Luminescent Properties of Eu^{3+} Doped γ-Bi_2MoO_6 Powder Prepared by Co-precipitation Method

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Abstract. Eu^{3+}doped γ-Bi_2MoO_6 red uminescent powder is prepared by co-precipitation method in this paper. Structure and constitution of powder samples are examined by DTA-TG, XRD and IR. Results showed that: quadrature phase α-$Bi_2Mo_3O_{12}$ is achieved when anneal temperature is 800 ℃ and pH is below 3; while quadrature phaseγ-Bi_2MoO_6 is achieved when pH is between 5 to 13. Under the monitoring of the 612 nm light, the sample γ-Bi_2MoO_6: the excitation spectrum of Eu^{3+} does not appear $Eu^{3+}\rightarrow O^{2-}$ charge transfer band and the wide absorption peak resulted from $Mo^{6+}\rightarrow O^{2-}$ charge transfer band, and similar linear transition peaks only located at 466 nm as well as 535 nm with little difference between the intensity of two excitation peaks. Under the stimulating of the 612 nm blue light, Eu^{3+} in γ-Bi_2MoO_6 matrix has considerable $5D^0\rightarrow 7F^2$ transition emission at 612 nm, and γ-Bi_2MoO_6： the illuminating intensity of Eu^{3+} is the strongest when pH is 5.

Introduction

With the progress of science and technology, optical functional materials have been put forward higher requirements and rare earth luminescent materials occupy a pivotal position in various applications in the field of rare earths. Among the rare earth luminescent materials, materials putting Eu^{3+} as well as Tb^{3+} as activator have become a major source of red light and green light, and have been extensively studied. Molybdate has excellent luminescent properties and it is a typical self-activated phosphors. It is showed that rare earth ions undoped molybdate can emit wide and strong spectrum between blue and green light under the monitoring of near ultraviolet or UV. While Eu^{3+} doped molybdate will transfer its energy to Eu^{3+} under the monitoring of UV and its inherent emission characteristics will disappear. As a result, Eu^{3+} can emit characterise red light, and studies for the rare earth luminescent materials of Eu^{3+} doped molybdate have been conducted endlessly in recent years. Bismuth molybdate chemical formula is Bi_2O_3•$nMoO_3$， and n=3, 2, 1 respectively corresponds to α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$ and γ-Bi_2MoO_6. Bismuth molybdate is a kind of molybdate with the luminescent, ion conductor and catalytic properties, and it has been increasingly favored by researchers. As the simplest one among perovskite-type compounds with special layered structure, γ-Bi_2MoO_6 has been reported many times. In this paper, the red luminescent material, Eu^{3+} doped γ-Bi_2MoO_6 is prepared by co-precipitation method, and its structure as well as luminescent properties have been studied.

Experimental

2.1 Reagents

Eu_2O_3, 99.99%, Baotou Rare Earth Research Institute; $Bi(NO_3)_3$ ·$5H_2O$, $(NH_4)_6Mo_7O_{24}$·$4H_2O$, A.R., Sinopharm Chemical Reagent Co., Ltd.; NH_3·H_2O, A.R., Tianjin Chemical Reagent Co., Ltd. Sheng Austria; experimental double-distilled water.

2.2 Preparation of samples

Weighing a certain amount of Eu_2O_3 with nitric acid (1:1) and

dissolved, evaporating excess nitric acid slowly, and after cooled to room temperature, moved it to flask, adding a secondary water volume, dubbed 0.1 mol·L^{-1} Eu $(NO_3)_3$ solution, setting aside.

In preparing γ-Bi_2MoO_6 doped 10% Eu^{3+} case to illustrate the course of the experiment. Weighing 0.9702 g Bi $(NO_3)_3$·5H2O was added to the deionized water, Stirring and adding 1.0 mL preparation of a good 0.1 mol / L $Eu(NO_3)_3$ solution, adding $(NH_4)_6MoO_6$ solution to form a homogeneous white suspension, adjusting the pH value of the mixed suspension to 5 With NH_3 • H_2O, The precipitate was filtered and washed, dried at 60 C for 6 h, gaining a pale yellow powder. Maintaining a high temperature furnace and heating at rate of 10 C / min. The samples were treated for 2 h at a certain annealing temperature, Naturally cooled to room temperature after a pale yellow sample γ-Bi_2MoO_6 doped Eu^{3+}.

