Journal of Non-Crystalline Solids 357 (2011) 83–87

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Short-wavelength upconversion luminescence of Yb^{3+}/Tm^{3+} co-doped glass ceramic containing SrF_2 nanocrystals

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ARTICLE INFO

Article history:
Received 17 May 2010
Received in revised form 8 September 2010

Keywords:
Glass ceramic;
Lanthanide ion;
Upconversion luminescence

ABSTRACT

The preparation process and upconversion luminescence properties of the Yb^{3+} and Tm^{3+} co-doped glass ceramic containing SrF_2 nanocrystals were investigated. In the glass ceramic, the SrF_2 nanocrystals were embedded uniformly in the glass matrix. The Yb^{3+} and Tm^{3+} ions could be enriched into the precipitated SrF_2 nanocrystalline phase, which provide much lower phonon energy than the glass matrix. The glass ceramic exhibited much stronger upconversion luminescence from ultraviolet to visible than the precursor glass. The upconversion luminescence mechanisms were mainly attributed to Yb^{3+}–Yb^{3+} cooperative upconversion, Yb^{3+}–Tm^{3+} energy transfer and Tm^{3+}–Tm^{3+} cross relaxation.

1. Introduction

Short-wavelength upconversion solid state lasers have been the subject of intense research in the last two decades for applications such as high-density data storage, medical diagnosis and treatment, underwater surveillance, and full color solid state displays [1–5]. Trivalent lanthanide (Ln^{3+}) doped upconversion materials can be utilized for realization of short-wavelength solid state lasers in both CW and pulsed modes without use of any nonlinear frequency conversion [6]. One of the most frequently-used Ln^{3+}-upconversion laser hosts is fluoride glasses, but they exhibit excellent luminescent properties together with their intrinsic problems, such as chemical instability and sensitivity to moisture [7]. Those problems were found to be well solved in oxyfluoride glass ceramic because such glass ceramic not only presented excellent upconversion luminescent properties related with fluoride crystals but also maintained the durability, formability and chemical stability corresponding to oxide glasses [8]. Avoiding toxic PbF_2 and CdF_2, we have developed a new series of alkaline earth fluorosilicate glass ceramic containing MF_2:Ln^{3+} nanocrystals (M = Ca^{2+}, Sr^{2+} and Ba^{2+}) by melting techniques [9–11]. In this work, we mainly report on preparation and upconversion luminescence of the Yb^{3+}/Tm^{3+} co-doped glass ceramic containing SrF_2 nanocrystals. Here, Yb^{3+} ions act as an efficient sensitive ion for Tm^{3+} because its strong 980 nm absorption cross section matches well with the standard wavelength of commercially available high-power InGaAs laser diode. The Yb^{3+}/Tm^{3+} co-doped glass ceramic exhibited intense upconversion luminescence, including ultraviolet and blue emission deduced from unusual efficient three- or four-step energy transfer from Yb^{3+} to Tm^{3+}.

2. Experimental

Yb^{3+}/Tm^{3+} co-doped glass with a composition (mol%) of $50SiO_2$–$10Al_2O_3$–$20ZnF_2$–$20SrF_2$–$4YbF_3$–$0.05TmF_3$ and Yb^{3+} single doped glass with a composition (mol%) of $50SiO_2$–$10Al_2O_3$–$20ZnF_2$–$20SrF_2$–$4YbF_3$, named respectively as GYbTm and GYb, were prepared from high purity SiO_2, Al_2O_3, ZnF_2, SrF_2, YbF_3 and TmF_3. After molten in covered corundum crucibles in the air for 45 min at 1400 °C, the melts were poured onto a brass plate and then pressed by another brass plate. DTA results showed the glass transition temperature (T_g) located around 590 °C and the first crystallization peak temperature (T_{c1}) located around 660 °C for both GYb and GYbTm glasses. Accordingly, the glass ceramic was obtained by heat treating GYbTm glass (named as GCYbTm) and GYb glass (named as GCYb) for 2 h at 600 °C. Glass and glass ceramic samples were then polished on a UNIPOL-802 precision lapping/polishing machine. All glasses and glass ceramic were transparent.

