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Luminescent characteristics of $Sr_{0.95}MoO_4$: $0.05Ln^{3+}$(Ln = Eu, Tb, Pr) phosphors

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ABSTRACT

The Eu^{3+}, Tb^{3+}, Pr^{3+} ions activated $SrMoO_4$ phosphors have been synthesized using a conventional solid-state reaction under the 600 ℃, starting from Eu_2O_3, Tb_4O_7, Tb_6O_{11} and $(NH_4)_2MoO_4$ as raw materials. The crystal structures of the products are characterized by Powders X-ray Diffraction (XRD). The results indicated that the nanoparticles crystallized in a tetragonal system of scheelite type. The typical emission spectrum of $Sr_{0.95}MoO_4$:$0.05Eu^{3+}$ phosphors consists of sharp lines peaking at 532, 553, 590, 611 and 649nm, which are assigned to $^5D_1$ -$^7F_1$, $^5D_0$ - $^7F_0$, $^5D_0$ - $^7F_1$, $^5D_0$ -$^7F_2$ and $^5D_0$ -$^7F_3$ respectively. When the Tb^{3+} is doped, the emission spectra composed of four emission peaks located at 487, 543, 579, and 617 nm, which are ascribed to the $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ transitions of Tb^{3+}. The characteristic green luminescence of the $Sr_{0.95}MoO_4$:$0.05Pr^{3+}$component on excitation at 241nm was attributed to the $^3P_0$ excited state of Pr^{3+}. The most intense lines with maxima at 486 and 643 nm correspond to the $^3P_0$-$^3H_4$ and $^3P_0$-$^3F_2$ transitions respectively.

Key words: inorganic compounds; chemical synthesis; optical properties

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Alkali rare earth molybdate $AMoO_4$:xLn^{3+}, where A=alkali metal ions, Ln^{3+}= rare earth ions) are of particular interest since their crystal structure (Fig.1) and potential application in areas such as laser hosts, phosphors, optical fibers, pigments, humidity sensors, magnetic materials, ionic conductors, catalysts[1,2]. Recently, molybdates have been extensively studied due to its attractive luminescence behavior and interesting structural and opto-electronic properties[3, 4].

Over the past several years, abundant effort has been focused on the development of new synthetic routes for the most efficient solid-state lighting sources in the lighting industry. Pochporch-making advancement has been made to the assembly nanocrystals for the fabrication of solid state lighting nanocrystal materials[5]. In general, dimensionality, shape, and size are vigorously related to the property of a material[6]. Up until now, many distinctive preparation techniques, such as solid-state reactions[7], Czochralski method[8], solvothermal procedures[9], microwave irradiation process[10], hydrothermal course[11], electrochemical routines [12] and sol-gel synthesis[13] are successfully used in the synthesis of different inorganic nanocrystal materials. In these various synthesis routes, the solid-state reactions play an important role in the plot and production of nanomaterial and have been successful in overcoming the complexity to the process. However, the fabrication of the $Gd_2(MoO_4)_3$: Eu^{3+} Nanostructures with well-controlled in shape, phase purity, chemical composition, and desired property remains as one of the main challenging issues by material's scientists. The controlled micro/nano architectures via chemical self-assembly routes still remains a challenge in materials chemistry research for its great application potential. Therefore, we report nanoparticles of $SrMoO_4$ doped with Eu^{3+}, Tb^{3+}, Pr^{3+} ions with perfectly crystalline morphology without any organic additives. In this paper, Trivalent praseodymium doped strontium molybdate ($SrMoO_4$) was synthesized by solid-state reactions and the crystal structure and luminescent properties were investigated. We also explore the luminescence by changing kinds of trivalent rare-earth ions at room temperature. The CIE chromaticity diagrams for $Sr_{0.95}MoO_4$:$0.05Ln^{3+}$ phosphors are investigated in detail.

