Short Communication

Synthesis and photoluminescence studies of one dimensional Sm$_2$MoO$_6$ nanofibers derived from electrospinning process

Kamal P. Mani, Vimal George, Biju P. Ramakrishnan, Cyriac Joseph*, Unnikrishnan N. Viswambharan, Ittyachen M. Abraham

School of Pure & Applied Physics, Mahatma Gandhi University, Kottayam, Kerala, India

ARTICLE INFO

Article history:
Received 30 September 2014
Accepted 13 January 2015
Available online 14 February 2015

Keywords:
Sm$_2$MoO$_6$
Electrospinning
Nanofiber
Photoluminescence
Energy transfer
CIE

ABSTRACT

A combined sol-gel and electrospinning process was employed to synthesize one-dimensional nanofibers of samarium molybdate (Sm$_2$MoO$_6$). X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL) and CIE chromaticity studies were used to characterize the resulting samples. XRD studies revealed the formation of crystalline phase of nanofibers on annealing. SEM analyses indicate that the fibers were of uniform size with length of 10–100 µm. Due to the efficient energy transfer from host molybdate groups to Sm$^{3+}$, Sm$_2$MoO$_6$ phosphors show their strong characteristic emission on exciting the molybdate group. The emission colors of Sm$_2$MoO$_6$ nanofibers are in the orange red region hence suggests its potential applications in fluorescent lamps and field emission displays (FEDs).

© 2015 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. All rights reserved.

1. Introduction

The one dimensional inorganic luminescent nanomaterials such as nanorods, nanobelts, nanofibers, nanowires, and nanotubes are of fundamental interest due to their fascinating size dependent optical, electronic, magnetic, thermal, mechanical, and chemical properties. From this point of view, they find potential applications in energy storage, fuel cells, nanomedicine, molecular computing, nanophotonics, tunable resonant devices, sensors etc. [1–3].

Among all the nanomaterials, rare earth compounds have been widely used in the fields of high-performance luminescent devices, catalysts and other functional materials based on their electronic, optical, and chemical characteristics arising from the 4f electrons [4,5]. Rare earth oxide phosphors, which are currently used in the screens of flat-panel displays (FPDs), VFDs, and FEDs have gained much interest due to their
better thermal and chemical stability as well as their environmental friendliness [6]. Therefore, more attention has been paid to the development of new rare earth oxide phosphor materials for their wide possible applications. Molybdates have been proved to be a useful host lattice for the luminescence of rare earth ions to produce phosphors emitting a variety of colors, due to the high luminescence quantum yields observed for the f–f transitions [7].

One dimensional nanomaterials with different compositions have been developed using various methods including the chemical or physical vapor deposition, laser ablation, solution, arc discharge, vapor-phase transport process, and a template-based method. Among which electrospinning is an effective and simple method to obtain one dimensional rare earth phosphors. Electrospinning generates one dimensional material with diameters ranging from tens of nanometers up to micrometers [8]. Here we chose a combination of sol–gel process and electrospinning method to prepare samples.

As the most frequently used activator ions in luminescent materials, Sm³⁺ mainly shows emission in the orange-red region at 567 nm (4G_{5/2}→4H_{5/2}), 606 nm (4G_{9/2}→4H_{15/2}) and 649 nm (4F_{9/2}→4H_{15/2}) respectively. To the best of our knowledge, one dimensional Sm₂MoO₆ nanofibers have not been reported until now. In this paper, we present the electrospinning preparation, structural and photoluminescence properties of Sm₂MoO₆ nanofibers.

2. Experimental

Samples were prepared by sol–gel process and electrospinning. 0.05 M of samarium nitrate (Sm(NO₃)₃·6H₂O) and 0.05 M of Ammonium hepta molybdate ((NH₄)₆Mo₇O₂₄) were dissolved in deionized water containing citric acid as a chelating agent for the metal ions. The molar ratio of metal ions to citric acid was 1:2. 9 wt.% of poly vinyl alcohol was added to adjust the viscoelastic behavior of the solution to make it suitable for electrospinning. The solution was stirred for 4 h to obtain a homogeneous hybrid sol to be used for electrospinning. The distance between the spinneret (a metallic needle) and collector (a grounded conductor) was fixed at 16 cm and the high-voltage supply was maintained at 15 kV. The spinning rate was controlled at 0.5 mL·h⁻¹ by a syringe pump. The prepared hybrid precursor samples were annealed at 600 °C for 2 h in air.

2.1. Characterization

X-ray diffraction patterns were collected in a 2θ range of 10–60° with an X’Pert Pro PANalytical X-ray diffractometer (Cu Kα1 = 1.54 Å). The microstructure, morphology and composition of the samples were investigated by means of scanning electron microscope (SEM) analysis. The SEM images were obtained on a JEOL 6500 instrument with an accelerating voltage 15 kV and 20,000× Zoom. Photoluminescence measurements were performed using a HORIBA, JobinYvon, Fluoro Max-4 spectrofluorometer, which uses a 450 W xenon lamp as the excitation source. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Structure and morphology studies

Fig. 1 displays the XRD patterns of the as-prepared precursor fiber for Sm₂MoO₆ and those annealed at 600 °C for 4 h. The XRD pattern of the precursor phase formed by electrospinning shows no diffraction peak except for a less intense broadband, ascribed to the semicrystalline nature of poly vinyl alcohol present in the sample. On annealing at 600 °C, the broad peak disappears and well-defined diffraction peaks appear, all of which can be indexed to the monoclinic phase of Sm₂MoO₆ according to the ICDD No. 24-0997.

