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Highly modulated structure and upconversion photoluminescence properties of $PbGd_2(MoO_4)_4:Er^{3+}/Yb^{3+}$ phosphors

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ABSTRACT

Double molybdate of $PbGd_{2-x}(MoO_4)_4:Er^{3+}/Yb^{3+}$ phosphors with the correct doping concentrations of Er^{3+} and Yb^{3+} ($x = Er^{3+} + Yb^{3+}$, $Er^{3+} = 0.05$, 0.1, 0.2 and $Yb^{3+} = 0.2$, 0.45) were successfully synthesized by microwave sol–gel process. The highly modulated structure and the upconversion photoluminescence properties were investigated in detail. The synthesized particles, formed after heat-treatment at 900 °C for 16 h, showed a well ctystallized morphology with particle sizes of 2–5 μm. Under excitation at 980 nm, the $PbGd_{1.7}(MoO_4)_4:Er_{0.1}Yb_{0.2}$ and $PbGd_{1.5}(MoO_4)_4:Er_{0.05}Yb_{0.45}$ particles exhibited a strong 525-nm emission band, a weak 550-nm emission band in the green region, and a very weak 655-nm emission band in the red region. The Raman spectra of the doped particles indicated the disordered structures of $PbGd_{2-x}(MoO_4)_4$ by the incorporation of the Er^{3+} and Yb^{3+} ions into the crystal lattice, which resulted in the highly modulated structure as well as a concentration quenching effect of Er^{3+} ions.

1. Introduction

Scheelite-structured compounds belonging to the molybdate family have attracted great attention because of their spectroscopic characteristics and excellent upconversion (UC) photoluminescence properties [1]. These UC photoluminescence particles have potential applications in various fields, including biomedical imaging, owing to their unique UC optical behaviors, which allow them to overcome many of the current limitations of traditional photoluminescence materials [2,3]. It is possible for the trivalent rare earth ions in the disordered tetragonal-phase to be partially substituted for by Er^{3+} and Yb^{3+} ions; these ions are effectively doped into the crystal lattices of the tetragonal phase due to the similar radii of the trivalent rare earth ions; this results in high emitting efficiency and superior thermal and chemical stability [4–6]. The $[MoO_4]^{2-}$ group has strong absorption in the near ultraviolet region, so that the energy transfer process from the $[MoO_4]^{2-}$ group to the rare earth ions can easily occur, which can greatly enhance the external quantum efficiency of rare-earth ion doped materials. Many lanthanides such as Er^{3+}, Tm, and Ho^{3+} are used as luminescent centers because their abundant electronic energy levels are very convenient for realizing the conversion of near infrared light to visible light. Among the lanthanide ions, the Er^{3+} ion as an activator is a promising UC luminescence center because of its unique luminescence in the visible range, when a sensitizer is used to enhance the UC luminescence efficiency. The Yb^{3+} ion is generally co-doped as a sensitizer owing to its strong absorption around 980 nm and can enhance the UC luminescence through energy transfer. Especially, due to the efficiency of the energy transfer from Yb^{3+} to Er^{3+}, co-doped Yb^{3+} and Er^{3+} ions can remarkably enhance the UC efficiency for the shift from infrared to visible light [7–10].

To prepare the double molybdates, several processes have been developed via specific preparation processes [11–23]. For practical application of UC photoluminescence in products such as lasers, three-dimensional displays, light-emitting devices, and biological detectors, features such as the homogeneous UC particle size distribution and morphology need to be well defined. Usually, molybdates are prepared by a solid-state method that requires high temperatures, a lengthy heating process and subsequent grinding, this results in a loss of the emission intensity and an increase in cost. The sol–gel process provides some advantages over the conventional solid-state method, including good homogeneity, low calcination temperature, small particle size and narrow particle size distribution optimal for good luminescent characteristics. However, the sol–gel process has a disadvantage in that it takes a long time for gelation. Compared with the usual methods, microwave synthesis has the advantages of a very short reaction time, small-size particles, narrow particle size distribution, and high purity of final polycrystalline samples. Microwave heating is delivered to the material surface by radiant and/or convection heating, which is transferred to the bulk of the material

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via conduction [24–27]. A microwave sol–gel process is a cost-effective method that provides high homogeneity and is easy to scale-up, and it is emerging as a viable alternative approach for the quick synthesis of high-quality luminescent materials [7,9,28,29]. However, the $PbGd_{2-x}(MoO_4)_4:Er^{3+}/Yb^{3+}$ phosphors prepared by the microwave sol–gel method have not been reported.

