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材料合成及性能

$\text{Ca}_{0.8}\text{La}_{0.2-x-y}\text{MoO}_4 : x\text{Tb}^{3+}, y\text{Eu}^{3+}$ 荧光材料的水热合成及多色发光性质

韩丽, 宋超, 刘桂霞, 王进贤, 董相廷

长春理工大学化学与环境工程学院 应用化学与纳米技术吉林省高校重点实验室, 吉林 长春 130022

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摘要： 采用水热法制备了 $\text{Ca}_{0.8}\text{La}_{0.2-x-y}\text{MoO}_4 : x\text{Tb}^{3+}, y\text{Eu}^{3+}$ 荧光材料, 并对其结构和发光性能进行了研究。X射线衍射(XRD)分析表明, 合成的样品为四方晶系的 CaMoO_4 白钨矿结构, 稀土离子 La^{3+} 、 Eu^{3+} 、 Tb^{3+} 的引入不会改变主晶格的结构。荧光光谱表明, 与 $\text{CaMoO}_4 : \text{Eu}^{3+}$ 荧光粉相比, 基质中掺杂 La^{3+} 后的 $\text{Ca}_{0.8}\text{La}_{0.15}\text{MoO}_4 : 0.05\text{Eu}^{3+}$ 样品的 616 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) 处的特征发射峰明显增强。在 285 nm 紫外光激发下, $\text{Ca}_{0.8}\text{La}_{0.16-y}\text{MoO}_4 : 0.04\text{Tb}^{3+}, y\text{Eu}^{3+}$ ($y=0.01, 0.03, 0.05, 0.07$) 系列样品在 545 nm 和 616 nm 处出现的发射峰, 分别对应于 Tb^{3+} 的 $^5\text{D}_4 \rightarrow ^7\text{F}_5$ 跃迁和 Eu^{3+} 的 $^5\text{D}_0 \rightarrow ^7\text{F}_2$ 跃迁, 并且随着 Eu^{3+} 掺杂量的增加, Tb^{3+} 的发射峰逐渐减弱, Eu^{3+} 的发射峰逐渐增强, 表明该荧光材料中存在着由 Tb^{3+} 到 Eu^{3+} 能量传递。随着 $\text{Ca}_{0.8}\text{La}_{0.16-y}\text{MoO}_4 : 0.04\text{Tb}^{3+}, y\text{Eu}^{3+}$ ($y=0.01, 0.03, 0.05, 0.07$) 系列样品中激活剂 Eu^{3+} 掺杂量的增加, 荧光粉实现了从绿色 \rightarrow 黄绿 \rightarrow 黄色 \rightarrow 红色的颜色可调。

关键词： $\text{Ca}_{0.8}\text{La}_{0.2}\text{MoO}_4$ 荧光材料 水热合成 多色发光

Hydrothermal Preparation and Multi-color Luminescence Properties of $\text{Ca}_{0.8}\text{La}_{0.2-x-y}\text{MoO}_4 : x\text{Tb}^{3+}, y\text{Eu}^{3+}$

HAN Li, SONG Chao, LIU Gui-xia, WANG Jin-xian, DONG Xiang-ting

Key Laboratory of Applied Chemistry and Nanotechnology at Universities of Jilin Province, School of Chemistry and Environmental Engineering, Changchun University of Science and Technology, Changchun 130022, China
Abstract: $\text{Ca}_{0.8}\text{La}_{0.2-x-y}\text{MoO}_4 : x\text{Tb}^{3+}, y\text{Eu}^{3+}$ fluorescent materials were prepared by hydrothermal method. The crystal structure and luminescence properties were studied. X-ray diffraction (XRD) patterns confirm that the crystal structure of the samples matches well with the tetragonal CaMoO_4 . The introduction of rare earth ions La^{3+} , Eu^{3+} , and Tb^{3+} doesn't change the structure of the host lattice. Comparing with $\text{CaMoO}_4 : \text{Eu}^{3+}$ phosphors, the characteristic emission peak in 616 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) of $\text{Ca}_{0.8}\text{La}_{0.15}\text{MoO}_4 : 0.05\text{Eu}^{3+}$ is enhanced obviously. The emission spectra of $\text{Ca}_{0.8}\text{La}_{0.16-y}\text{MoO}_4 : 0.04\text{Tb}^{3+}, y\text{Eu}^{3+}$ ($y=0.01, 0.03, 0.05, 0.07$) exhibit two emission peaks at 545 nm and 616 nm under 285 nm UV excitation, corresponding to the transition of $^5\text{D}_4 \rightarrow ^7\text{F}_5$ of Tb^{3+} and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ of Eu^{3+} . It is found that the emission intensity of Eu^{3+} increases and the emission intensity of Tb^{3+} decreases with the increasing of Eu^{3+} content, indicating that there is energy transfer of $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$. Moreover, the luminescence colors of the $\text{Ca}_{0.8}\text{La}_{0.16-y}\text{MoO}_4 : 0.04\text{Tb}^{3+}, y\text{Eu}^{3+}$ ($y=0.01, 0.03, 0.05, 0.07$) samples can be tuned from green, green-yellow and yellow to red by simply adjusting the relative doping concentrations of the activator ion of Eu^{3+} under a single wavelength excitation.
Keywords: $\text{Ca}_{0.8}\text{La}_{0.2}\text{MoO}_4$ luminescent material hydrothermal preparation multi-color emitting

