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ScienceDirect
Ceramics International 36 (2010) 1091–1094
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Structure and luminescence of Eu^{3+} doped glass ceramics embedding ZnO quantum dots

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Received 23 September 2009; received in revised form 12 October 2009; accepted 24 November 2009
Available online 4 January 2010

Abstract

Eu^{3+} doped glass ceramics embedding ZnO quantum dots (QDs) were successfully prepared by a sol–gel method. High-resolution transmission electron microscopy (HRTEM) observations revealed that ZnO QDs with size of 3–6 nm precipitated homogeneously among the SiO_2 glassy matrix after thermal treatment of the precursor sample. Such glass ceramics show a high transparency in the visible-infrared range due to the much smaller size of the ZnO QDs than the wavelength of the visible light. The emission and excitation spectra of the samples with various ZnO contents were studied. Based on Judd–Ofelt theory, the intensity parameter Ω_2 was evaluated to investigate the change of the environment around Eu^{3+} in samples with and without QDs.

Keywords: D. Glass ceramics; C. Optical properties; Eu^{3+} ions

1. Introduction

In recent years, rare earth (RE) ions doped semiconductor quantum dots (QDs) have attracted an increasing attention because of their novel optical properties potentially applicable in flat plane displays, biosensors, and so on [1–3]. Generally, RE luminescence in this new class of nano-materials might be efficiently sensitized by QDs host, which is an effective way to overcome the low absorptions of parity-forbidden f–f transitions of RE ions [4–6]. However, QDs might continuously grow and agglomerate during storage, which restricts their practical applications [7,8]. A good solution would be the RE ions doped glass ceramics with semiconductor QDs embedding among an oxide glassy matrix. Such materials possess not only the merits of glassy matrix, such as excellent chemical and mechanical performance and flexibility in size and shape, but also unique physical properties originating from the semiconductors QDs, for instance, quantum confinement and size-dependent optical properties.

ZnO is a well-know wide band gap semiconductor ($E_g = 3.37$ eV [9]) and a desirable candidate as the host material for luminescence centers [10,11]. The optical properties of the ZnO nano-crystals doped with various RE species have been previously studied, which indicated that energy transfer from the host to RE ions may take place when the synthesis and microstructure of the material are well designed and controlled [10–13]. In this paper, the Eu^{3+} doped glass ceramics embedding various contents of ZnO QDs were successfully prepared by a sol–gel method, and their structures and optical properties were investigated.

2. Experiments

The sol was prepared in two parts. For the first one, ethyl orthosilicate (TEOS), distilled water and ethanol were mixed in a molar ratio of 1:10:4. Europium nitrate was used as the Eu^{3+} source, and traces of nitric acid were added as a catalyst for the hydrolysis. The mixture solution was stirred for 4 h at room temperature to complete the hydrolysis. For the second one, zinc acetate di-hydrate and ethanolamine were dissolved in isopropanol with a molar ratio of 1:1:2.5. The sols were formed after continuous stirring the solutions at 65 °C for 4 h. Two parts of sols were slowly mixed together and stirred for another 4 h, resulting in a clear sol which was then poured into vessels to form gels. The gels were then aged at room temperature for one week, and finally dried at different

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0272-8842/$36.00
doi:10.1016/j.ceramint.2009.12.007

temperatures (30–200 °C) for another one week to obtain bulk xerogels with compositions of xZnO-$(100-x)$$SiO_2$:$y$$Eu^{3+}$ (in mol%, $x = 0$, 5, 10, 15, 20; $y = 1$, 2, respectively). To precipitate the ZnO QDs, the xerogels were heat-treated at 500 °C for 2 h. The final samples were transparent bulk monolithic pieces.

The microstructures of the samples were investigated by transmission electron microscopy (TEM, JEM-2010) operated at 200 kV. TEM specimens were prepared by dispersing fine power grinded from bulk sample in ethanol, followed by ultrasonic agitation, and then depositing onto a carbon enhanced copper grid. The transmittance spectra were recorded in an UV near-infrared spectrophotometer (Lambda900). The photoluminescence excitation (PLE) and photoluminescence (PL) spectra, under the excitation of a xenon lamp equipped with a grating monochromator, were recorded by a PMT detector (R928).

3. Results and discussions

TEM micrograph of the as-made xerogel with composition of 1Eu^{3+}:90SiO_2–10ZnO is exhibited in Fig. 1a, demonstrating a typical amorphous structure. After heat-treated at 500 °C for 2 h, the homogenously distributed ZnO spherical crystallites with 3–6 nm in size precipitated from the glassy matrix, as shown in Fig. 1b. Fig. 2 reveals that, despite the difference in refractive index between the ZnO QDs (∼2.0) and the surrounding glassy matrix (∼1.55), the transmittance of the glass ceramic reaches as high as 90% in the visible-infrared range, which is due to the much smaller size of the precipitated crystals than the wavelength of the visible light [14,15].