X-ray powder diffraction (D8-Advance model, Bruker Germany ray source was CuKa, 1.5406, tube voltage of 40KV, tube current of 40mA). Fluorescence spectroscopy is a Japanese type Hitachi F-4500 Fluorescence Spectrophptometer, with a Xe lampas(150W) as laser source, and the photomultiplier tube voltage was 400V.Differential thermal analyzer is Shimadzu DTG-60H.

Results and discussion

3.1Eu^{3+} doped Bismuth molybdate with

Figure 1 shows the DTA-TG of the precursor of bismuth molybdate doped with Eu^{3+} (molar fraction of 10%). As shown in the figure, a broad endothermic peak appeared at about 100C to 200C, because of the absorption at the surface of water. At about 200C to 1000C, no obvious endothermic or exothermic peaks. There is a slow process of weightless in the about 200C to between 600C. When the anneal temperature is higher than 600C, the weight of the sample remains almost unchanged, it showed the crystal structure has been basically stable. the choice of more than 600C temperature calcination of the samples is reasonable.

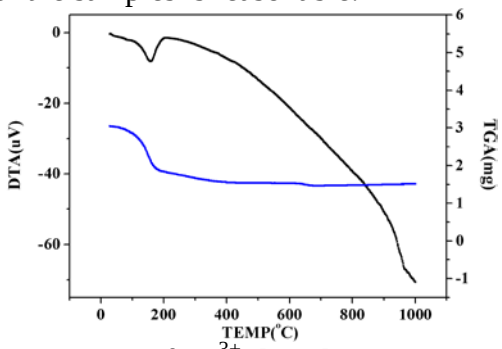
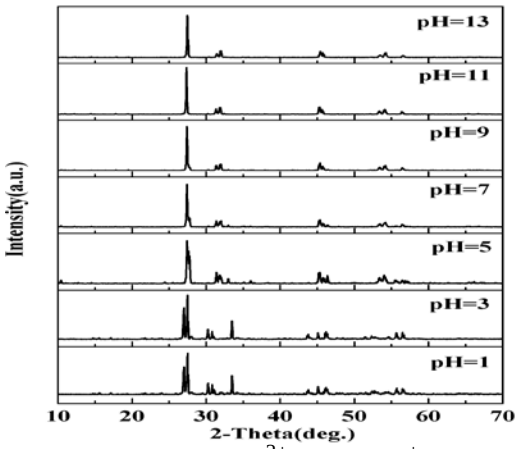


Fig. 1 DTA-TG spectra of Eu^{3+}-doped Bi_2O_3·$nMoO_3$ precursor

Figure 2 indicated the XRD patterns of the samples of Eu^{3+} doped bismuth molybdate at different pH value. (mole fraction of Eu^{3+} is 10%, the annealing temperature is 800C). As shown in Figure 2, when the pH value is 1 or 3, all diffraction peaks for the sample is in according to the standard card JCPDS:P210103, and no the other impurity peaks exist, the samples is detected to be orthogonal phase of α-$Bi_2Mo_3O_{12}$, When the pH value is 5, 7, 9, 11 or 13, the diffraction peaks for the sample is found in the standard card JCPDS:210102, it indicated the preparation sample is γ-Bi_2MoO_6 required. Therefore, when the pH value is above than 5, it is easy to obtain γ-Bi_2MoO_6.