EXPERIMENTAL SECTION

1.1 Synthesis of $Sr_{0.95}MoO_4$:0.05Ln^{3+}(Ln = Eu, Tb, Pr)

The analytical grade chemicals were used without treating further for purification. $Sr_{1-x}MoO_4$:xLn^{3+}(Ln = Eu, Tb, Pr) phosphors were prepared by a standard solid-state technique. High-purity starting materials such as Eu_2O_3, Tb_4O_7, Tb_6O_{11} 99.99%), $(NH_4)_2MoO_4$ (Aldrich, 99.9%) and $SrCO_3$ (Aldrich, 99.9%) were used. Assuming a complete reaction and in accordance with the stoichiometric ratio, the materials were weighted and sufficiently grounded until the mixture became the homogeneous and viscous precursor. Then, the samples were sintered at 850°C for five h. Finally, they were ground slightly to obtain the phosphor powder.

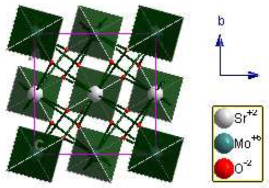

Fig. 1 Crystal structure of $SrMoO_4$

1.2 Characterization

The crystal structures and morphologies of the products were characterized by X-ray powder diffraction method (XRD). XRD analysis was carried out on a BRUKER D8 Advance powder diffractometer using Cu K_α radiation (λ=0.1541874 nm). The applied current and the accelerating voltage were 40 mA and 40 kV, respectively. The 2θ ranges of all the data sets are from 10° to 70° with a step size of 0.05°. The photoluminescence spectra were recorded using a Perkin Elmer (LS-55) instrument. All the measurements were performed at room temperature.

RESULTS AND DISCUSSION

2.1 XRD characterization of the $Sr_{0.95}MoO_4$:0.05Ln^{3+} (Ln = Eu, Tb, Pr) phosphor

Fig. 2 presents the XRD patterns of the $Sr_{0.95}MoO_4$:0.05Ln^{3+} powders containing 5.00% of Eu^{3+},Tb^{3+}, and Pr^{3+} phosphors annealed at 600 °C for 5h. According to the JCPDS(NO.08-0482) database, all diffraction peaks were indexed as a scheelite-like single phase of the $SrMoO_4$ presenting the tetragonal symmetry with a space group I41/a (88) indicating no impurity phase is found when the Ln^{3+} dopant concentration is 5mol %.

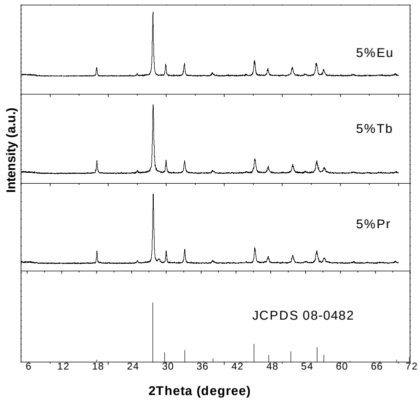

Fig.2 XRD patterns of $Sr_{0.95}MoO_4$:0.05Ln^{3+}phosphors

2.2 Luminescent properties of the $Sr_{0.95}MoO_4$:0.05Ln^{3+} (Ln= Eu, Tb, Pr)

Fig. 3 gives the excitation spectra of $Sr_{0.95}MoO_4$:0.05Eu^{3+} powders heat treated at 600 °C for 5h at the room temperature, which were obtained setting the Eu^{3+} emission maximum at 612 nm.The excitation peaks of samples consist of a broad band region (200–320 nm) and groups of sharp peaks located at 320–500 nm. The dominant broad excitation band at 200–320 nm is attributed to the charge-transfer (CT) transition from 2p orbital of O^{2-} ions to the 4f orbital of Eu^{3+} ions. It was noticed the characteristic sharp peaks occurring in the longer wavelength region are assigned to the intra-configuration 4f–4f transitions of Eu^{3+} ions in the host lattice of $Sr_{0.95}WO_4$:0.05$Eu^{3+}$and the $^7F_0$-$^5L_6$ and $^7F_0$-$^5D_3$ transitions at 394 nm and 417 nm, respectively. The emission spectra of $Sr_{0.95}MoO_4$:0.05Eu^{3+} phosphors under 225 and 259 nm excitation are shown in Fig. 4. Due to the similar photoluminescent character of $Sr_{0.95}MoO_4$:0.05Eu^{3+} with different excitation wavelength, we just take the 225nm excitation wavelength spectra for example. The typical spectrum essentially consists of sharp peaks at wavelengths from 500 to 700 nm. The corresponding emission spectrum consists of the characteristic transitions of Eu^{3+} within its $4f^6$ configuration, i.e., $^5D_1$ -$^7F_1$ (532 nm), $^5D_0$ - $^7F_0$ (553 nm), $^5D_0$ - $^7F_1$ (590 nm), $^5D_0$ -$^7F_2$ (611nm) and $^5D_0$ -$^7F_3$ (649 nm). The strongest one is located at 611 nm.