In this study, $PbGd_{2-x}(MoO_4)_4:Er^{3+}/Yb^{3+}$ phosphors with the correct doping concentrations of Er^{3+} and Yb^{3+} ($x = Er^{3+} + Yb^{3+}$, $Er^{3+} = 0.05$, 0.1, 0.2 and $Yb^{3+} = 0.2$, 0.45) phosphors were prepared by the microwave sol–gel process, followed by heat treatment. The synthesized particles were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Pump power dependence and Commission International de L'Eclairage (CIE) chromaticity of the UC emission intensity were evaluated in detail. The optical properties were examined comparatively using photoluminescence (PL) emission and Raman spectroscopy.

2. Experimental

In this study, stoichiometric amounts of $Pb(NO_3)_2$ (99%, Sigma–Aldrich, USA), $Gd(NO_3)_3 \cdot 6H_2O$ (99%, Sigma–Aldrich, USA), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (99%, Alfa Aesar, USA), $Er(NO_3)_3\cdot 5H_2O$ (99.9%, Sigma–Aldrich, USA), $Yb(NO_3)_3\cdot 5H_2O$ (99.9%, Sigma–Aldrich, USA), citric acid (99.5%, Daejung Chemicals, Korea), NH_4OH (A.R.), ethylene glycol (A.R.) and distilled water were used to prepare $PbGd_2(MoO_4)_4$, $PbGd_{1.8}(MoO_4)_4:Er_{0.2}$, $PbGd_{1.7}(MoO_4)_4:Er_{0.1}Yb_{0.2}$ and $PbGd_{1.5}(MoO_4)_4:Er_{0.05}Yb_{0.45}$ compounds with the correct doping concentrations of Er^{3+} and Yb^{3+} ($Er^{3+} = 0.05$, 0.1, 0.2 and $Yb^{3+} = 0.2$, 0.45). To prepare the compounds $Pb(NO_3)_2$ and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ were dissolved in 20 mL of ethylene glycol and 80 mL of 5 M NH_4OH under vigorous stirring and heating. Subsequently, $Gd(NO_3)_3\cdot 6H_2O$ $6H_2O$ with $Er(NO_3)_3\cdot 5H_2O$, $Yb(NO_3)_3\cdot 5H_2O$ and citric acid (with a molar ratio of citric acid to total metal ions of 2:1) were dissolved in 100 mL of distilled water under vigorous stirring and heating. Then, the solutions were mixed together vigorously and heated at 80–100 °C. At the end, highly transparent solutions were obtained and adjusted to pH = 7-8 by the addition of NH_4OH or citric acid. The transparent solutions were placed for 30 min into a microwave oven operating at a frequency of 2.45 GHz with a maximum output-power of 1250 W. The working cycle of the microwave reaction was controlled very precisely using a regime of 40 s on and 20 s off for 15 min, followed by further treatment of 30 s on and 30 s off for 15 min. The samples were dried at 120 °C in a dry oven to obtain black dried gels. The black dried gels were ground and heat-treated at 900 °C for 16 h at 100 °C. Finally, white particles were obtained for the pure $PbMoO_4$ and pink particles were obtained for the doped compositions.

