}$ was not unequivocally observed due to the possible overlap of the charge transfer band with that of the molybdate group[8,12,16]. The sharp lines in the 360nm to 500nm range are intra-configurational 4f-4f transitions of Eu^{3+} in the host lattice[12]. The strong excitation bands at ~395nm and ~465nm can be attributed to the $^7F_0 \rightarrow ^5L_6$ and $^7F_0 \rightarrow ^5D_2$ transitions of Eu^{3+}, respectively[12,13,16]. Excitation with 395nm irradiation produces the well-known $^5D_0 \rightarrow ^7F_J$ (J=0,1,2, etc) emission lines of Eu^{3+} ions with the strong emission for J=2 at 616nm[12,13].

The excitation spectra of the $M_{0.76}Eu_{0.24}MoO_4$, (where M = Mg, Ca, Sr and Ba) phosphor samples scanned between 200nm and 500nm are presented in Figure 1. Their normalised spectra, cut between 200nm and 350nm and between 350-500nm, are presented in Figures 2 and 3.
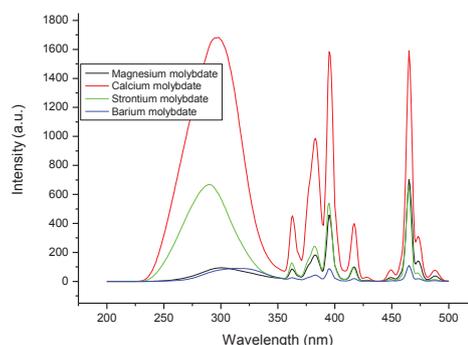
Fig. 1. Excitation spectra of the Eu^{3+} doped alkaline earth metal molybdates
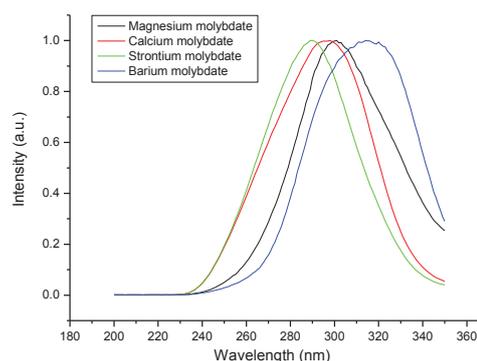
Fig. 2. Excitation spectra of the Eu^{3+} doped alkaline earth metal molybdates (200-350nm) normalised.

In Figure 2 the short wave regions of these phosphors are presented. These bands have been ascribed as being O→-Mo charge transfer (CT) bands.

there are significant differences in their peak excitation wavelengths viz 300nm, 295nm, 290nm, and 315nm respectively.[9, 11-14] However, at the higher wavelength region (Figure. 3), the two most intense peak excitation wavelengths coincide at 395nm and 465nm.
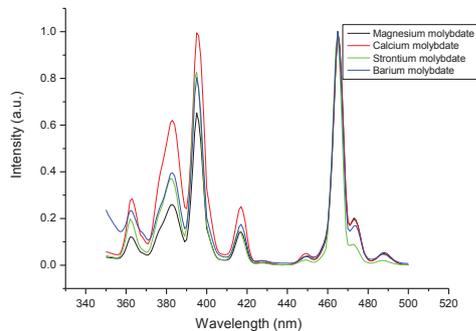
Fig. 3. Excitation spectra of the Eu³⁺ doped alkaline earth metal molybdates (350-500nm) normalised.

