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Short communication

Synthesis and luminescence properties of Eu^{3+}-activated $NaLa(MoO_4)(WO_4)$ phosphor

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Abstract

$NaLa_{1-y}(MoO_4)_{2-x}(WO_4)_x{:}yEu^{3+}$ series red-emitting phosphors have been synthesized by a combustion route and their crystal structure, optical and luminescent properties have been investigated. Their emission spectra show an intense red emission at 616 nm due to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}. As the tungstate content increases, the intensity of $^5D_0 \rightarrow {}^7F_2$ emission of Eu^{3+} activated at wavelength of 467 nm is found to increase and reaches a maximum when the relative ratio of Mo/W is 1:1. Also, the effect of Eu^{3+} concentration on the luminescence behavior of the solid solutions is examined. The optical properties of $NaLa_{0.9}Eu_{0.1}(MoO_4)(WO_4)$ phosphor make it attractive for the application in white-light-emitting diodes (LEDs), in particular for near-UV InGaN-based white-LEDs.

Keywords: Phosphors; Tungstomolybdate; Photoluminescence properties

1. Introduction

Eu^{3+} doped phosphors, particularly in the host with noncentrosymmetric site, have been widely used due to their intense $^5D_0 \rightarrow {}^7F_2$ emission in the red spectral region. Double molybdates $ALn(MoO_4)_2$ (A = alkali metal ions; Ln = trivalent rare earth ions), which share scheelite-like ($CaWO_4$) isostructure, show excellent thermal and hydrolytic stability and are considered to be efficient luminescent hosts [1]. In these compounds, Ln^{3+} occupy the lattice sites without centrosymmetry, and these compounds show unusual optical properties: no concentration quenching, thus these double molybdates are excellent red phosphor hosts [2]. Eu^{3+}-activated double molybdates are of practical interest as efficient, high color rendering phosphors. Such molybdates are used as materials for luminescent lamps, gain media, and luminescent display panels [3,4]. Most of these compounds have been prepared by solid-state method that needs high temperature, long heating time and subsequent grinding. In this work, we report on these red phosphors prepared by a combustion route. This synthesis approach has some advantages over the reported method, such as good homogeneity, lower calcinations temperature and shorter heating time.

Complex molybdate–tungstates $ALn(MO_4)_2$ (A = alkali metal ions; Ln = trivalent rare earth ions, M = Mo, W) have become the hot spot for the atoms Mo and W, which have similar ionic radius, to substitute each other [5–10]. In this paper, a series of phosphors, $NaLa(MoO_4)_{2-x}(WO_4)_x{:}Eu^{3+}$ have been synthesized by a facile combustion process. Their crystal structure and photoluminescence (PL) are reported.

2. Experimental procedures

2.1. Samples preparation

The red phosphors $NaLa(MoO_4)_{2-x}(WO_4)_x{:}yEu^{3+}$ were prepared by the combustion route using Eu_2O_3 and La_2O_3 (99.99%, Shanghai Yuelong Nonferrous Metals Ltd.), HNO_3 (Analytical Reagent, AR), $NaNO_3$ (AR), $H_{40}N_{10}O_{41}W_{12}$ (AR), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (AR) as raw materials. $CO(NH_2)_2$ (AR grade) was used as fuel. First, metal oxides were dissolved in dilute HNO_3 (AR) under vigorous stirring. A suitable volume of deionized water was added to above solutions. $CO(NH_2)_2$ (AR) was added to the solution as fuel. Then stoichiometric amount

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of $NaNO_3$, $H_{40}N_{10}O_{41}W_{12}$ and $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ were added to the solution. A highly transparent solution was obtained after stirring for a few minutes. The solution was put into a furnace for pre-calcination at 600 °C for 5 min and then calcined at 900 °C for 3 h to obtain the phosphor samples.

2.2. Characterization

The X-ray power diffraction (XRD) pattern of the products was recorded on a Bruker D8 X-ray diffractometer (Bruker Co. Ltd., Karlsruhe, Germany) equipped with Cu Kα radiation (λ = 1.5406 Å). X-ray photoelectron spectroscopy (XPS) was recorded on a VG MultiLab2000 MK Spectrometer (Thermo Electron Corp., UK), using the monochromatic Al Kα radiation (1486.6 eV, 300 W) as the excitation source. The excitation and emission spectra were measured using a Perkin-Elmer LS-55 (Perkin-Elmer Corporation, USA) luminescence spectrophotometer equipped with a xenon discharge lamp as an excitation source. All measurements were performed at room temperature.