The excitation spectra monitored at 614 nm (Eu^{3+}:$^5D_0 \rightarrow {}^7F_2$ transition) for the 1 mol% Eu^{3+} doped glass ceramics embedding various contents of ZnO QDs are displayed in Fig. 3. Several peaks ascribing to Eu^{3+} transitions are observed in all the samples, while a broad UV band appears in the samples with ZnO QDs, owing to the generation of excitons in the ZnO QDs and subsequent energy transfer to Eu^{3+} ions residing in the QDs or near them [16]. It is noted that the center of the broad UV bands does not shift obviously with increasing ZnO content, suggesting that the band gap of QDs, related to the size of the QDs, keeps almost unchanged. This is in agreement with TEM observations where the mean grain radius remains almost a constant for the samples with different ZnO contents.

The PL spectra for the 1 and 2 mol% Eu^{3+} doped samples containing various contents of ZnO were measured under excitation at 330 nm. The intensities of Eu^{3+} emission at 614 nm as functions of ZnO content for the samples doped with 1 and 2 mol% Eu^{3+}, respectively, are displayed in Fig. 4. For the 1 mol% Eu^{3+} doped samples, the emission intensifies with increasing of ZnO content from 0 to 15%, and it remains nearly constant when ZnO content further extends to 20 mol%. Interestingly, for the 2 mol% Eu^{3+} doped samples, the emission intensity enhances monotonously with increasing of ZnO content from 0 to 20 mol%. These results suggest that the

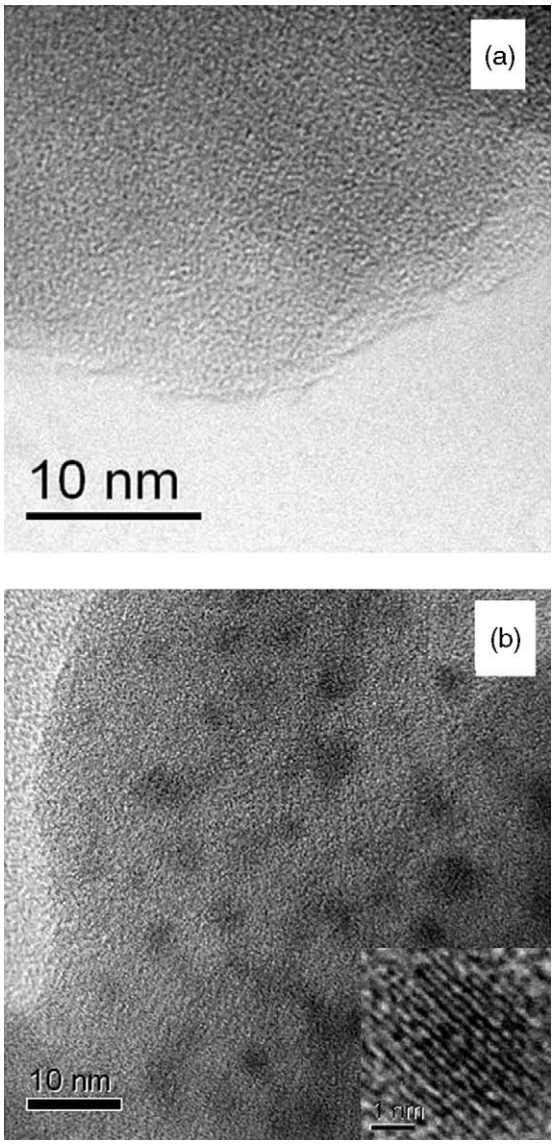

Fig. 1. TEM micrographs of (a) the as-made dry xerogel, and (b) the glass ceramic. Inset in (b) shows the HRTEM image of an individual ZnO QD.

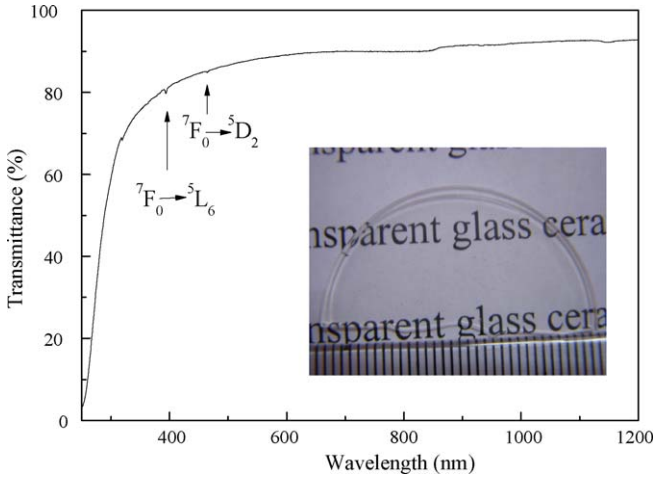

Fig. 2. Transmittance spectrum of the glass ceramic; inset shows photograph of the corresponding sample.