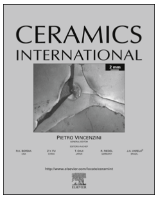
Ceramics International 42 (2016) 14086–14093

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint



Luminescent properties and energy transfer mechanism of $NaGd(MoO_4)_2$:Sm^{3+}, Eu^{3+} phosphors

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ARTICLE INFO

Article history:
Received 27 May 2016
Received in revised form
3 June 2016
Accepted 3 June 2016
Available online 7 June 2016

Keywords:
Hydrothermal synthesis
Molybdate
Luminescent properties
Energy transfer

ABSTRACT

Sm^{3+} singly doped $NaGd(MoO_4)_2$ and Sm^{3+}, Eu^{3+} co-doped $NaGd(MoO_4)_2$ phosphors by using sodium citrate as chelating agent were synthesized via hydrothermal method. The structure and morphology were characterized by means of X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM). During the synthesis process, the Na_3Cit concentration plays a crucial role in determining the morphology and particle size of the products. The optimal doping concentration in Sm^{3+} singly doped $NaGd(MoO_4)_2$ phosphor was confirmed. The relevant parameters of energy transfer in the $NaGd(MoO_4)_2$:Sm^{3+}, Eu^{3+} phosphors have been calculated based on the fluorescent dynamic analysis. Finally, on the analysis of luminescent spectra and fluorescent dynamics, the main energy transfer mechanism between Sm^{3+} and Eu^{3+} in $NaGd(MoO_4)_2$ phosphor is confirmed to be electric dipole-dipole interaction, and energy transfer pathway is from $^4G_{5/2}$ state of Sm^{3+} to $^5D_0$ state of Eu^{3+} rather than $^5D_1$ of Eu^{3+} ions.

1. Introduction

In recent years, white LED has been widely used as a new generation of light source, with advantages of long lifetime, low energy consumption, small size, green and high efficiency of environmental protection. In the research of white LED phosphor, blue and green phosphor are relatively mature but the luminous efficiency, stability and useful life of red phosphor are not satisfactory, which seriously affect the performance and quality of white LED [1–6].

With the research of red phosphors for LED, molybdate red phosphor has become a very promising kind. The molybdate system has good luminescent performance, thermal stability and chemical stability, so it can become a research hot spot. The molybdate phosphors have a strong and wide charge transfer band in the near ultraviolet region. Especially molybdate red phosphors doped Eu^{3+} ions in red light band has a strong emission spectra, which has become an important content of the current research and development. However the method of hydrothermal synthesis on molybdate red phosphors preparation is a kind of new preparation method [7–11]. The molybdate red phosphors prepared by using hydrothermal method have advantages of high purity, fine morphology and the particle size distribution is uniform [12].

On the basis of the above reasons, in this work, we synthesized Sm^{3+} doped $NaGd(MoO_4)_2$ and Sm^{3+}, Eu^{3+} co-doped $NaGd(MoO_4)_2$ phosphors by using a facile hydrothermal method. The photoluminescent properties and energy transfer process of the phosphors were also studied.

2. Experiment

2.1. Synthesis

Sm^{3+} singly doped $NaGd(MoO_4)_2$ and Sm^{3+}, Eu^{3+} co-doped $NaGd(MoO_4)_2$ phosphors were synthesized by hydrothermal method. In this work, we added Na_3Cit as chelating agent in order to better control the shape of particles and improve the stability of nanocrystallines. The steps are as follows. First, Na_3Cit, $Re(NO_3)_3 \cdot 6H_2O$ and $Na_2MoO_4 \cdot 2H_2O$ (RE = Gd , Sm, Eu , the Re^{3+} is 0.005 mol totally) were weighted according to the molar ratio of 1:1:2. Then, Na_3Cit was dissolved in 50 ml deionized water. $Re(NO_3)_3 \cdot 6H_2O$ and $Na_2MoO_4 \cdot 2H_2O$ were dissolved in 10 ml deionized water, respectively. The $Re(NO_3)_3$ solution was poured into Na_3Cit solution. A white precipitate was immediately observed in the glass beaker. The $Na_2MoO_4 \cdot 2H_2O$ solution was dripped into the above mixed solution slowly by using a dropper . The precursor solution was stirred 20 min. Then the precursor solution was transferred into a 100 ml autoclave which was sealed and maintained at 180 °C for 24 h, then cooling the autoclave to room temperature naturally. Finally, the product was put into centrifuge to wash by using deionized water, after that maintain the samples drying 3 h at 70 °C. A series of Sm^{3+} singly doped $NaGd(MoO_4)_2$ and Sm^{3+},

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http://dx.doi.org/10.1016/j.ceramint.2016.06.017

Eu^{3+} co-doped $NaGd(MoO_4)_2$ phosphors with different concentration were synthesized by hydrothermal method .

