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Luminescence properties of Eu^{3+} doped $BaMoO_4$ transparent glass ceramics

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ABSTRACT

Eu^{3+} doped transparent glass ceramics (GCs) are obtained via melt- quenching technique and subsequent heating. The structure and morphology of the samples were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). XRD and SEM results showed that tetragonal barium molybdate ($BaMoO_4$) crystals are precipitated in the glass matrix. The excitation spectrum of $BaMoO_4$:Eu^{3+} GCs are composed of Eu^{3+} ions characteristic excitation peaks. The emission spectra of $BaMoO_4$:Eu^{3+} GCs consists of several sharp emission bands center at 592 nm, 615 nm, 653 nm and 702 nm, respectively. Among them, the strongest one was located at 615 nm due to $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} generating bright red light. The quantum efficiency of $BaMoO_4$:Eu^{3+} GC is 46.3%, and the fluorescence lifetime is 2.0716 ms, when the Eu^{3+} ions doping concentration is 0.7 mol%.The results show that Eu^{3+} doped $BaMoO_4$ glass ceramics exhibit a potential to act as a kind of red phosphor for white light-emitting diodes (W-LEDs).

1. Introduction

Recently, white light-emitting diodes (W-LED) have been used as substitute for traditional light sources (fluorescent lamps and incandescent lights) due to their high brightness, quick response, reliability, long lifetimes, low power consumption and shock resistance [1–3]. At present, there are two approaches for obtaining W-LEDs. The first is to use ultraviolet InGaN to excite blue, green, and red phosphors to produce white light [4]. The W-LEDs fabricated with this method has higher color rendering index (CRI) value, negatively, the luminous efficiency is low due to reabsorption of blue light. The commercial phosphors for the current leading white fluorescent LEDs are usually used in 450–470 nm blue InGaN LED chip, which is covered by yellow phosphor coating, usually using $Y_3Al_5O_{12}$:Ce^{3+} (Ce:YAG). In order to homogeneously distribute the phosphor on the LED chip and keep the shape, the matrix material is essential to the phosphor particles. So far, curable silicone is the most common carrier material of phosphor in wavelength converter, which has high optical transmittance and low manufacturing temperature. However, there will be a loss of light and chromaticity distortion after a period of operation [5–7]. The second way is combining a blue-emitting LED with a yellow-emitting $Y_3Al_5O_{12}$:Ce^{3+} (YAG:Ce^{3+}) phosphor to obtain white light [8]. It has benefit in low cost and high brightness, however, this combination exhibits a poor color rendering index and a high correlated color temperature due to lacking of red component. To solve this problem, research and development of transparent glass ceramics as the potential red phosphor for white light-emitting diodes,which has become a hot research topic in many fields, such as materials, chemistry, and physics [9]. Impressively, such GC based W-LED shows less deterioration of the silicone resin-based W-LED, including the loss of transmittance, lumen loss, chromaticity drift, and peak emission intensity, resistance to thermal aging [10].

It is known that glass ceramics (GCs) are a multiphase material by making up of a glassy phase and a crystalline phase, ordinarily obtained by high-temperature melting method with the subsequent annealing process. Glass ceramics have the advantages of crystal, and also retained the high transmittance of the glass and simple preparation process. It has good thermal stability and chemical stability, and improved optical properties through lower phonon energy. In recent years, transparent glass ceramics have been widely studied as luminescent materials [11–13]. Such as Hyun-A Park et al. prepared the Eu^{3+} and Pr^{3+} doped SiO_2-B_2O_3-RO phosphor-in-glasses, and the chromaticity has been improved, but due to the high phonon energy of silicate glasses, the red conversion efficiency was lower [14]. Weihuan Zhang et al. synthesized the Sm^{3+} doped $BaGdF_5$ transparent glass ceramic and enhanced the luminescent properties, but the CIE chromaticity coordinates located in red-orange [15]. Molybdate material has drawn the great attention of researchers due to its excellent optical, chemical

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stability and structural properties. The molybdate group (MoO_4^{2-}) has an intense broad absorption band, which is due to the charge transfer from the central molybdates atom of oxygen ligands to t the MoO_4^{2-} groups in the ultraviolet region, and the absorbed energy can be effectively transferred to the trivalent lanthanide activator ion [16, 17].