In the reaction process, two kinds of ions of Bi^{3+} and BiO^{+} can be formed. BiO^{+} slightly soluble in water, so the bismuth is precipitated in the form of Bismuth oxygen salt. The following is simple analysis of the forming mechanism[6].

$$Bi^{3+} + H_2O \leftrightarrow BiO^{+} + 2\,H^{+} \quad (1)$$

The behavior of Mo (VI) in the solution depends on the degree of polymerization of Mo (VI). According to the pH value of the solution, the concentration of molybdenum, Molybdenum anion can be clustered for preparing a series of heavy molybdenum ions such as $(MoO_4)^{2-}$, $(Mo_2O_7)^{2-}$, $(Mo_3O_{10})^{2-}$.

$$2\,(MoO_4)^{2-} + 2\,H^{+} \leftrightarrow (Mo_2O_7)^{2-} + H_2O \quad (2)$$

$$3\,(MoO_4)^{2-} + 4\,H^{+} \leftrightarrow (Mo_3O_{10})^{2-} + 2H_2O \quad (3)$$

At the higher concentrations of molybdenum and the lower pH value, $(MoO_4)^{2-}$ is prone to poly, Mo mainly forms $(Mo_3O_{10})^{2-}$, the precipitation is mainly α-$Bi_2Mo_3O_{12}$.

$$2BiO^{+} + (Mo_3O_{10})^{2-} \rightarrow Bi_2Mo_3O_{12}\downarrow \quad (4)$$

When the pH value increased gradually, part of the H^{+} was neutralized by OH^{-}, the molybdate ion from poly, molybdenum in solution mainly in the form of $(MoO_4)^{2-}$, the precipitation mainly for γ-Bi_2MoO_6

$$2BiO^{+} + (MoO_4)^{2-} \rightarrow Bi_2MoO_6\downarrow \quad (5)$$

3.2Infrared spectra of Eu^{3+} doped bismuth molybdate

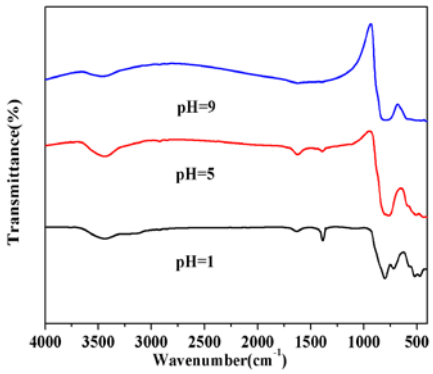


Fig. 3 IR spectra of Eu^{3+}-doped $Bi_2O_3 \cdot nMoO_3$ under different pH

Figure 3 shows the IR spectra of Eu^{3+} doped bismuth molybdate with different pH values. (The mole fraction of Eu^{3+} was 10%, The annealing temperature is 800C). Figure 3 shows that when the pH is equal to 1, the sample has the O-H stretching vibration peak at about 3440 cm^{-1} and have the O-H bending vibration peak at 1630 cm^{-1}, this is attributed to the combined water contained in the samples. There is a N-H bending vibration peak at about 1386 cm^{-1} which is mainly attributed to the $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ is used as the source of molybdenum in the experimental process,$NH_3 \cdot H_2O$ is used to adjust the pH value of the solution. The strong absorption peak which located around 802 cm^{-1} is due to the stretching vibration of polymer $(Mo_3O_{10})^{2-}$; The strong absorption peak which is located around 718 cm^{-1} is MoO_6 eight surface body ν_1 and ν_3 stretching vibration (Mo-O stretching vibration); The absorption peak which is located about 518 cm^{-1} and 470 cm^{-1} is due to stretching vibration and bending vibration of Mo-O-Bi. Combined with XRD analysis results , the

samples were prone to poly when the preparing circumstance with the low pH value, which is consistent with the results of IR analysis. When the pH value is 5, O-H bending vibration peak and O-H stretching vibration peak the of samples located around 3440 cm^{-1} and 1630 cm^{-1} respectively are basically unchanged; The N-H bending vibration peak at about 1386 cm^{-1} decreased; The ν_1 and ν_3 stretching vibration (Mo-O stretching vibration) of MoO_6 eight surface body located around 764 cm^{-1} strengthened; Stretching vibration and bending vibration of Mo-O-Bi is located about 506 cm^{-1} and 470 cm^{-1} respectively also strengthened. When the pH value is 9,the O-H bending vibration peak and the O-H stretching vibration peak of samples at about 3440 cm^{-1} and 1630 cm^{-1} respectively decreased, N-H bending vibration peak at about 1386 cm^{-1} disappeared, Mo-O characteristic absorption peak below 1000 cm^{-1} is weakened. Combined with XRD analysis results, the molybdate ion were prone to removal of poly when the pH value is high, mainly in the form of $(MoO_4)^{2-}$. Thus, different values of pH affects the sample's forming process, in order to obtain the γ-Bi_2MoO_6 required for the proper regulation of pH value of the solution.