The morphology of the sample was investigated by SEM. Fig. 2a and b shows the SEM micrographs of as-prepared samples. From the SEM micrographs it can be seen that the samples consist of uniform fibers with lengths of several tens to hundreds of micrometers. Also, the as-formed fibers are smooth with diameters ranging from 100 to 300 nm. After annealing at 600 °C, the fiber diameters decrease greatly due to the decomposition of the organic species and the resulting formation of inorganic phase as shown in the high resolution SEM image in Fig. 2c. The diameters of the nanofibers annealed at 600 °C for 4 h gets reduced to 80–150 nm. The EDS spectra shown in Fig. 2d confirm the presence of Sm, Mo and O as constituent elements in the present sample.

3.2. Photoluminescence studies

The excitation spectrum of the samples was recorded by monitoring the 4G_{9/2}→6H_{15/2} emission transition of Sm³⁺ at 606 nm and is shown in Fig. 3a. The spectra consists of a wide excitation band ranging from 320 to 360 nm due to the excitation of the molybdate host lattice and an excitation peak at 405 nm due to transition of Sm³⁺ ions from its 6H_{5/2} → 4F_{7/2} level [9,10]. The strong charge transfer absorption band of the molybdate group in the excitation spectrum on monitoring the emission.
transition of Sm$^{3+}$ clearly suggests the efficient energy transfer from host to the Sm$^{3+}$ ion.

The excitation and emission process of Sm$_2$MoO$_6$ under UV radiation includes three major steps. The first one is absorption of UV radiation by MoO$_6^{6-}$ and is subsequently transferred to Sm$^{3+}$ ions by resonance interactions and the final one is the deexcitation process of excited Sm$^{3+}$, which yields their characteristic orange red emissions. The emission spectrum of the sample was recorded in the range 320–360 nm is comparable to the energy of the $^6P_{7/2}$ level of Sm$^{3+}$ ion. Therefore, when excited in the charge transfer band of MoO$_6^{6-}$, the electrons are pumped into the excited energy states of MoO$_6^{6-}$ and then move to the lowest excited energy states through relaxation, followed by transfer of energy to the 4f level of Sm$^{3+}$. As there are several 4f levels for samarium with smaller energy differences, efficient non radiative relaxation leading to the population of the $^4G_{5/2}$ state which relaxes to $^4G_{5/2} \rightarrow ^6H_{5/2}(560 \text{ nm})$, $^4G_{5/2} \rightarrow ^6H_{7/2}(606 \text{ nm})$, $^4G_{5/2} \rightarrow ^6H_{9/2}(648 \text{ nm})$ and $^4G_{5/2} \rightarrow ^6H_{11/2}(709 \text{ nm})$ levels through radiative transition [10]. The emission intensity

**Fig. 2** – SEM images of the as-formed precursor for Sm$_2$MoO$_6$ nanofibers (a) images with low magnification and (b) high magnification: SEM and EDS patterns of the 600 °C annealed sample (c) SEM image (d) EDS pattern.

**Fig. 3** – Photoluminescence (a) excitation and (b) emission spectra for Sm$_2$MoO$_6$ nanofibers.
corresponding to the transition \( ^{4}G_{5/2} \rightarrow ^{6}H_{7/2} \) is very strong and it controls the emission color of the phosphor material. In the luminescence spectra no emission from the \( \text{MoO}_6^{6-} \) group is observed suggesting that the energy transfer from \( \text{MoO}_6^{6-} \) to \( \text{Sm}^{3+} \) is quite efficient. Fig. 4 shows the CIE chromaticity diagram and the digital photographs of the photoluminescence colors for \( \text{Sm}_2\text{MoO}_6 \) nanofiber. The chromaticity coordinate for \( \text{Sm}_2\text{MoO}_6 \) is found to be \( x = 0.58 \) and \( y = 0.33 \), which falls in orange–red of the CIE hue diagram.

4. Conclusions

In summary, samarium molybdate nanofibers are successfully synthesized via electrospinning technique. The as-formed hybrid precursor exhibits uniform fiber like morphology with smooth surface. After annealing the precursors at 600°C, the samples are well crystallized with the monoclinic structure of \( \text{Sm}_2\text{MoO}_6 \). Upon excitation into the \( \text{MoO}_6^{6-} \) groups, \( \text{Sm}^{3+} \) ions show their characteristic strong emissions due to an efficient energy transfer from the \( \text{MoO}_6^{6-} \) group to \( \text{Sm}^{3+} \) ions. In addition, the CIE chromaticity coordinate analysis revealed that the emission color of the nanofiber is located in the orange red region of the CIE hue diagram. These studies indicate that electrospinning is a facile and novel route for the development of one dimensional luminescent nanomaterials, which finds application in many lighting and color display devices.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

The authors are thankful to UGC (Govt. of India) and DST (Govt. of India) for the financial assistance through SAP-DRS (No. F.530/12/DRS/2009 (SAP-1)) and DST-PURSE PURSE (SR/S9/Z-23/2010/22) (C,G) programs, respectively. The authors Kamal P. Mani and Vimal G. are thankful to University Grants Commission, Govt. of India for the award of RFSMS fellowship.

References