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通讯作者: 刘桂霞, E-mail: liuguixia22@yahoo.com.cn

作者简介: 韩丽(1987-), 女, 山西太原人, 主要从事稀土发光材料的研究。E-mail: aicaobaihe7887@163.com

作者Email: liuguixia22@yahoo.com.cn

参考文献:

- [1] Zhao D, Seo S J, Bae B S. Full-color mesophase silicate thin film phosphors incorporated with rare earth ions and photosensitizers [J]. *Adv. Mater.*, 2007, 19(21): 3473-3479.
- [2] Zhao Y S, Fu H B, Hu F Q, et al. Multicolor emission from ordered assemblies of organic 1D nanomaterials [J]. *Adv. Mater.*, 2007, 19(21): 3554-3558.
- [3] Li G G, Geng D L, Shang M M, et al. Color tuning luminescence of $\text{Ce}^{3+}/\text{Mn}^{2+}/\text{Tb}^{3+}$ -triacivated $\text{Mg}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2$ via energy transfer: Potential single-phase white-light-emitting phosphors [J]. *J. Phys. Chem. C*, 2011, 115(44): 21882-21892 [crossref](#)
- [4] Wang T, Jing Y J, Zhu Y H, et al. Progress of the research on tungstate and molybdate red phosphor for white-LED [J]. *China Light & Lighting* (中国照明电器), 2008, 2(4): 16-20 [crossref](#)
- [5] Lin X, Qiao X S, Fan X P. Synthesis and luminescence properties of a novel red $\text{SrMoO}_4 : \text{Sm}^{3+}, \text{R}^{3+}$ phosphor [J]. *J. Solid State Sci.*, 2011, 13(3): 579-583.
- [6] Liu X R. Phosphor for white led solid state lighting [J]. *Chin. J. Lumin.* (发光学报), 2007, 28(3): 291-301 (in Chinese).