The emission spectra of $M_{0.76}Eu_{0.24}MoO_4$, (where M = Mg, Ca, Sr and Ba) excited at 395nm (Fig 4) and 465nm (Fig. 5) are very similar though the relative intensities vary. In both figures 4 and 5 the highest emission is found for the calcium molybdate phosphor.
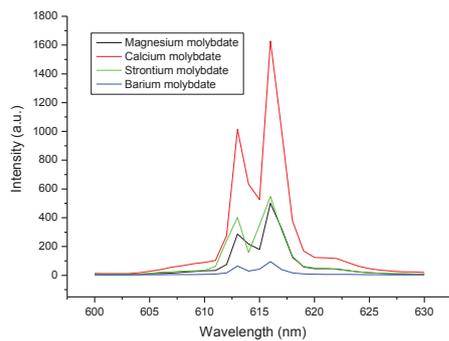
Fig. 4. Emission spectra of of the Eu³⁺ doped alkali earth metal molybdates excited at 395nm.
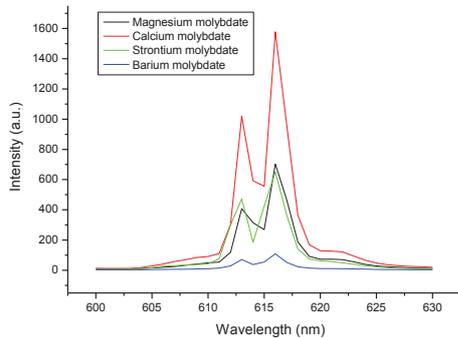
Fig. 5. Emission spectra of of the Eu³⁺ doped alkali earth metal molybdates excited at 465nm.

The excitation spectra of the $AgLa_{0.70}Eu_{0.30}(MoO_4)_2$ and $AgGd_{0.70}Eu_{0.30}(MoO_4)_2$ phosphor samples were scanned between 200nm and 500nm and in Figure 6 they are shown in the range between 335-500nm. The bands below 350nm are the O-Mo CT bands, but the most notable differences in the excitation spectra between figures 3 and 6 is the relative intensities of the bands around 395nm and 465nm due to the ($^7F_0$-$^5D_2$) and ($^7F_1$-$^5D_1$) transitions respectively.
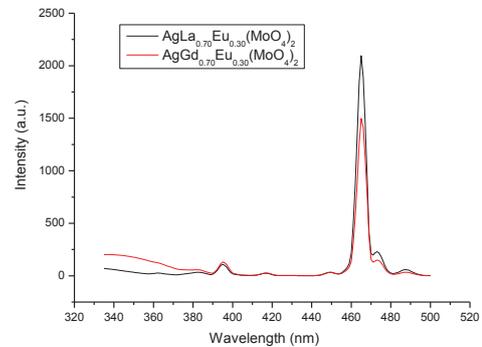
Fig. 6. Excitation spectra of $AgLa_{0.70}Eu_{0.30}(MO_4)_2$ and $AgGd_{0.70}Eu_{0.30}(MO_4)_2$, monitored at 616 nm.
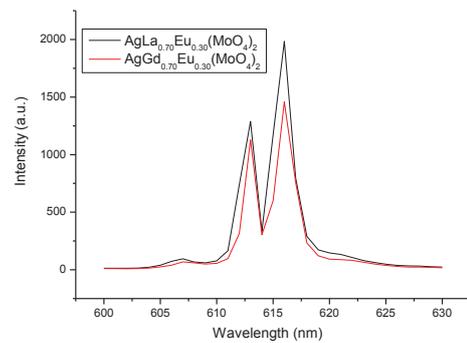
Fig. 7. Emission spectra of $AgLa_{0.70}Eu_{0.30}(MO_4)_2$ and $AgGd_{0.70}Eu_{0.30}(MO_4)_2$, excited at 465 nm.