2.2. Characterization

The XRD spectra were measured by a RIGAKU D/max2600 (λ=0.15406 nm) radiation of Cu Kα1. The scanning range is from 10° to 70° with scanning step of 0.02. The structure and morphology were examined by using a HITACHI S-4800 Field Emission Scanning Electron Microscopy. The emission, excitation spectra and fluorescent decay curves of the phosphor were determined by an EDINBURG GH-LFS920 spectrophotometer equipped with a 450W xenon lamp as excitation source.

3. Results and discussion

3.1. Structural and morphology characterization of the phosphor

Fig. 1 shows the XRD spectra of $NaGd(MoO_4)_2$ phosphors which are Sm^{3+} singly doped $NaGd(MoO_4)_2$ with different molar ratios of Cit^{3-}/Re^{3+} and co-doped with 2 mol% Sm^{3+}, X mol% Eu^{3+} (X=5,10,20). As shown in Fig. 1(a), it can be seen when the ratio (N) of Cit^{3-}/Re^{3+} is 0, 0.5 and 1 all of the diffraction peak position of $NaGd(MoO_4)_2$: Sm^{3+} are consistent with the JCPDS card #250828. From the JCPDS card, it can be concluded that the sample is body centered tetragonal. No other diffraction peaks can be observed in the patterns and proved the dopant ions do not change the crystal structure of hosts. However, in the sample of Cit^{3-}/Re^{3+} is 2, there are other diffraction peaks can be found obviously and the 112 peak is weaker than other samples. So this sample is not pure phase. Fig. 1(b) shows the samples of $NaGd(MoO_4)_2$: 2 mol% Sm^{3+}, X mol% Eu^{3+} (Cit^{3-}/Re^{3+} is 1:1). They are also consistent with the JCPDS card #250828. No other diffraction peaks can be observed in the patterns, indicating these co-doped samples are also pure phase. From Fig. 1(b) obvious change of diffraction peak position can not be discovered. The reason of the phenomenon above is the ion radius of Eu^{3+} and Gd^{3+} are 1.07 Å and 1.05 Å, respectively. The values are very close. So doping Eu^{3+} does not cause obvious change of diffraction peak position.

Many organic additives are made use of for control crystal's morphology [13,14]. In this work, Na_3Cit was adopted as chelating agent, and by controlling the molar ratio (N) of Cit^{3-}/Re^{3+} (N=0, 0.5, 1, 2) to investigate the effect of Na_3Cit on the shape evolution. Fig. 2 shows the FE-SEM images of the $NaGd(MoO_4)_2$: 2 mol% Sm^{3+} with different molar ratios of Cit^{3-}/Re^{3+}. As shown in Fig. 2(a), the sample is in the absence of Na_3Cit, which is composed of flake-like particles. They are attached each other and in an irregular arrangement. When the molar ratio of Cit^{3-}/Re^{3+} is up to 0.5, it can be found that olivary particles has come out, as shown in Fig. 2(b). With a further increase of the ratio of Cit^{3-}/Re^{3+} to 1, the phosphor is composed of olivary particles with perfect uniformity, as shown in Fig. 2(c). When the ratio of Cit^{3-}/Re^{3+} is up to 2, some particles are agglomerated into bulk. Through the above analysis indicates that the amount of Na_3Cit plays a key role in the $NaGd(MoO_4)_2$ samples. Based on the analysis results of XRD and SEM, we finally confirm the molar ratio of Cit^{3-}/Re^{3+} is 1 in the next experiment preparation process.

Fig. 3 shows the FE-SEM images of the $NaGd(MoO_4)_2$: 2 mol% Sm^{3+} , X mol% Eu^{3+} (X=5,10 or 20) and all the molar ratio of Cit^{3-}/Re^{3+} is 1. Fig. 3(a) and (b) are the concentration of 2 mol% Sm^{3+}, 5 mol% Eu^{3+}, Fig. 3(c) and (d) are 2 mol% Sm^{3+}, 10 mol% Eu^{3+} , and Fig. 3(e) and (f) are 2 mol% Sm^{3+}, 20 mol% Eu^{3+}, respectively. It can be seen that under the low-magnification the phosphor particles are almost uniform and consist of a large quantity of olivary microstructures, as shown in Fig. 3(a), (c) and (e). From Fig. 3(b), (d) and (f) images, it can be found that under the high-magnification each phosphor particle has regular morphology and olive shape. The olivary microstructures have diameters of 600 nm.