The phase composition of the synthesized particles was identified using XRD (D/MAX 2200, Rigaku, Japan). The microstructure and surface morphology of the synthesized particles were observed using SEM/EDS (JSM-5600, JEOL, Japan). The PL spectra were recorded using a spectrophotometer (Perkin Elmer LS55, UK) at room temperature. Pump power dependence of the upconversion emission intensity was measured at levels of working current from 20 to 110 mW. Raman spectra measurements were performed using a LabRam Aramis (Horiba Jobin-Yvon, France) with the spectral resolution of 2 cm^{-1}. The 514.5-nm line of an Ar ion laser was used as an excitation source; to avoid sample decomposition, the samples were exposed to a power level that was maintained at 0.5 mW.

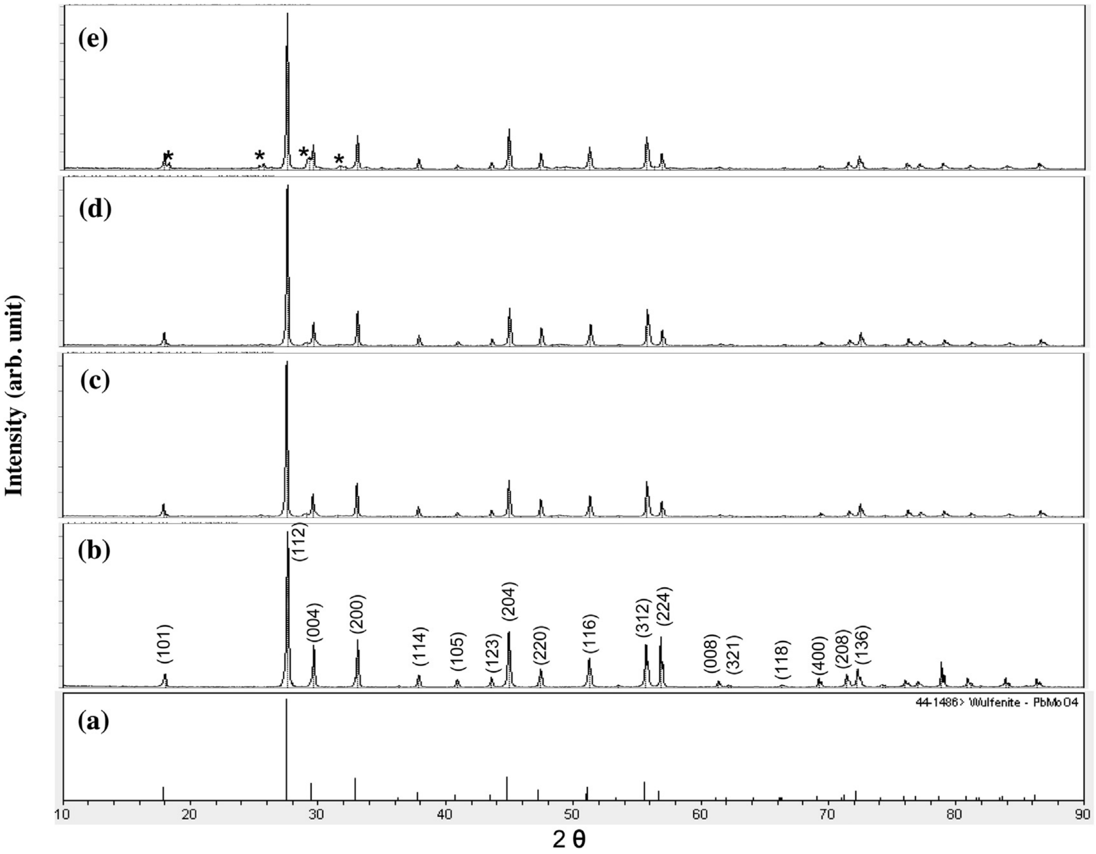

Fig. 1. X-ray diffraction patterns of (a) JCPDS 44-1486 pattern of $PbMoO_4$, and the synthesized (b) $PbGd_2(MoO_4)_4$, (c) $PbGd_{1.8}(MoO_4)_4:Er_{0.2}$, (d) $PbGd_{1.7}(MoO_4)_4:Er_{0.1}Yb_{0.2}$, and (e) $PbGd_{1.5}(MoO_4)_4Er_{0.05}Yb_{0.45}$ particles.