

Preparation and Luminescence Properties of Eu^{3+} doped Transparent Glass Ceramics Containing CaMoO_4 crystals

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Keywords: glass ceramics, CaMoO_4 , rare-earth doped, luminescence properties

Abstract. Eu^{3+} doped transparent molybdate glass ceramics containing CaMoO_4 were successfully fabricated by melt-quenching technique. The optimal heat-treated system for the glass sample was determined by DSC, XRD and SEM (710° for 2.5h). The grain size of the glass ceramics gradually increased with the increasing of heat treatment time. The UV-Vis-NIR spectra indicated that the sample transparency was approximately up to 80% in visible light range. The effect of different Eu^{3+} doping concentration on the luminescence properties of the glass ceramics under the condition of the same heat treatment by fluorescence spectrum. The experimental result indicated that the Eu^{3+} doping concentration was 5mol%, the sample has the maximum fluorescence intensity.

Introduction

Recently, rare earth doped glass ceramics possess higher chemical and mechanical stability, higher doping concentration, lower phonon energy, and the possibility of preparing materials in large sizes and different shapes have attracted much attention in the luminescent materials field, such as optical communication, solid-state display, light emitting diodes and so on. Among various materials, RE^{3+} ion doped calcium molybdate nanocrystal materials have advantageous as their remarkable optical, thermal, chemical properties and superior photo-stability, which is widely used in various fields [1-4]. Among various rare earth ions, Eu^{3+} becomes widely used in red emitting materials which has the strong luminescence intensity and high color purity. In recent years, because molybdate can produce efficient red light as important applications in the white LED [5,6]. Molybdate as a matrix, Up-conversion luminescence intensity of materials is increasingly emphasized. In 2010 by professor Cheng Lihong group [7,8] prepared $\text{Y}_2(\text{MoO}_4)_3:\text{Yb}^{3+}/\text{Er}^{3+}(\text{Tm}^{3+})$ by high temperature solid state method and co-precipitation method and up-conversion luminescence characteristics were analyzed. In 2012, tetragonal rare earth doped $\text{NaLn}(\text{MoO}_4)_2$ nanoparticles were synthesized by hydrothermal method by Wang Guofeng et al [9,10] and strong green light was observed under the excitation of 980 nm. In 2015, Qingyun et al [11] prepared $\text{CaMoO}_4:\text{Eu}^{3+}$ phosphor by microwave-assisted liquid phase method and studied its properties.

The current research on the rare earth molybdate as matrix material. $\text{CaMoO}_4:\text{Eu}^{3+}$ glass ceramics have not been reported. In this paper, Tb^{3+} doped molybdate glass ceramics containing CaMoO_4 nanocrystals were successfully prepared by the conventional melting and thermal treatment methods and the luminescence properties of Tb^{3+} ions in the glass ceramics were investigated.

Experimental

Preparation of Samples

The glass sample was prepared with the following composition in mol% of $26\text{CaO}-41\text{SiO}_2-13\text{H}_3\text{BO}_3-8\text{MoO}_3-9\text{CaF}_2-2\text{Sb}_2\text{O}_3-1\text{Eu}_2\text{O}_3$. The mixed raw materials were melted in a covered alumina crucible at 1350°C for 2 h. The glass melt was quenched into a preheated brass mold. The quenched sample C was annealed at 450°C for 2 h and then cooled slowly down to the room temperature. The composition of matrix glass sample shown in Table 1. Controlled crystallization of glass samples at a certain temperature obtain transparent glass ceramics.

Table 1 The composition of matrix glass sample (mol%)

CaCO_3	MoO_3	SiO_2	H_3BO_3	Sb_2O_3	CaF_2	Eu_2O_3
26	8	41	13	2	9	1

Performance Test

Differential scanning calorimeter (DSC) of matrix glass samples was carried out at the temperature range of 200°C to 1000°C with the heating rate of $10^\circ\text{C}/\text{min}$ by using SDT2960 thermal analyzer. X-ray diffraction(XRD) measurements were performed by Japan Rigaku 2500PC with Cu-K α 1 radiation at scanning rate of $4^\circ\text{C}/\text{min}$. The microscopic structures of samples were observed by a SPI3800N scanning electron microscope(SEM) produced by Japanese SII. Fluorescence spectra of samples were tested by using high resolution laser spectroscopy with the model of FI9000 produced by British BIO-RAID company, with measurement range of 400-700nm.