3.3Analysis of luminescence properties of Eu^{3+}-doped γ-$Bi_2M_oO_6$

3.3.1 The excitation spectra of Eu^{3+}-doped γ-Bi_2MoO_6

Fig.4 shows PL excitation spectra of Eu^{3+}-doped γ-Bi_2MoO_6 particles with the monitoring wavelength at 614nm.From Fig.4, when the sample is not a broad absorption peak $Eu^{3+}\rightarrow O^{2-}$ the charge transfer (CT) band, and $Mo^{6+}\rightarrow O^{2-}$ charge transfer band is formed, only there presence of a strong class of linear transition peak at 535nm and 466nm and two excitation peak intensity less. They correspond to the $^7F_0\rightarrow{}^5D_2$ and $^7F_0\rightarrow{}^5D_1$ transition of Eu^{3+}, respectively. Which is the outer layer of the f-f transition 5s and 5p electronic shielding produced.

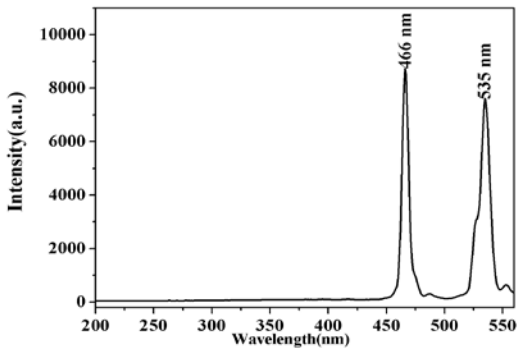


Fig. 4 The excitation spectra of Eu^{3+}-doped

For the commonly excitation materials by Eu^{3+}, charge transfer excitation spectrum intensity at 395nm or $^7F_0\rightarrow{}^5L_6$ transition are much higher than $^7F_0\rightarrow{}^5D_2$ and $^7F_0\rightarrow{}^5D_1$ transition intensity and our preparation obtained Eu^{3+} doped γ-Bi_2MoO_6, Eu^{3+} was very special, which may be due molybdate matrix itself characteristics and preparation methods of the symmetry of the crystal lattice of the matrix is changed resulting in the formation, and the mechanism for this change to be further studied.

This indicated that we use to control the pH of the circumstance, by co-precipitation method successfully Eu^{3+} ion was introduced into γ-Bi_2MoO_6, the excitation spectrum of the sample prepared in $Mo^{6+}\rightarrow O^{2-}$ charge transfer band disappeared, which show that after the γ-Bi_2MoO_6 matrix absorb energy. This energy effectively transfer to the activator Eu^{3+}, Eu^{3+} and γ-Bi_2MoO_6 matrix-matched, luminous performance be raised.

3. 3. 2 The emission spectra of Eu^{3+}-doped γ-Bi_2MoO_6

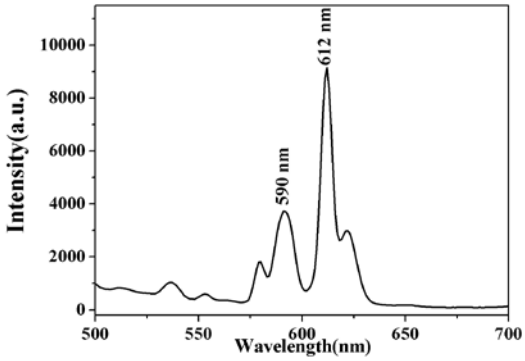


Fig. 5 The emission spectra of Eu^{3+}-doped γ-Bi_2MoO_6

Fig.5 shows emission spectra of Eu^{3+}-doped γ-Bi_2MoO_6 particles with the emission wavelength of $\lambda_{em} = 466\text{nm}$. The emission peaks located at 590nm and 612nm were assigned to the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+}, respectively, splitting occurred and the intensity of $^5D_0 \rightarrow {}^7F_1$ transition lower than the intensity of $^5D_0 \rightarrow {}^7F_2$ transition, that is electric dipole transitions more prominent than the magnetic dipole transitions. This shows that the doped into γ-Bi_2MoO_6 matrix Eu^{3+}, partially in the center of symmetry, a portion deviated from the center of symmetry, the sample presence of a plurality the center of light-emitting and red light is emitted.