In this work, we have been synthesized Eu^{3+} ions doped transparent glass ceramics containing $BaMoO_4$ crystals for the first time. The structural and luminescent properties of precursor glass and glass ceramics were investigated in detail. The influence of heat treatment system on the morphology of samples was analyzed. The luminescence properties of Eu^{3+} doped GCs were investigated and the reasons of fluorescence enhancement for GCs were explained. The obtained information will help to research as the potential red phosphor for white light-emitting diodes.

2. Experimental

The matrix glass samples with composition of 14BaO-7MoO_3-34B_2O_3-28SiO_2- 8NaF-8Na_2O-1Sb_2O_3 (in mol%) doped with xEu_2O_3 (x = 0.1, 0.3, 0.5, 0.7, 0.9, 1.1 mol%) were prepared by melt-quenching method and subsequent heating. The raw materials were uniformly mixed and placed in the platinum crucibles, and melted at 1500 °C for 1 h in silicon molybdenum furnace. The melt was poured onto the preheated copper plate and then pressed by another plate to get glass samples. Then the glass samples were immediately transferred to a resistance furnace at 450 °C for 3 h to release internal stresses and natural cooling to room temperature. To prepare the GCs, the precursor glasses (PG) are subjected to heat treatment and crystallization. The obtained samples were polished optically for further characterization.

Differential scanning calorimetry (DSC) of glass powder was carried out by a SDT2960 thermal analyzer at the temperature range of 200 °C–900 °C with the heating rate of 10 °C/min. For DSC measurement, the bulk glass samples were ground to fine powders in an agate mortar. The measurements of the X-ray diffraction (XRD) were performed on a diffractometer (Rigaku 2500 PC, Japan) with Cu-Kα1 radiation over the angular range 10° ≤ 2θ ≤ 90°. The optical transmittance of the glass ceramics was measured by UV-VIS spectrophotometer (SHIMADZU, UVmini-1240). The Fourier transform infrared spectra of the samples were taken using a FTIR-8400S spectrometer in the wave number range of 1500–400 cm^{-1}. KBr pellets were used to record the FTIR spectra of the samples. The morphology and particle size of samples were measured by a SPI3800N scanning electron microscope produced by Japanese SII. The photoluminescent (PL) excitation and emission spectra were observed on Sunlite EX OPO produced by American Continuum company, with the measurement range of 200–800 nm. The quantum efficiency of samples was measured by using an Absolute Photoluminescence Quantum Efficiency Measurement System (C9920–02, Hamamatsu Photonics K. K., Japan).

3. Results and discussion

3.1. Phase and structure characterization

Fig. 1 shows the DSC curve of the matrix glass. It can be seen that the crystallization temperature of matrix glass T_x is around 675 °C, and the crystallization peak T_p is at 685 °C. It can be initially determined that the crystallization temperature range is between 670 and 700 °C. The PG samples were heat-treated at 670 °C, 680 °C, 690 °C and 700 °C for 1 h, respectively, and subsequent the optimum crystallization temperature was determined by the X-ray diffraction (XRD) pattern.