3. Results and discussion

The X-ray diffraction (XRD) pattern of $NaLa_{0.9}Eu_{0.1}(MoO_4)(WO_4)$ powders is shown in Fig. 1. All of the diffraction peaks are in good agreement with the standard data of $NaLa(MoO_4)_2$ (JCPDS Card No. 24-1103) [11], which can be rationalized by the almost identical ionic radius of Mo^{6+} (0.41 Å) and W^{6+} (0.42 Å). No second phase is detected at this doping level, indicating that the Eu^{3+} ions can be effectively incorporated into the sites of La^{3+} ion of $NaLa(MoO_4)(WO_4)$ matrix.

Interpretation of the XPS spectra can provide the chemical state of the elements in the $NaLa_{0.9}Eu_{0.1}(MoO_4)(WO_4)$ particles. The XPS data are shown in Fig. 2 using C 1s as reference at 284.6 eV. No peaks of other elements except W, Mo, O, La, Na, and Eu are observed in the spectrum, indicating the high purity of the product and suggesting that Eu enter into the $NaLa(MoO_4)(WO_4)$ crystalline host lattice.

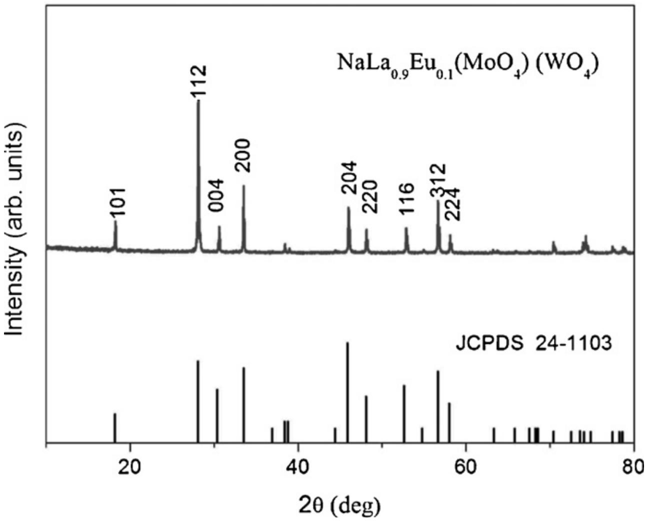

Fig. 1. X-rays diffraction patterns of $NaLa_{0.9}Eu_{0.1}(MoO_4)(WO_4)$.

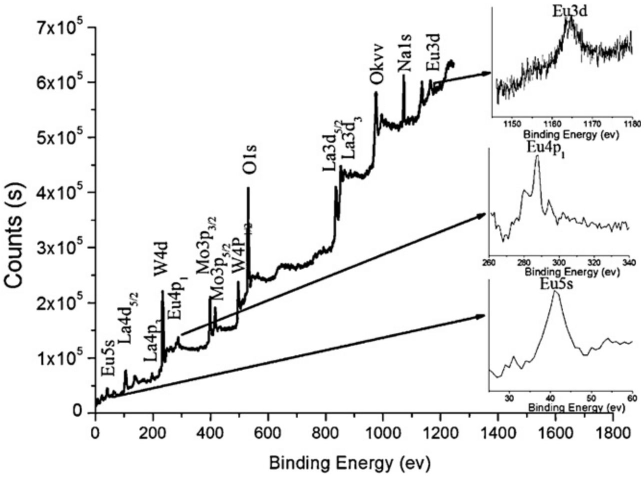

Fig. 2. X-ray photoelectron spectroscopy of $NaLa_{0.9}Eu_{0.1}(MoO_4)(WO_4)$.

Fig. 3 shows the PL spectra of phosphors $NaLa_{1-y}Eu_y(MoO_4)(WO_4)$ (y = 4–14%) as a function of doped Eu content (i.e., y) under the excitation of 467 nm blue light. For the samples excited by 467 nm, two typical emission peaks of Eu^{3+} are located mainly in the red region of the spectrum (594 and 616 nm) and are attributable to the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions, respectively. Among all emission lines of each phosphor, the shapes of emission spectra are similar. And the strongest red emission line peaked at 616 nm owing to the electric dipole transition $^5D_0 \rightarrow {}^7F_2$, which suggested the sites that Eu^{3+} substitutes for is noncentrosymmetric [10,12,13], while the relative weak emission lines at 594 nm is owing to the transitions of $^5D_0 \rightarrow {}^7F_1$.