3.3.3 Different effects of pH on Eu^{3+} luminescence properties of doped γ-Bi_2MoO_6

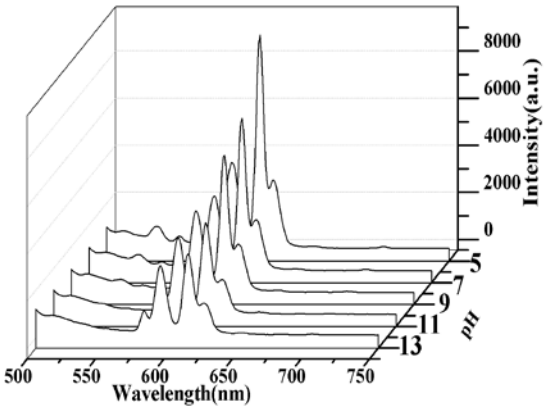


Fig. 6 The emission spectra of different pH of the samples Eu^{3+}-doped γ-Bi_2MoO_6

Fig.6 shows emission spectra of different pH of the samples Eu^{3+}-doped γ-Bi_2MoO_6 with the emission wavelength of $\lambda_{em} = 466\text{nm}$,in experimental range, with the increase of pH, light intensity at first increased and then decreased. When pH is 5, the reaction is carried out fully, the maximum luminous intensity. Further illustrate controlled the pH of the reaction can be to control the sample luminescence properties.

Conclusion

The red luminescent material Eu^{3+} doped γ-Bi_2MoO_6 is prepared by co- precipitation method. When annealed at 800C and pH is low(pH is 1 and 3), Eu^{3+} doped α-$Bi_2Mo_3O_{12}$ is obtained; while required Eu^{3+} doped γ-Bi_2MoO_6 is obtained when pH is high (pH is 5,7,9,11 and 13). Through the excitation and emission spectrum, it is found that similar linear transition peaks only locate at 466 nm as well as 535 nm with little difference between the intensity of two peaks. The red luminescent material Eu^{3+} with the topic of $^5D_0 \rightarrow {}^7F_2$ transition and excellent luminescent properties can be obtained when excitation energy is provided by the fine excitation wavelength 466 nm light, and luminous intensity of the sample is strongest when pH is 5.

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References

[1] Fu C C，Li G S，Zhao M L，et al. Solvent-Driven Room-Temperature Synthesis of Nanoparticles BiPO4:Eu3+ [J]. Inorg. Chem.，2012，51：5869−5880.

[2] Wu X, You H, Cui H, et al. Vacuum ultraviolet optical properties of (La, Gd)PO4: RE3+(RE = Eu, Tb) [J]. Mater. Resear. Bull., 2002，37: 1531-1538.

[3] Jin Y, Zhang J H, LüS Z, et al. Fabrication of Eu3+ and Sm3+ Codoped Micro/Nanosized MMoO4(M=Ca, Ba and Sr) via Facile Hydrothermal Method and Their Photoluminescence Properties through Energy [J]. Journal of Physical chemistry, 2008, 112: 5860-5864.

[4] Xia Z G, Sun J, Du H Y, et al. Luminescence properties of double-perovskite Sr2Ca1-2xEuxNaxMoO6 red-emitting phosphors prepared by the citric acid-assisted sol–gel method [J]. Mater. Sci., 2010, 45: 1553-1559.

[5] Yan S X, Zhang J H, Zhang Xia, et al. Enhanced Red Emission in CaMoO4:Bi3+，Eu3+ [J]. Journal of Physical Chemistry, 2007，111: 13256-13260.

[6] Tian G. H., Chen Y. J., Pan W., et al. Facile solvothermal synthesis of hierarchical flower-like Bi2MoO6 hollow spheres as the high performance visible-light photocatalysts [J]. Mater. Chem., 2011, 21(3): 887-592.