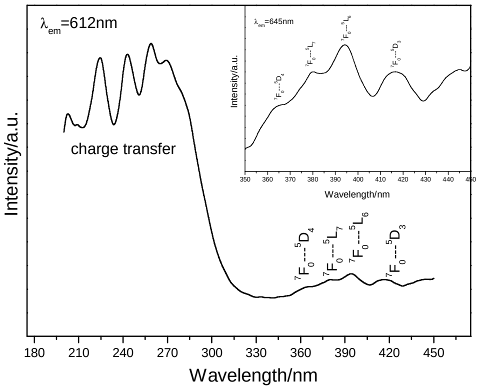

Fig.3 Excitation spectrum of $Sr_{0.95}MoO_4$:0.05Eu^{3+}

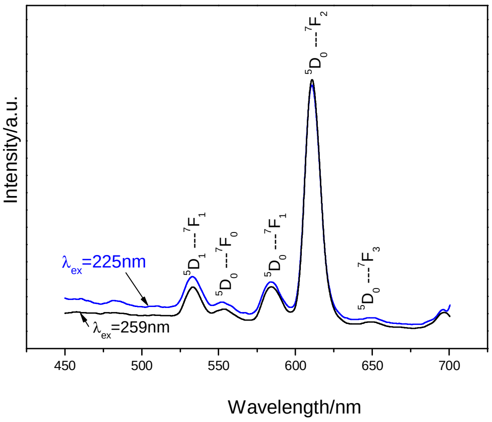

Fig. 4 Emission spectrum of $Sr_{0.95}MoO_4$:0.05Eu^{3+}

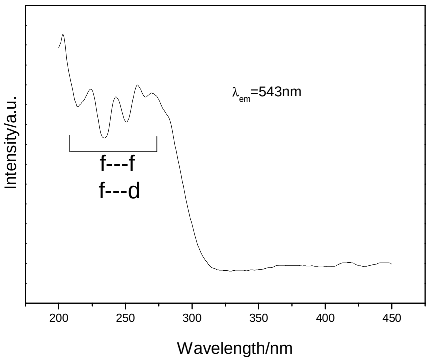

Fig. 5 Excitation spectrum of $Sr_{0.95}MoO_4$:0.05Tb^{3+}

The excitation and emission spectra of $Sr_{0.95}MoO_4$:0.05Tb^{3+} phosphors are shown in Fig. 5, Fig. 6, respectively. It can be seen that the excitation spectrum monitored at 543 nm exhibits a wide band from 220 to 280 nm. The broad band can be ascribed to $4f^8 \rightarrow 5f^7d^1$ (f→d) transition of Tb^{3+} ion, which is caused by the dipolar electric parity allowed transition. The emission spectrum excited by 260,223 nm look very similar, which composed of four emission peaks located at 487, 543, 579, and 617 nm, which are ascribed to the $^5D_4$-$^7F_6$, $^5D_4$-$^7F_5$, $^5D_4$-$^7F_4$ and $^5D_4$-$^7F_3$ transitions of Tb^{3+} respectively and the green $^5D_4$-$^7F_5$ emission located at 543 nm is dominant. The excitation spectrum of $Sr_{0.95}MoO_4$:0.05Pr^{3+} phosphor (λ_{em}=645nm) is shown in Fig. 7. The excitation spectrum of the $^3P_0$-$^3F_2$