It is generally accepted that effect of Eu^{3+} concentration plays an important role in the luminescence properties of the red-emitting phosphor. Lower doping concentrations lead to weak luminescence while higher doping concentrations cause concentration quenching of the Eu^{3+} emission. The variations of luminescence properties of Eu^{3+} concentration-dependent $NaLa_{1-y}Eu_y(MoO_4)(WO_4)$ have been investigated in this study. The increasing concentrations of the Eu^{3+} ion bring no

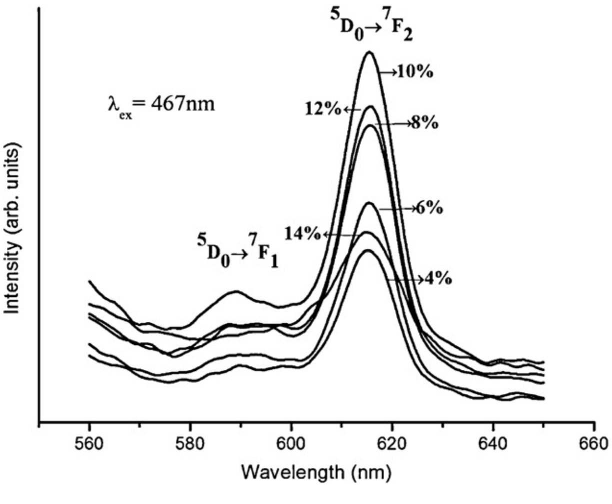

Fig. 3. Emission spectra of $NaLa_{1-y}Eu_y(MoO_4)(WO_4)$ (y = 4–14%) phosphor upon 467 nm excitation.

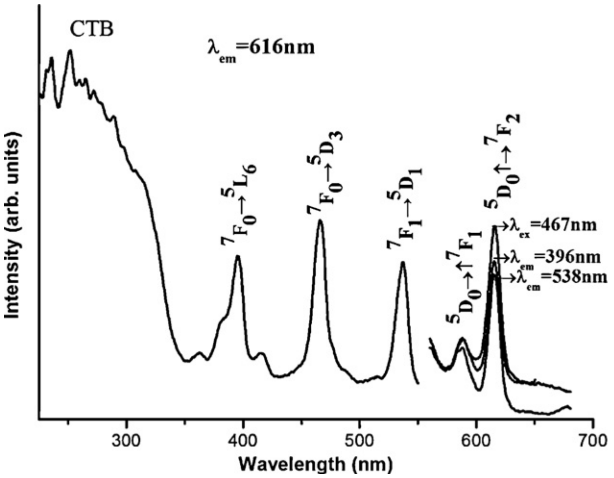

Fig. 4. Excitation and emission spectra of $NaLa_{0.9}Eu_{0.1}(MoO_4)(WO_4)$.

alteration in the shape of the photoluminescent spectra of the samples. The emission intensity is found to be maximum for the phase $NaLa_{0.9}Eu_{0.1}(MoO_4)(WO_4)$. It is well known that lower doping concentrations lead to weak luminescence while higher doping concentrations cause concentration quenching of the Eu^{3+} emission. Blasse and Grabmaier [14] proposed that the quenching mechanism was associated with the exchange interaction, which results in the energy transfer and ultimately quenches the emission from the $^5D_0$ level of the Eu^{3+} ion.

