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Photoluminescent Properties of Phosphors in the System $Ca_rCd_{1-r}MoO_4:Eu^{3+}, Li^+$

Jiaguo Wang,^{a,b} Xiping Jing,^{b,z} Chunhua Yan,^b Jianhua Lin,^b and Fuhui Liao^b

^aCollege of Chemistry and Materials Science, Wenzhou Normal University, Wenzhou 325027,

China

^bThe State Key Laboratory of Rare Earth Materials Application and Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

The luminescent properties of the new red phosphors in the solid solution system $Ca_xCd_{1-x}MoO_4:Eu^{3+}$, Li⁺ are reported. Their dominating emission peaks are at 615 nm, which satisfies color purity. Under the excitation of ~320 nm UV light, some selected samples have luminescent intensity 30% higher than that of the commercial red phosphor $Y_2O_2S:Eu^{3+}$. Therefore, it is a promising material for N_2 plasma display application.

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Choi *et al.*¹ have put forward a plasma display panel (PDP) with N₂ and Ne mixture as discharge gas, which emits UV light in the wavelength range 300-400 nm. Compared to conventional PDP devices, which emit vacuum UV with the wavelengths 147 and 173 nm from Xe, the longer emitting wavelength in the new device, named N₂-PDP, is beneficial to energy efficiency, because in this device, the phosphors have smaller Stokes shift. Moreover, due to excitation by lower energy radiation, the phosphors may have better duration in this device. N2-PDP requires phosphors having effective excitations in the wavelength range 300-400 nm. Due to the excitation spectra of blue phosphors $Sr_{10}(PO_4)_6Cl_2:Eu^{2+}$ and MgBaAl₁₀O₁₇:Eu²⁺ extending over 400 nm, they can be employed as the blue components for the N₂-PDP devices. The green phosphor, MgBaAl₁₀O₁₇:Mn²⁺, Eu²⁺, also has an excitation band in the range 300-400 nm; thus, it may be utilized as the green component. Because both YVO_4 :Eu³⁺ and Y_2O_2S :Eu³⁺ show their excitation peaks at around 330 nm, they may be considered as red components. Our group patented molybdate as red phosphor matrices^{2,3} previously. In the present work, we report the detailed luminescent properties of the phosphors in the system $Ca_rCd_{1-r}MoO_4:Eu^{3+}$, Li⁺. They emit saturated red light with good color purity. Some of them show better efficiency than the commercial phosphors YVO₄:Eu³ and $Y_2O_2S:Eu^{3+}$.

Experimental

Raw materials Eu_2O_3 (99.99%), MoO₃ (99.5%), CdO (analytical reagent), CaCO₃ (>99%), and Li₂CO₃ (analytical reagent) were used for the sample preparation. They were weighed and ground by using an agate mortar and pestle. A small amount of ethanol was added during the grindings in order to obtain homogenous mixtures. The samples were heated in a muffle furnace at 550°C for 10 h and then at 800°C for another 2 h. Finally, the samples were ground into powders for characterization.

Phase purities were analyzed by using a Rigaku D/max2000 X-ray diffractometer. Photoluminescences were measured using a Hitachi F4500 fluorescent spectrophotometer and the luminescent decay curves were recorded by using a lab-established yttrium aluminum garnet (YAG):Nd laser system with an excitation wavelength of 266 nm.

Results and Discussion

Both CaMoO₄ and CdMoO₄ belong to Scheelite⁴ structure, which has a tetragonal unit cell with space group $I4_1/a$, Z = 4, the unit cell parameters a = 0.5226 nm, c = 1.1430 nm for the former, and a = 0.5170 nm, c = 1.1190 nm for the latter. In this structure, Mo⁶⁺ occupies the tetrahedral sites constructed by O²⁻, and MoO₄²⁻ tetrahedrons are isolated. Bivalent cations are eight-coordinated by