To identify the crystalline phase in glass ceramic, X-ray diffraction (XRD) measurements were performed on an XD-98 diffractometer with Cu-K_α radiation at 4°/min scanning rate. Crystal sizes were then calculated from XRD patterns and their errors were evaluated with Jade (Materials Data, Inc.). Transmission electron microscopy (TEM) and high resolution TEM images were taken on a JEOL JEM-2010HR microscopy. The analysis of HRTEM images was carried out with DigitalMicrograph (Gatan Inc.). Upconversion luminescence measurements were performed with a Hitachi F-4500 fluorescence spectrophotometer, using an excitation of 980 nm from a laser diode. Luminescence decay curves were measured with an Edinburgh FLS920P spectrometer, using an excitation of a microsecond flashlamp at 300 nm. All spectral measurements were performed at room temperature and systematical errors were minimized by calibrating instruments with standard samples. Spectra analysis was carried out

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0022-3093/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2010.09.008

with Origin (OriginLab Coporation) and the errors of lifetime and photon number absorbed during upconversion processes were also evaluated simultaneously.

3. Results

Fig. 1 shows the XRD patterns of the glasses and glass ceramics. Both Yb^{3+} single doped and Yb^{3+}/Tm^{3+} co-doped glasses were completely amorphous with no diffraction peaks. But sharp diffraction peaks for GCYbTm and GCYb could be identified, which were easily assigned to the cubic SrF_2 phase (JCPDS-PDF# 06-0262). From the obtained peak width of the XRD pattern, the average size of SrF_2 nanocrystals in GCYbTm and GCYb was respectively calculated as 12.5 ± 0.2 nm and 13.7 ± 0.1 nm by the Scherrer formula. Fig. 2(a) shows the TEM image of GCYbTm glass ceramic. Glassy and crystalline phase showed different contrasts. The isolated dark circle domains corresponded to the crystalline phase and the gray background to the glassy phase, which revealed that the nanocrystals embedded homogenously in the glass host. The size of these crystalline particles was 10–20 nm, which was consistent with the Scherrer-calculated diameter from the XRD result. Due to much smaller size of precipitated SrF_2 nanocrystals than the visible-near infrared wavelength, such glass ceramic containing SrF_2 nanocrystals still had high transparency. Fig. 2(b) shows a magnified lattice image from the high resolution transmission electron microscopy (HRTEM) image of GCYbTm glass ceramic. Using the Fourier transform method, the associated interplanar spacing could be determined as 0.3295 nm with an error range estimated as about $\pm 1.5\%$, which could be assigned to the (111) plane of cubic SrF_2. It was consistent with the value of 0.3324 ± 0.0001 nm from XRD. But it was still smaller than the standard value of 0.3352 nm (see JCPDS card # 06-0262). It might be attributed to the enrichment of Yb^{3+} and Tm^{3+} ions into the precipitated SrF_2 crystalline phase because the Yb^{3+} (0.095 nm) and Tm^{3+} (0.096 nm) has smaller ionic radius than Sr^{2+} (0.121 nm) when the coordinate number was six [12].

Fig. 3 shows the upconversion luminescence spectra (excited with 980 nm) of Yb^{3+} doped and Yb^{3+}/Tm^{3+} co-doped glasses and glass ceramics. For Yb^{3+} doped samples, both GYb and GCYb present their strongest upconversion peaks at 479 nm, which could be assigned to the cooperative upconversion process of Yb^{3+}: $^2F_{7/2} + {}^2F_{7/2} \rightarrow {}^2F_{5/2} + {}^2F_{5/2}$.