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- [7] Chen Y J, Liu T T, Geng X J, *et al.* Influence for matrix composition of molybdates-tungstates phosphors and annealing process on photoluminescent properties [J]. *J. Chin. Soc. Rare Earths* (中国稀土学报), 2012, 30(1):56-60 (in Chinese).
- [8] Khanna A, Dutta P S. Narrow spectral emission $\text{CaMoO}_4:\text{Eu}^{3+},\text{Dy}^{3+},\text{Tb}^{3+}$ phosphor crystals for white light emitting diodes [J]. *J. Solid State Chem.*, 2013, 198: 93-100.
- [9] Xu Z H, Li C X, Li G G, *et al.* Self-assembled 3D Urchin-like $\text{NaY}(\text{MoO}_4)_2:\text{Eu}^{3+}/\text{Tb}^{3+}$ microarchitectures: Hydrothermal synthesis and tunable emission colors [J]. *J. Phys. Chem. C*.2010, 114(6):2573-2582 [crossref](#)
- [10] Jiang Y Y, Liu G X, Wang J X, *et al.* Preparation and luminescence properties of $\text{NaGd}(\text{MoO}_4)_2:\text{Dy}^{3+},\text{Eu}^{3+}$ white-light phosphors [J]. *Chem. J. Chin. Univ.*(高等学校化学学报), 2013, 34(4):794-799 (in Chinese).
- [11] Liao J S, Zhou D, Yang B, *et al.* Sol-gel preparation and photoluminescence properties of $\text{CaLa}_2(\text{MoO}_4)_4:\text{Eu}^{3+}$ phosphors [J]. *J. Lumin.*, [crossref](#)
- [12] Yang Y L, Li X M, Feng W, *et al.* Co-precipitation synthesis and photoluminescence properties of $(\text{Ca}_{1-x-y}\text{Ln}_y)\text{MoO}_4:\text{xEu}^{3+}$ ($\text{Ln}=\text{Y}, \text{Gd}$) red phosphors [J]. *J. Alloys Compd.*, 2010, 505(1):239-242.
- [13] Zeng Q H, He P, Liang H B, *et al.* Luminescence of Eu^{3+} -activated tetra-molybdate red phosphors and their application in near-UV InGaN-based LEDs [J]. *Mater. Chem. Phys.*, 2009, 118(1):76-80.
- [14] Yang Y L, Li X M, Feng W L, *et al.* Co-precipitation synthesis and photoluminescence of $(\text{Ca}_{1-x-y}\text{Lu}_y)\text{MoO}_4:\text{xEu}^{3+}$ red phosphors [J]. *Chin. J. Inorg. Chem.*(无机化学学报), 2011, 27(2):276-280 (in Chinese).
- [15] Cao F B. Sol-gel synthesis of red-emitting phosphor $\text{Ca-Sr-Mo-W-O}-(\text{Eu}^{3+},\text{La}^{3+})$ powders and luminescence properties [J]. *Ind. Eng. Chem. Res.*, 2012, 51(9):3569-3574.
- [16] Cao F B, Li L S. La^{3+} acting on host to Eu^{3+} energy transfer in $(\text{Ca-Sr-Eu-La})(\text{Mo-W})\text{O}_4$ under NUV excitation [J]. *J. Electrochem. Soc.*, 2011, 158(10):997-1001.
- [17] Li X, Yang Z P, Guan L, *et al.* Synthesis and luminescent properties of $\text{CaMoO}_4:\text{Tb}^{3+},\text{R}^+(\text{Li}^+, \text{Na}^+, \text{K}^+)$ [J]. *J. Alloys Compd.*, 2008, 478(1-2):684-686.
- [18] Sheng T Q, Fu Z L, Wang X J. Solvothermal synthesis and luminescence properties of BaCeF_5 , and $\text{BaCeF}_5:\text{Tb}^{3+},\text{Sm}^{3+}$ nanocrystals: An approach for white light emission [J]. *J. Phys. Chem. C*.2012, 116(36):19597-19603 [crossref](#)
- [19] Huang C H, Chen T M. A novel single-composition trichromatic white-light $\text{Ca}_3\text{Y}(\text{GaO})_3(\text{BO}_3)_4:\text{Ce}^{3+},\text{Mn}^{2+},\text{Tb}^{3+}$ phosphor for UV-light emitting diodes [J]. *J. Phys. Chem. C*.2011, 115(5):2349-2355 [crossref](#)
- [20] Wu Y T, Ding D Z, Pan S K, *et al.* Luminescence characteristics of $\text{Lu}_{0.8}\text{Sc}_{0.2}\text{BO}_3:\text{RE}^{3+}$ ($\text{RE}=\text{Eu}, \text{Tb}$) polycrystalline powders [J]. *J. Alloys Compd.*, 2011, 509(25):7186-7191.
- [21] Zhang J H, Lyu W, Hao Z D, *et al.* Color-tunable white-light emitting $\text{BaMg}_2\text{Al}_6\text{Si}_9\text{O}_{30}:\text{Eu}^{2+},\text{Tb}^{3+},\text{Mn}^{2+}$ phosphors *via* energy transfer [J]. *Chin. Opt.*(中国光学), 2012, 5(3):203-208 (in Chinese).
- [22] Xie Y, Wang T, Wang H B. Luminescence properties of $\text{Y}(\text{VP})\text{O}_4:\text{Eu}^{3+}$ phosphor doped with alkali earths and rare earths [J]. *Chin. J. Liq. Cryst. Disp.*(液晶与显示).2011, 26(5):587-591 [crossref](#)