The XRD pattern of the PG was heat-treated at 670 °C, 680 °C, 690 °C and 700 °C for 1 h, as shown in Fig. 2(a). After heat treatment at 670 °C for 1 h, there were no discrete diffraction peaks indicating an amorphous structure. The XRD patterns of glass ceramics heat-treated at 680 °C, 690 °C and 700 °C for 1 h show intense diffraction peaks, which are assigned to space group $I4_1/a$ structure of the tetragonal $BaMoO_4$

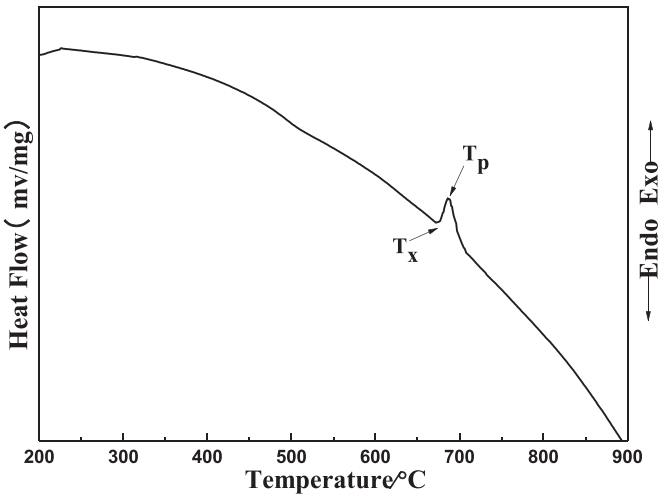

Fig. 1. DSC curve of the glass sample.

(PDF#29-0193), which was directly confirming the formation of $BaMoO_4$ crystals in glass ceramic sample. Meanwhile, in order to obtain glass ceramics with uniform crystal particle and high crystallinity, the temperature 680 °C is chosen as the best annealing temperature.

The PG was heat-treated at 680 °C for 1 h, 1.5 h, 2 h and 2.5 h, respectively, as shown in Fig. 2(b). The diffraction peak of XRD diffraction peak did not change with the increase of heat treatment time, but the peak intensity increased and then tends to be stable. The peak intensity reached the maximum at 680 °C for 2 h, indicating gradually $BaMoO_4$ crystal precipitation in the glass matrix. In this system, the relatively rapid growth of crystallites from a limited number of nuclei was observed, which an early termination of the crystallization process due to their collision. The crystal size of $BaMoO_4$ crystals in GCs can be calculated by Scherrer equation [18]:

$$D = \frac{k\lambda}{\beta cos\theta} \quad (1)$$

Where k is 0.89, λ is 0.154056 nm represents the wavelength of X-ray, β is the corrected half-maximum of diffraction peak and θ is the angle of diffraction. The grain size of the $BaMoO_4$:0.1%Eu^{3+} GC sample was calculated to be approximately 281 nm.

Fig. 3 shows the SEM images of Eu^{3+} doped $BaMoO_4$ glass ceramics undergone different heat treatment time. It is found that the crystal is uniformly and randomly distributed in the glass matrix from the SEM pictures. The SEM pictures reveal that the crystals growing constantly with the increase of crystallization time, the larger crystal is obvious when the heat treatment time is 2.5 h. The average crystal size of $BaMoO_4$ is about 273 nm when the heat treatment is 680 °C 2 h, which is consistent with the diameter estimated by Scherrer's equation.

By using Fourier transform infrared (FTIR) spectroscopy, it is able to detect samples relevant information in the form of functional groups. Fig. 4 shows the FTIR spectrum of PG and GCs doped with different concentrations of Eu^{3+} in the range of 400–1300 cm^{-1}. Assignment of FTIR bands of the samples is listed in Table 1. The FTIR intense absorption band centered at about 1020 cm^{-1} is due to the O—Si—O asymmetric vibrations of silicate groups associated with non-bridging oxygens. The band observed around 702 cm^{-1} and 456 cm^{-1} can be ascribed to stretching vibration Si—O—Si linkages of silicate structural units and Si—O—Si bending vibration, respectively [19, 20]. The glass ceramics have the significant absorption band in 813 cm^{-1} than the precursor glass, which can be attributed to the Mo—O stretching vibration in the MoO_4^{2-} tetrahedrons. Therefore, the enhancement of the photoluminescence intensity of glass ceramics is probably related to the Mo—O stretching vibration of MoO_4^{2-} group appearance at 813 cm^{-1} compared with the precursor glass [21, 22].