Results and Discussion

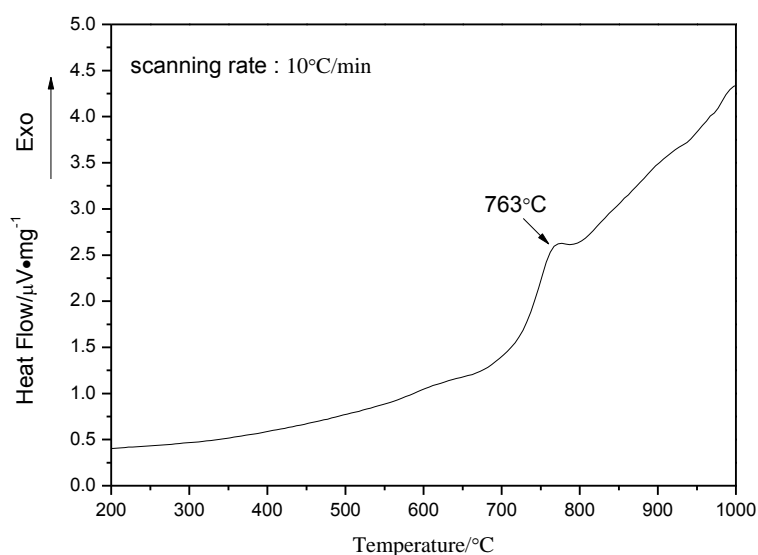


Fig. 1 DSC curve of matrix glass

The DSC curves of matrix glass is shown in Fig. 1, which exhibits a unique exothermal peak centered at about 763°C corresponding to the crystallization of the crystal. So we make a heat-treatment system of glass ceramics as shown in Table. 2.

Table 2 Heat-treating processes of glass

Sample	Temperature/°C	Time/h	Transpareny
C1	700°C	2h	transparent
C2	710°C	2h	transparent
C3	720°C	2h	translucent
C4	730°C	2h	opaque
D1	710°C	2h	transparent
D2	710°C	2.5h	transparent
D3	710°C	3h	opaque
D4	710°C	3.5h	opaque

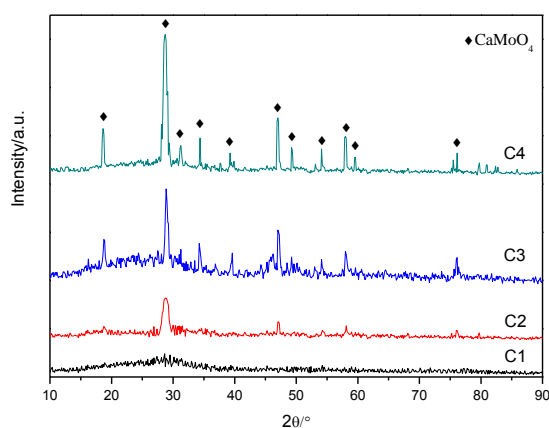


Fig.2 XRD patterns of glass-ceramics C1~C4

Fig. 2 shows the XRD patterns of glass ceramics C1~C4. The diffraction peaks of the all samples were compared with those of the JCPDS NO. 29-0351 standard card, and the crystal phase was determined to be CaMoO_4 .

By comparing the XRD patterns of glass ceramic samples C1 ~ C4, there was no diffraction peak in C1 samples, Obvious diffraction peaks were observed in the sample C2, however, it was observed that the sample C3 became translucent and the sample C4 became opaque, due to the heat treatment temperature of these two samples is too high, resulting in too large number of crystals in the samples .So 710 °C is chosen as heat treatment temperature . The heat treatment time of 2h, 2.5h, 3h and 3.5h samples were numbered as D1, D2, D3, D4 respectively. The heat-treatment system of glass ceramics of matrix glass as shown in Table 2.

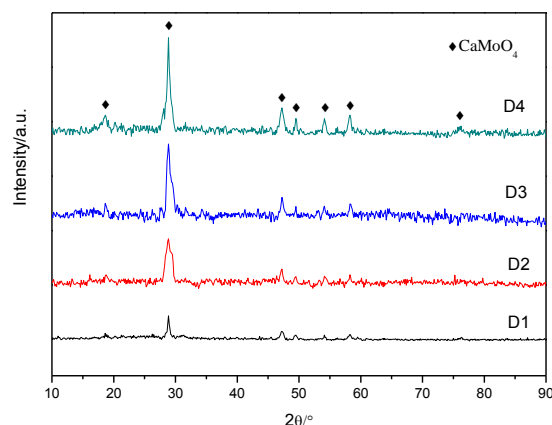


Fig.3 XRD patterns of glass-ceramics D1 ~D4

Fig. 3 shows the XRD patterns of glass ceramic samples D1 ~ D4. The diffraction peaks of the all samples were compared with those of the JCPDS NO. 29-0351 standard card, can determine the crystal phase of CaMoO_4 . The crystal phase of the samples did not change with the increase of heat treatment time but the diffraction peaks gradually enhance. The above analysis shows that different heat treatment system does not generate the formation of new crystalline phases in the samples.