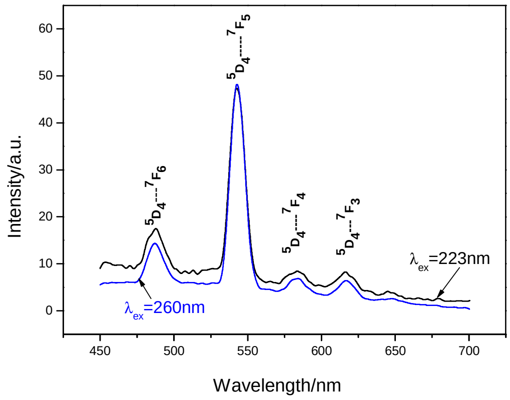

Fig. 6 Emission spectrum of $Sr_{0.95}MoO_4$:0.05Tb^{3+}

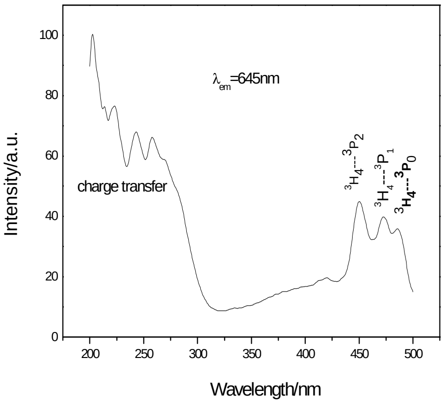

Fig.7 Excitation spectrum of $Sr_{0.95}MoO_4$:0.05Pr^{3+}

Fig. 8 shows the excitation spectrum dependence of the emission spectra of $Sr_{0.95}MoO_4$:0.05Pr^{3+} at 254 transition of Pr^{3+} is composed of the host broadband in the UV regions which were assigned to the 4f-5d transition of Pr^{3+} or a charge transfer transition from Pr^{4+}-O^{2-} to Pr^{3+}-O^{1-}[14,15]. The manifold of sharp lines peaking at 450, 472, and 487 nm are assigned to the $^3H_4$-$^3P_2$, $^3H_4$-$^3P_1$, and $^3H_4$-$^3P_0$ absorption transitions of Pr^{3+} respectively [16-18]. and 241nm. Upon the two excitation wavelength, similar behaviors are observed for crystals. They present a series of relatively sharp features mainly originating in the $^3P_0$ excited state of Pr^{3+}. The most intense lines with maxima at 486 and 643 nm correspond to the $^3P_0$-$^3H_4$ and $^3P_0$-$^3F_2$ transitions, respectively. The weaker multiplet in the 510–580 nm range is assigned to the $^3P_0$-$^3H_5$ and that in the 590–630 nm range to the $^3P_0$-$^3H_6$ and $^1D_2$-$^3H_4$ transitions.The Commission Internationale de I'Eclairage (CIE)-1931 chromaticity coordinates of $Sr_{0.95}MoO_4$:0.05Ln^{3+}(Ln = Eu, Tb, Pr) phosphors were calculated using a ColorCoordinate.exe program.

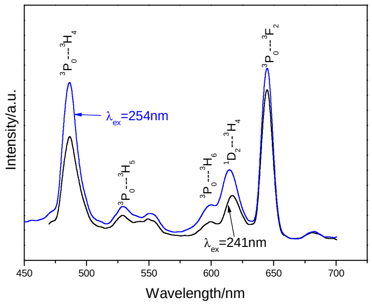

Fig. 8 Emission spectrum of $Sr_{0.95}MoO_4$:0.05Pr^{3+}

As shown in Fig. 9, when we doped Eu^{3+},Tb^{3+}, Pr^{3+} ions in $Sr_{1-x}MoO_4$, the color tones change from buff (CIE coordinates x= 0.456, y=0.380) to white (CIE coordinates x= 0.375, y=0.364) and yellowish green (CIE coordinates x=0.297, y=0.506) by adjusting the kind of doping rare earth.