O²⁻, which forms dodecahedrons; the dodecahedrons connect to each other by sharing edges. Each O²⁻ bonds one Mo⁶⁺ and two bivalent cations. When doped with Eu3+, an equal amount of Li+ was codoped for the charge balance. Phase analysis indicated that all samples, doped and undoped, were phase pure, which suggested that the doped samples formed solid solutions. The doping mechanism should be: $Eu^{3+} + Li^+ \leftrightarrow 2Ca^{2+}(Cd^{2+})$. $Eu^{3+}(106.6 \text{ pm})$ has similar radius to Ca²⁺ (112 pm) and Cd²⁺ (110 pm);⁵ thus, Scheelite structure was kept when doping Eu^{3+} and Li^+ to both $CaMoO_4$ and $CdMoO_4$, even if all Ca^{2+} or Cd^{2+} was replaced by Eu^{3+} and Li^+ , though Li⁺ has a small radius. In our experimental results, Eu_{0.5}Li_{0.5}MoO₄ had a similar unit cell to CaMoO₄, and with the unit cell parameters a = 0.5201 nm, c = 1.1332 nm, the values were significantly smaller than those of CaMoO₄. The unit cell parameters of $Eu_0 Li_0 MOO_4$ were considerably larger than those of CdMoO₄. This may be due to the particular structure features of this bivalent cation wholly replaced sample. Actually, the dodecahedron located by the bivalent cation is too large for the small cation Li⁺ (92 pm) and it is an unstable structure for Li⁺ to place at this site. Thus Li⁺ tends to deviate from the center and shift to one side of the dodecahedrons. This structural feature may be related to the unit cell increase. A similar structural feature was also found in another molybdate, Li₀₅₆₂₅Li_{0.3125}MoO₄.⁶ The variation of unit cell volume with doping content in the system Cd_{1-x}Eu_{0.5x}Li_{0.5x}MoO₄ is shown in Fig. 1. The Eu3+-doped CaMoO4 was discussed in our previous paper.⁷ Furthermore, Ca^{2+} and Cd^{2+} have almost the same radii; hence, the system Ca_xCd_{1-x}MoO₄ formed solid solutions over the whole range. The variation of the unit cell volume with Cd²⁺ content is also represented in Fig. 1.

Reference 8 shows that undoped CaMoO₄ emits faint green light with an emission peak at 520 nm under excitation of ~295 nm UV. Similarly, CdMoO₄ also emits green light at the same wavelength with the excitation peak at ~335 nm, but its intensity is even weaker (see Fig. 2). The red shifts for the excitation peaks from CaMoO₄ to CdMoO₄ are attributed to the difference of the electronegativity between Ca (1.0) and Cd (1.7); smaller electronegativity difference between the bivalent cation elements and oxygen make the electrons in the lattice more delocalized and the excitation energy lower. Groenink *et al.* and Abraham *et al.* reported the intrinsic optical properties of CaMoO₄ to CdMoO₄, respectively.^{9,10} In both hosts, the complex ions MoO₄^{2–} are considered as the luminescent centers. Their excitation and emission are due to the chargetransfer transitions of Mo⁶⁺-O^{2–}. As a potential laser material, CaMoO₄ doped with other rare earth ions (Nd³⁺, Dy³⁺) was reported in the past few years.^{11,12}

Figure 2 also represents the excitation and emission spectra of the Eu³⁺ and Li⁺ codoped sample Cd_{0.96}Eu_{0.02}Li_{0.02}MoO₄, which shows typical Eu³⁺ red emissions with color coordinates x = 0.665 and y = 0.335. The excitation spectrum may be divided into two regions. The strong and wide band below 360 nm may be assigned

^z E-mail: xpjing@pku.edu.cn



Figure 1. Variation of unit cell volume with Eu^{3+} and Li^+ or Ca^{2+} content in the systems $Cd_{1-x}Eu_{0.5x}Li_{0.5x}MoO_4$ or $Ca_xCd_{0.9-x}Eu_{0.1}Li_{0.1}MoO_4$.

to the combination of the charge-transfer transitions of Eu³⁺-O²⁻ and Mo⁶⁺-O²⁻. Compared with the profile of the excitation spectrum of the undoped sample, it can be seen that the excitation transition of the Eu³⁺-doped sample is mainly due to the charge-transfer transition of Mo⁶⁺-O²⁻ and Eu³⁺ doping making the band slightly wider to the short wavelength side. The weak and narrow peaks above 360 nm may be assigned to the f-f transitions of Eu^{3+} . The emission spectrum of the codoped samples are dominated by the red peaks at 613 and 615 nm due to the electric dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, which indicates that Eu^{3+} occupies a site lacking inversion symmetry.¹³ Though in the host matrix the sites of bivalent cations have inversion symmetry, the introduction of trivalent Eu^{3+} makes the inversion symmetry disappear. The orange peak at 592 nm due to the magnetic dipole transition ${}^5\mathrm{D}_0 \to {}^7\mathrm{F}_1$ also appears with weak intensity. The intensity ratio of 615 nm emission to 592 nm emission (normally named as the ratio of red/orange) is 10. To be a red component of the tricolor phosphors for display devices, the color purity of this phosphor is better than those of YVO₄:Eu³⁺ and Y2O2S:Eu3+. Excited by the optimized wavelengths of (325 nm) and commercial phosphor emission intensity for Cd_{0.7}Eu_{0.15}Li_{0.15}MoO₄ is about 85% of that of the latter.