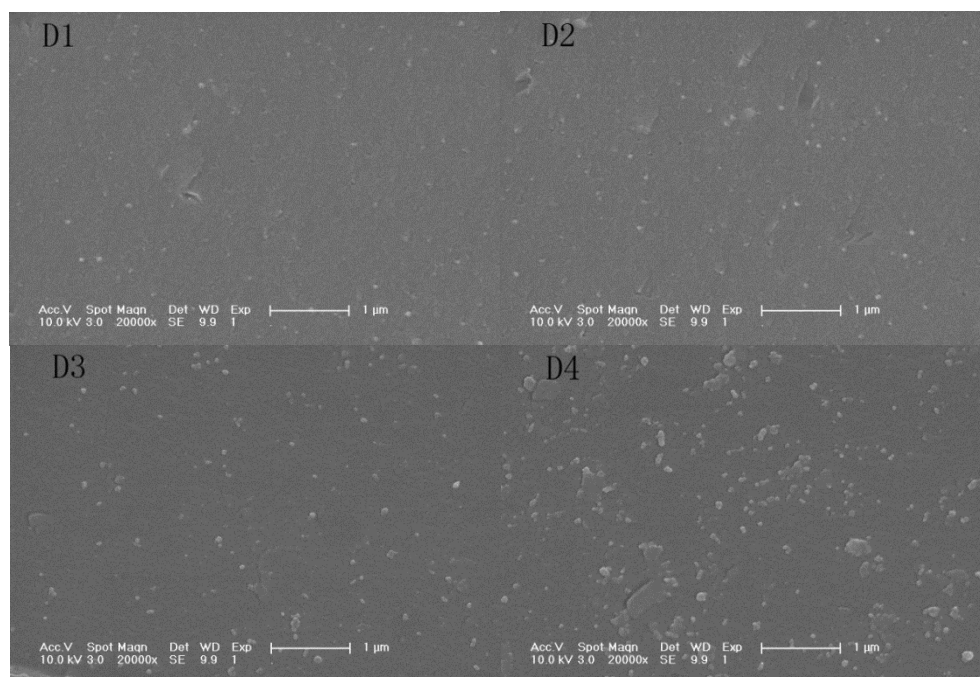


Fig.4 SEM images of glass-ceramic specimen D1~D4

Fig.4 shows the scanning electron microscope photograph of glass ceramic sample D1 ~ D4. It can be seen from the figure, grain formation begins in sample D1. The particle size of D2 crystals gradually increased and the number increased. The results show that the grain growth rate can be increased with the increase of heat treatment time. Grain aggregation occurred in sample D3. The grain size of the sample D4 was agglomerated when the heat treatment time was too long.

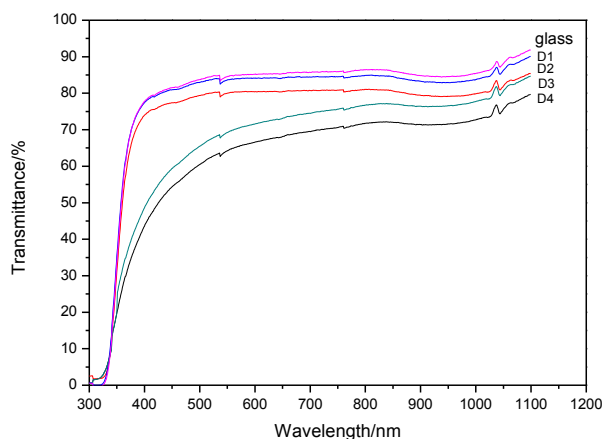


Fig.5 UV-vis-NIR spectroscopy for samples

Fig. 5 shows the transmittance curves of glass sample C and glass ceramics D1 ~D4. It can be seen from the figure that the transmittance of the glass-ceramic samples G1 to G4 in the visible region is gradually reduced from 85% to 68%. With the increase of heat treatment time, the grain size increases and the increase in the number, the distance between grain and grain becomes smaller, the probability of light scattering and diffraction increases. The loss of light increases and the transmittance decreases.