3.2. Photoluminescent properties of the Sm^{3+} singly doped $NaGd(M_oO_4)_2$ phosphor

Fig. 4 is the excitation spectra monitoring 646.5 nm of $NaGd(MoO_4)_2$ phosphors doped 2 mol% Sm^{3+}. The scanning range is from 220 nm to 450 nm. The spectrum shows a wide band and a series of sharp lines, the former is in the range of 220–330 nm and the latter is range from 340 nm to 450 nm. The wide band is O-Sm and O-Mo charge transfer band. The sharp lines correspond to the characteristic 4–4 f transitions of Sm^{3+} ions which are $^6H_{5/2}$-$^4K_{17/2}$, $^6H_{5/2}$-$^4H_{7/2}$, $^6H_{5/2}$-$^4P_{7/2}$, $^6H_{5/2}$-$^4K_{11/2}$ and $^6H_{5/2}$-$^6P_{5/2}$, respectively. From all of them the stronger transition is the $^6H_{5/2}$-$^4K_{11/2}$ at 405 nm [15,16].

Fig. 5 shows the emission spectrum excited by 405 nm of $NaGd(MoO_4)_2$: 2 mol% Sm^{3+} and these emission lines positions can be observed, which are 564 nm, 607 nm, 646.5 nm and 708 nm. The positions are corresponding to the transition of $^4G_{5/2}$-$^6H_{5/2}$, $^4G_{5/2}$-$^6H_{7/2}$, $^4G_{5/2}$-$^6H_{9/2}$, and $^4G_{5/2}$-$^6H_{11/2}$, respectively. Fig. 6 shows the emission spectra excited by 405 nm of NaGd $(MoO_4)_2$ phosphors doped with X mol% Sm^{3+} (X=0.5,1,1.5,2,2.5,3,4) and the scanning rage is from 500 nm to 750 nm. From Fig. 6 it can be found

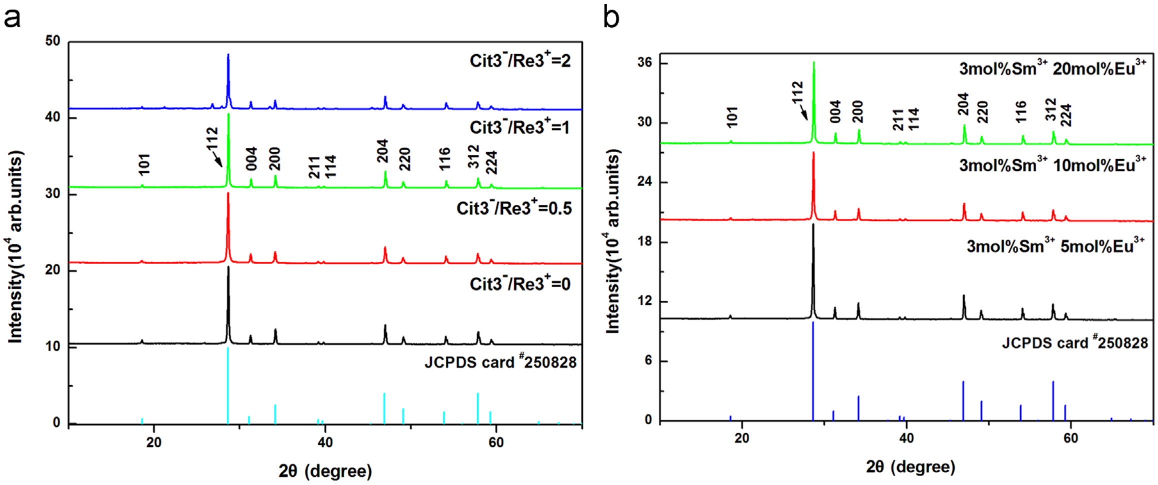

Fig. 1. (a) X-ray diffraction pattern of $NaGd(MoO_4)_2$:2 mol% Sm^{3+} corresponding to different concentrations of Na_3Cit. (I) In the absence of Na_3Cit (II) Cit^{3-}/Re^{3+}=1:2 (III) Cit^{3-}/Re^{3+}=1:1 (IV) Cit^{3-}/Re^{3+}=2:1. (b) X-ray diffraction pattern of $NaGd(MoO_4)_2$:2 mol% Sm^{3+}, X mol% Eu^{3+} while the Cit^{3-}/Re^{3+} is 1:1.(X=5,10,20).