Fig. 4 shows the excitation and emission spectra of the phosphor $NaLa_{0.9}Eu_{0.1}(MoO_4)(WO_4)$. The excitation spectra for monitoring the $^5D_0 \rightarrow {}^7F_2$ emission of Eu^{3+}($\lambda_{em} = 616$ nm) show a broad charge transfer (O → Mo or O → W) band (CTB) along near 250 nm. However, the CT band of Eu^{3+}–O^{2-} is not clearly observed in the excitation spectra, which can be due to possible overlap of the CT band with that of tungstate or molybdate group. The sharp lines in 350–550 nm range are due to intra-configurational 4f–4f transitions of Eu^{3+} in the host lattice, and three of the strongest excitation peaks are at ~396 nm ($^7F_0 \rightarrow {}^5L_6$), ~467 nm ($^7F_0 \rightarrow {}^5D_2$), and ~538 nm ($^7F_1 \rightarrow {}^5D_1$), respectively [10,15]. The strong CTB from host tungstate or molybdate group is favorable for the effective energy transfer and luminescence of Eu^{3+}. The Eu^{3+} transitions in $NaLa_{0.9}Eu_{0.1}(MoO_4)(WO_4)$ excitation spectra show effective absorption at near-UV (396 nm) and blue (467 nm), and these wavelengths coincide with those of commercial GaN-based LED. Upon excitation with 396 nm UV irradiation, the emission spectrum shows a weak emission at 594 nm and a strong emission line at 616 nm, which arise from the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+}, respectively. There are no differences observed for the emission band shape and position under different Eu^{3+} excitation ($\lambda_{ex} = 467$ and 538 nm) other than the luminescent intensity.

The emission spectra of the phosphors $NaLa_{0.9}Eu_{0.1}(MoO_4)_{2-x}(WO_4)_x$ ($x = 0$–2) by exciting at 467 nm are shown in Fig. 5. The intensity of $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+} was all found to increase with the increasing W/Mo content. However, the relative ratio of $^5D_0 \rightarrow {}^7F_1/{}^5D_0 \rightarrow {}^7F_2$ was found to change insensibly with W/Mo content. The variation of the relative emission intensity of Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ transition with the value of x in $NaLa_{0.9}Eu_{0.1}(MoO_4)_{2-x}(WO_4)_x$ are also shown in Fig. 5. It is found that the maximum emission intensity corresponds to $x = 1$ composition in $NaLa_{0.9}Eu_{0.1}(MoO_4)_{2-x}(WO_4)_x$. The reason for this observation may be due to the advent of ion pair interaction between Eu^{3+} ions, which is expected to be much stronger in molybdate than tungstate crystal because of the differences in the Eu^{3+}–Eu^{3+} distance in molybdate [average distance 3.86(6) Å] and that in tungstate (average distance 3.9(1) Å) phosphors. One of the possibilities is that the distance between two Eu^{3+} ions can affect the energy transfer between the two ions [15].

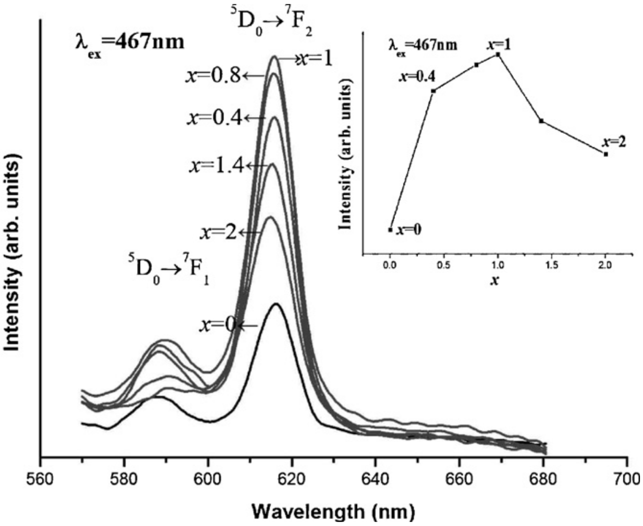

Fig. 5. Emission spectra of $NaLa_{0.9}Eu_{0.1}(MoO_4)_{2-x}(WO_4)_x$ ($x = 0$, 0.4, 0.8, 1, 1.4, 2) phosphors under 467 nm excitation; the inset is the dependence of the peak intensity $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+}) on W^{6+} concentration (x).

4. Conclusions

Intense red phosphor $NaLa_{0.9}Eu_{0.1}(MoO_4)(WO_4)$ was successfully synthesized by combustion route. XRD results show that phosphors $NaLa_{0.9}Eu_{0.1}(MoO_4)_{2-x}(WO_4)_x$ ($x = 0$–2) have only one scheelite-like structure. The photoluminescence studies on $NaLa_{0.9}Eu_{0.1}(MoO_4)(WO_4)$ show that a dominant red emission line at around 616 nm is observed under different Eu^{3+} excitation (396, 467, and 538 nm). Under 467 nm excitation, different Eu^{3+} concentrations and different W^{6+} concentrations affecting the emission spectra of the samples were studied. All these suggest composition-optimized $NaLa_{0.9}Eu_{0.1}(MoO_4)(WO_4)$ phosphor to be a suitable candidate for white-LEDs application.