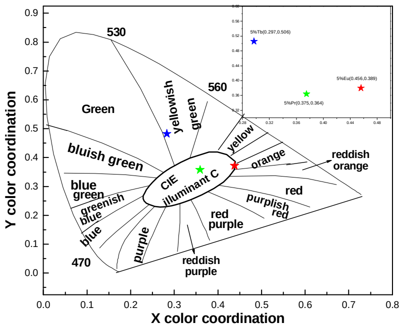

Fig. 9 CIE chromaticity diagram for $Sr_{1-x}MoO_4$:xPr samples

CONCLUSION

In summary, rare earth doped $Sr_{0.95}MoO_4$:$0.05Ln^{3+}$ (Ln = Eu, Tb, Pr) phosphors have been synthesized by solid-state technique. All the investigated samples were characterized by XRD and PL. The XRD patterns showed no impurity phase is found when the Ln^{3+} dopant concentration is 5mol %. The corresponding emission spectrum consists of the characteristic transitions of Eu^{3+}, Tb^{3+} and Pr^{3+} ions.

Acknowledgements

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REFERENCES

[1]. Florin Tudorache, Iulian Petrila, Karin Popa et al. *Applied Surface Science*, **2014**, 303(6),175-179.
[2] Polishchuk S A, Ignat’eva L N，Marchenko YV. et al. *TenPhysics and Chemistry*, **2011**,37(2),1-20.
[3] Tang Z W, Zhou Liqun, Wang Fen et al. *Acta Part A: Molecular and Biomolecular Spectroscopy*, **2009**,72(2,),348-355.
[4] Titipun Thongtem, Sukjit Kungwankunakorn, Budsabong Kuntalue et al. *Journal of Alloys and Compounds*, **2010**,506(1), 475-481.
[5] Zhang Fan, Zhao Dongyuan, *Nano Research*, **2009**, 2(4)292-305.
[6] Tsunenobu Onodera, Hitoshi Kasai, Hidetoshi Oikaw et al. *Advances in Materials Research*, **2009**,13,81-100.
[7] V.D. Zhuravlev, O.G. Reznitskikh, Yu.Aet al. *Journal of Solid State Chemistry*, **2011**, 184(10),2785-2789.
[8] Spassky D.A., Mikhailin V.V., Savon A.E. et al. *Optical Materials*, **2012**, 34(11),1804-1810.
[9] L. Krishna Bharat, Bandi Vengala Rao, Jae Su Yu, *Chemical Engineering Journal*, **2014**,255(11): 205-213.
[10] Pradeep Verma, Takahito Watanabe, Yoichi Honda et al. *Bioresource Technology,* 2011, 102(4):3941-3945.
[11] Byrappa K, Masahiro Yoshimura, Molybdates，*Related Compound，Handbook of Hydrothermal Technology*, 2001, 618-690.
[12] Chen Lianping, Gao Yuanhong, *Materials Research Bulletin*, **2007**, 42(10)2,1823-1830.
[13]. Mohamed Benchikhi, Rachida El Ouatib, Sophie Guillemet-Fritsch, et al. *Ceramics International*, **2014**, 40(4), 5371 - 5377.
[14] Zhu Fang, Xiao Zhisong, Zhang Feng et al. *Journal of Luminescence,* **2011**, 131(1):22-24.
[15] M.J. Martínez-Lope, J.A. Alonso, D. Sheptyakov et al. *Journal of Solid State Chemistry*, **2010**, 183(12),2974-2978.
[16] V.V. Atuchin, V.G. Grossman, S.V. Adichtchev et al.*Optical Materials*, **2012**, 34(5),812-816.
[17] Enrico Cavalli, Fabio Angiuli, Philippe Boutinau et al. *Journal of Solid State Chemistry*, **2012**, 185(1),136-142.
[18] ZhanS.B. g, Sun Y.P., Zhao B.C., et al. *Solid State Communications*, **2006**,138(3), 123-128.