Figure 2. Excitation and emission spectra of $Cd_{0.96}Eu_{0.02}Li_{0.02}MoO_4$ (solid line, labeled P) and CdMoO₄ (normalized, dash line, labeled H).



Figure 3. Luminescent decay curves of Eu^{3+} in $Cd_{0.98}Eu_{0.01}Li_{0.01}MoO_4$ and MoO_4^{2-} in $CaMoO_4.$

Figure 2 again shows that the emission from the MoO₄²⁻ group overlaps the f-f excitation of Eu³⁺. Therefore, it may be deduced that when the codoped sample is excited by UV light in the range of the wide excitation band, first the energy is mainly absorbed by the MoO₄²⁻ group and then transferred to Eu³⁺. This process is similar to that in the phosphor YVO₄:Eu³⁺ (Ref. 14). Decay time (τ) was measured, which fit well with the single exponential decay function (see Fig. 3). MoO₄²⁻ emission in CaMoO₄ (the emission of CdMoO₄ is too weak for the decay time measurement) has a decay time of $\tau = 0.17$ ms. The decay time measurements for Eu³⁺ emissions were conducted on the system Cd_{1-x}Eu_{0.5x}Li_{0.5x}MoO₄ with the Eu³⁺ content x < 0.15. The measurements showed that the decay time $\tau =$ ~ 0.45 ms for the samples was not obviously influenced by the Eu³⁺ content.

The variations of the luminescent properties with Eu^{3+} content were investigated (Fig. 4). The peak position of the band excitation shifts toward shorter wavelength with the increase of Eu^{3+} content (from 335 nm for $Cd_{0.98}Eu_{0.01}Li_{0.01}MoO_4$ to 285 nm for $Eu_{0.5}Li_{0.5}MoO_4$); this also can be understood by the electronegativity differences between cation elements (Eu, ~1.2, Li, 1.0) and oxygen. The optimized Eu^{3+} content for the luminescent intensity is about 0.075.



Figure 4. Variations of the luminescent intensity and the excitation peak wavelength with Eu^{3+} content *x* in the system $\text{Cd}_{1-x}\text{Eu}_{0.5x}\text{Li}_{0.5x}\text{MoO}_4$.



Figure 5. Variations of the luminescent intensities with Ca^{2+} content *x* in the system $Ca_xCd_{0.9-x}Eu_{0.05}Li_{0.05}MoO_4$ and $Ca_xCd_{0.8-x}Eu_{0.1}Li_{0.1}MoO_4$.

The luminescent properties of the solid solution systems $Ca_xCd_{0.9-x}Eu_{0.05}Li_{0.05}MoO_4$ and $Ca_xCd_{0.8-x}Eu_{0.1}Li_{0.1}MoO_4$ were also studied (see Fig. 5). Solid solution was formed whether Cd^{2+} was partially or wholly replaced by Ca^{2+} . The luminescent intensities for the system Eu^{3+} content 0.05 were more sensitive to the Ca^{2+} content. The introduction of Ca^{2+} remarkably enhanced the luminescent intensities. For the system $Ca_xCd_{0.9-x}Eu_{0.05}Li_{0.05}MoO_4$, compared to the end member $Cd_{0.9}Eu_{0.05}Li_{0.05}MoO_4$, the intensity was increased 80% at the optimized Ca^{2+} content x = 0.3. For the system $Ca_xCd_{0.8-x}Eu_{0.1}Li_{0.1}MoO_4$, at optimized composition x = 0.3, the intensity increased about 30% compared to the end member $Cd_{0.8}Eu_{0.1}Li_{0.1}MoO_4$. Compared with commercial $Y_2O_2S:Eu^{3+}$, the

emission intensity of the sample $Ca_{0.3}Cd_{0.6}Eu_{0.05}Li_{0.05}MoO_4$ was about 30% higher. The excitation peak wavelength has blue shift from 330 to 285 nm with the increase of Ca^{2+} content.

Conclusion

The phosphors in the system $Cd_{1-x}Ca_xMoO_4:Eu^{3+}$, Li^+ have intense red emissions with good color purities. The phosphors may be considered as a red component for N₂-PDP.

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