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References

[1] Z. Wang, H. Liang, M. Gong, Q. Su, Novel red phosphor of Bi^{3+}, Sm^{3+} co-activated $NaEu(MoO_4)_2$, Opt. Mater. 29 (7) (2007) 896–900.

[2] F. Shi, J. Meng, Y. Ren, Structure and luminescent properties of three new silver lanthanide molybdates, J. Solid State Chem. 121 (1996) 236–239.

[3] A.V. Zaushitsyn, V.V. Mikhailin, Yu.A. Romanenko, E.G. Khaikina, O.M. Basovich, V.A. Morozov, B.I. Lazoryak, Luminescence study of $LiY_{1-x}Eu_x(MoO_4)_2$, Inorg. Mater. 41 (7) (2005) 766–770.

[4] C. Guo, S. Wang, T. Chen, L. Luan, Y. Xu, Preparation of phosphors $AEu(MoO_4)_2$ (A = Li, Na, K and Ag) by sol–gel method, Appl. Phys. A 94 (2009) 365–371.

[5] V. Sivakumar, U.V. Varadaraju, Intense red-emitting phosphors for white LEDs, J. Electrochem. Soc. 152 (2005) H168–H171.

[6] X.-H. He, M.-Y. Guan, J.-H. Sun, N. Lian, T.-M. Shang, Synthesis and photoluminescence properties of $LiEu(W,Mo)_2O_8:Bi^{3+}$ red-emitting phosphor for white-LEDs, J. Mater. Sci. 45 (2010) 118–123.

[7] B. Yan, L. Lin, J. Wu, F. Lei, Photoluminescence of rare earth phosphors $Na_{0.5}Gd_{0.5}WO_4:RE^{3+}$ and $Na_{0.5}Gd_{0.5}(Mo_{0.75}W_{0.25})O_4:RE^{3+}$ (RE = Eu, Sm, Dy), J. Fluoresc. 21 (2011) 203–211.

[8] A. Xie, X. Yuan, Y. Shi, F. Wang, J. Wang, Photoluminescence characteristics of energy transfer between Eu^{3+} and Bi^{3+} in $LiEu_{1-x}Bi_x(WO_4)_{0.5}(MoO_4)_{1.5}$, J. Am. Ceram. Soc. 92 (10) (2009) 2254–2258.

[9] K.-S. Hwang, S. Hwangbo, J.-T. Kim, Sol–gel synthesis of red-emitting $LiEuW_2O_8$ powder as a near-ultraviolet convertible phosphor, Ceram. Int. 35 (2009) 2517–2519.

[10] C.-H. Chiu, C.-H. Liu, S.-B. Huang, T.-M. Chena, White-light-emitting diodes using red-emitting $LiEu(WO_4)_{2-x}(MoO_4)_x$ phosphors, J. Electrochem. Soc. 154 (7) (2007) J181–J184.

[11] A. Jayaraman, S.Y. Wang, S.K. Sharma, Pressure-induced amorphization in $NaLa(MoO_4)_2$: a high pressure Raman and IR absorption study, Solid State Commun. 93 (11) (1995) 885–890.

[12] G. Blasse, A. Bril, W.C. Nieuwpoort, On the Eu^{3+} fluorescence in mixed metal oxides: Part I. The crystal structure sensitivity of the intensity ratio of electric and magnetic dipole emission, J. Phys. Chem. Solids 27 (1966) 1587–1592.

[13] G. Jia, C. Wang, S. Xu, Local site symmetry determination of scheelite-type structures by Eu^{3+} spectroscopy, J. Phys. Chem. C 114 (2010) 17905–17913.

[14] G. Blasse, B.C. Grabmaier, Luminescent Materials, Springer-Verlag, Berlin, 1994.

[15] C.-H. Chiu, M.-F. Wang, C.-S. Lee, T.-M. Chen, Structural, spectroscopic and photoluminescence studies of $LiEu(WO_4)_{2-x}(MoO_4)_x$ as a near-UV convertible phosphor, J. Solid State Chem. 180 (2007) 619–627.