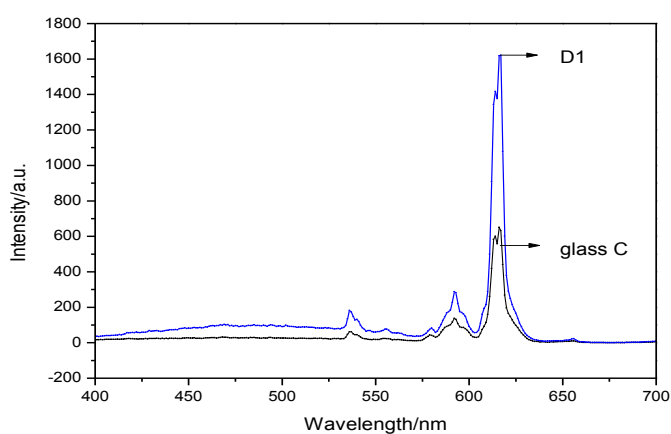


Fig.6 Emission spectra of glass and glass-ceramic specimen D1

Fig. 6 shows the fluorescence spectra of the samples of glass and glass ceramics D1. By observing the emission spectrum, there are two weak emission peaks at 535nm and 590nm, corresponding to Eu^{3+} ions of $^5\text{D}_1-^7\text{F}_0$, $^5\text{D}_0-^7\text{F}_1$ transition. There is a strong emission peak are found in 615nm, corresponding to the $^5\text{D}_0-^7\text{F}_2$ transition of Eu^{3+} ions. From the graph, the intensity of D1 emission peak of glass ceramics samples is higher than that of glass matrix samples, and the emission peak is sharp, but the position of the emission peak did not change.

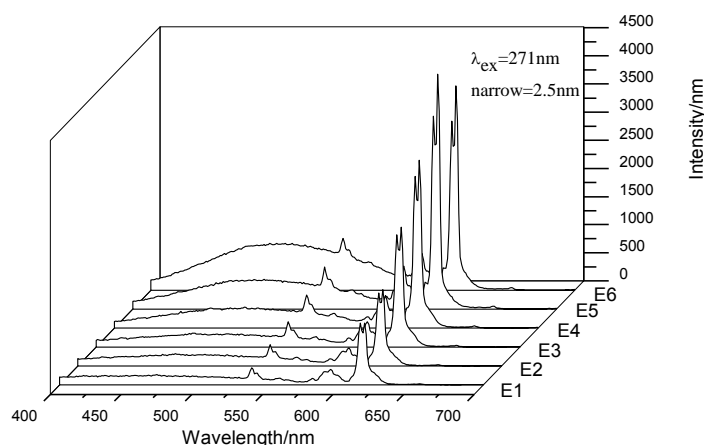


Fig.7 Emission spectra of E1 ~E6 different Eu^{3+} ions in glass-ceramics

Figure 7 is the emission spectra of glass ceramics samples with different amounts of europium dopant E1 ~ E6. The percentage of Eu^{3+} doped material (mol%) was 1%, 2%, 3%, 4%, 5%, and 6%. Glass ceramic samples were recorded as E1, E2, E3, E4, E5, E6. It was observed that with the increase of the mass fraction of Eu^{3+} , some Eu^{3+} ions enter into the crystal to replace some Ca^{2+} ions [12]. The peak of the emission peak increases with the increase of the luminescence centers of rare earth ions, up to 5 mol%, the peak value reached the maximum. Continue to improve the doping concentration, concentration quenching occurs, the peak becomes smaller. Therefore, the optimum doping concentration of Eu^{3+} was determined to be 5 mol%.

Conclusion

- (1) Eu-doped transparent molybdate glass-ceramics were prepared by melt-crystallization method.
- (2) The crystal phase of the glass-ceramics is CaMoO_4 , the optimal heat treatment is 710°C , crystallization 2.5h, the transmittance can reach 80%.
- (3) Eu^{3+} doped glass ceramics samples showed strong red light. The optimum doping concentration was determined to be 5 mol%.

Acknowledgement

This work was financially supported by the National 863 Project (2011AA030204), Key research Project of Jilin Provincial Science and Technology Department (20150204051GX) 、 (20160204027GX).

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