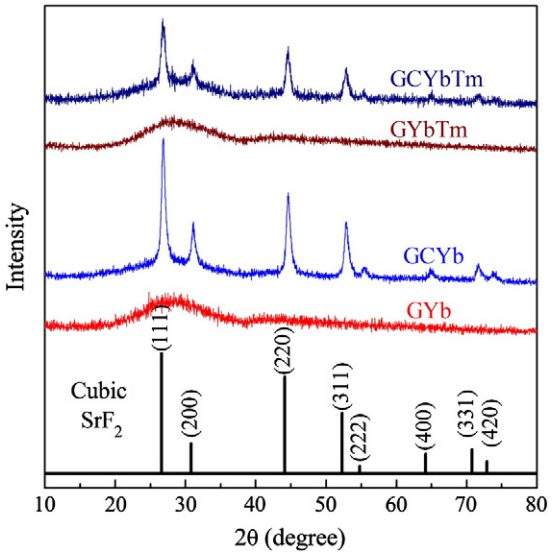

Fig. 1. XRD patterns of Yb^{3+} doped glass and glass ceramic and Yb^{3+}/Tm^{3+} co-doped glass and glass ceramic.

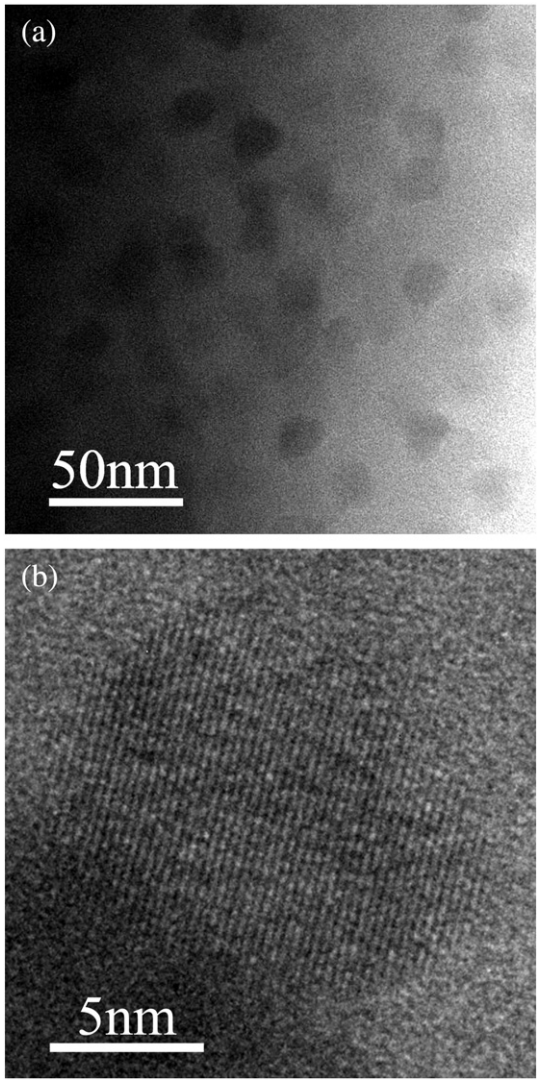

Fig. 2. TEM image (a) and HRTEM image (b) of GCYbTm glass ceramic.

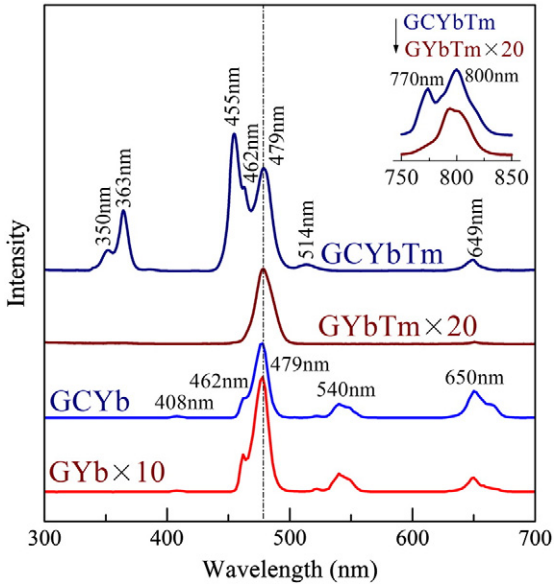

Fig. 3. Upconversion luminescence spectra of Yb^{3+} doped and Yb^{3+}/Tm^{3+} co-doped glass and glass ceramic, pumping with a 980 nm laser diode. (The inset shows upconversion spectra around 800 nm of Yb^{3+}/Tm^{3+} co-doped glass and glass ceramic.)