The emission spectra of $AgLa_{0.70}Eu_{0.30}(MO_4)_2$ and $AgGd_{0.70}Eu_{0.30}(MO_4)_2$, excited at 465nm (Fig. 7) are very similar though the relative intensities vary. The spectra are similar to those displayed in figures 4 and 5.
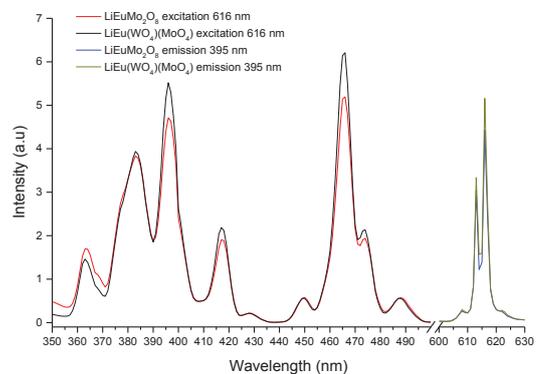
Fig. 8. Excitation and emission spectra of $LiEu(MoO_4)_2$ and $LiEu(MoO_4)(WO_4)$ phosphors

The excitation and emission spectra of $LiEu(MoO_4)_2$ and $LiEu(MoO_4)(WO_4)$ phosphors are presented in Figure 8. The relative intensities of the bands in the excitation spectra are similar to those shown in Figure 3, and the emission spectra are similar to those of Figures 5 and 7. Thus all the emission spectra of the phosphors reported herein are very similar as would be expected for materials having the same structure with the activators in the same lattice sites. It should be noted however that the intensities of the emission spectra differ and these will depend on the binding in the site.

The luminous efficacies of these phosphors are presented in Table 2. Where the values are less than 15lm/W they are not given because of accuracy limitations. Clearly although $Ca_{0.76}Eu_{0.24}MoO_4$ is the best of the alkaline earth molybdates it is poor when compared with the $LiEu(MoO_4)_2$ and $LiEu(MoO_4)(W0_4)$. It is of interest that the latter two phosphors have the smallest cell volume and that $Ca_{0.76}Eu_{0.24}MoO_4$ has the next smallest volume of the phosphors studied in this work. It thus appears that the tightness of the lattice site is all important in making an efficient phosphor.

Table 2 Luminous efficacies of the Phosphors and their Firing Temperatures

Phosphor	L_{eff} (lm/W) Ex 390 nm	L_{eff} (lm/W) Ex 460 nm)	Firing Temp. Atmosphere
$Zn_{0.76}Eu_{0.24}MoO_4$	(!)	(!)	700°C Air
$Mg_{0.76}Eu_{0.24}MoO_4$	21.97	(!)	700°C Air
$Sr_{0.76}Eu_{0.24}MoO_4$	(!)	(!)	700°C Air
$Ca_{0.76}Eu_{0.24}MoO_4$	49.18	76.57	700°C Air
$Ba_{0.76}Eu_{0.24}MoO_4$	(!)	(!)	700°C Air
$AgLa_{0.70}Eu_{0.30}(MoO_4)_2$	(!)	(!)	800°C H_2/N_2
$AgGd_{0.70}Eu_{0.30}(MoO_4)_2$	(!)	(!)	800°C H_2/N_2
$LiEu(MoO_4)_2$*	163.33	199.28	800° C Air
$LiEu(MoO_4)(WO_4)$*	236.38	243.78	800° C Air

(!) values of L_{eff} (lm/W) not given as less than 15 and not accurate.
*the L_{eff} (lm/W) of the Li compounds were measured at 395nm and 465nm but it is considered that they are still comparable.

As the intensities of the red emission is found to be related to the lattice size (cell volume), and the smaller cells in which the Eu^{3+} activator cations are tightly bound have the best luminous efficacies, then the implications of this for the design of new very bright phosphors are obvious. For a given phosphor lattice there will be a cell size where the emission is optimised.

4. CONCLUSIONS

A number of findings have resulted from this work: A range of Eu^{3+} doped metal molybdate phosphors has been prepared. Their spectral emission properties have been reported compared and discussed. A relationship between their structures, cell sizes and the intensity of their emission bands has been observed. The implications of the study for the design of efficient Eu^{3+} activated phosphors and probably all other rare earth

cation activated phosphors are therefore to design lattice sites that bind the activators as tightly as possible.

6. REFERENCES

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