Journal of Alloys and Compounds 511 (2012) 189–194

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

A study on microstructure and luminescent properties of oxyfluoride silicate glass-ceramics with (Ho^{3+},Yb^{3+}):$NaYF_4$ crystallites

G. Dominiak-Dzik*, R. Lisiecki, W. Ryba-Romanowski, L. Krajczyk

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, ul. Okólna 2, 50-950 Wrocław, Poland

ARTICLE INFO

Article history:
Received 1 July 2011
Received in revised form 7 September 2011
Accepted 8 September 2011
Available online 16 September 2011

Keywords:
Glass-ceramics
$NaYF_4$ nanocrystals
(Ho^{3+}/Yb^{3+}) luminescence
Excited-state dynamics

ABSTRACT

Glass-ceramics containing $NaYF_4$ nanocrystals were prepared by heat-treatment from oxyfluoride silicate-based glass doped with Ho^{3+} and Yb^{3+} ions. The formation of crystalline fluoride phase was confirmed by X-ray diffraction and transmission electron microscopy. Absorption and emission spectra revealed that a fraction of Ho^{3+} and Yb^{3+} ions is incorporated into the $NaYF_4$ ordered lattice influencing spectroscopic features of glass-ceramics in comparison with those of precursor glass. Green up-conversion emission (545 nm) originating in the $^5S_2$ level in glass-ceramics and up-converted red emission (650 nm) originating in the $^5F_5$ level in *as-melted* glass were observed under optical pumping into Yb^{3+} absorption band and analyzed. Although both emissions in both materials are achieved by two-photon excitations, the relation between green and red emission intensity in glass-ceramics and glass implies that processes relevant to up-conversion phenomena are different. Based on a careful analysis of relaxation dynamics of Ho^{3+} and Yb^{3+} excited states, the mechanisms involved in conversion of the infrared radiation into the visible emission in these materials are proposed and discussed.

1. Introduction

Oxyfluoride glass-ceramics systems doped with rare earth ions have been researched widely in the last decade since they possess not only higher chemical and mechanical stability than fluoride glasses but also lower phonon energy than oxide ones. It has been reported in numerous papers that nano-sized crystalline phase like PbF_2, $Pb_{1-x}Cd_xF_2$, MeF_2 (Me = alkaline earth cations), LaF_3 or $NaYF_4$ can be created in glasses by controlled thermal treatment without loss of transparency. An interest in luminescent properties of trivalent holmium ion is related to laser emission achieved in the $^5I_7 \rightarrow {}^5I_8$ transition around 2.2 μm (eye-save spectral region) and to the visible emission achieved in up-converted processes. Since a direct excitation of Ho^{3+} with diode lasers is inefficient, Ho^{3+} ion is usually sensitized with Yb^{3+} that shows a very strong and broad absorption band at around 1.0 μm, easy available for commercial laser diodes. Energy exchange from Yb^{3+} to Ho^{3+} allows to pump holmium luminescent states for the infrared and visible emissions. Numerous published paper were devoted to luminescence properties of Ho^{3+} and (Ho^{3+},Yb^{3+}) in various multicomponent glasses [1–4] and glass-ceramics containing LaF_3, PbF_2 or $Pb_{1-x}Cd_xF_2$ crystal phase [5–7]. However, to the best of our knowledge, optical studies of Ho^{3+} sensitized with Yb^{3+} in glass-ceramics systems with the nanocrystalline phase of $NaYF_4$ have not been reported. The $NaYF_4$ has been recognized as very efficient up-conversion matrix [8] especially for Er^{3+} or Tm^{3+} with Yb^{3+} as a codopant [9,10]. These reported results were motivation to investigate spectroscopic features of silicate glass-ceramics with (Ho^{3+},Yb^{3+}):$NaYF_4$ crystallites.

In this paper, we report the morphology of silica-based glass-ceramics with $NaYF_4$ nanocrystals, single- and double-doped with Ho^{3+} and Yb^{3+}, and emission properties of Ho^{3+}–Yb^{3+} co-doped glass and glass-ceramics materials under optical pumping into Ho^{3+} or Yb^{3+} absorption bands. Particular attention has been directed to relaxation dynamics of holmium and ytterbium excited states in order to explain mechanisms responsible for up-converted green emission originating in the $^5S_2$ level in the glass-ceramics and red emission from the $^5F_5$ state in glass.

2. Experimental

The mixture of high purity (4 N, Sigma–Aldrich) reagents were melted to obtain the glass samples with the batch composition in mol%: $40SiO_2$–$25Al_2O_3$–$18Na_2CO_3$–7NaF–$(10-x-y)YF_3$–$xHoF_3$–$yYbF_3$ (x = 0, 0.5 and y = 0, 1, 4). The anhydrous Na_2CO_3, NaF, YF_3 and LnF_3 (Ln = Ho, Yb) were used. Owing to a fluorine loss that may occur in the preparation procedure, a 10 mol% excess of YF_3 was used. The 20 g of starting reagents, thoroughly mixed and put in a covered corundum crucible in dry box, were introduced into a resistance furnace at 1450 °C and melted for one hour and fifteen minutes in normal atmosphere. The glassy liquid was poured into copper plate. To obtain glass-ceramics samples, the precursor (*as-melted*) glass ingots were cut into pieces and heat-treated at temperature ranging from 610 °C to 640 °C and time ranging from 2 to 4 h to find optimal crystallization conditions.

* Corresponding author. Tel.: +48 713954173; fax: +48 71 344 10 29.
E-mail address: G.Dominiak-Dzik@int.pan.wroc.pl (G. Dominiak-Dzik).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.09.026

The X-ray powder diffraction spectra were recorded with X'Pert PRO X-ray diffractometer (Cu, $K\alpha_1$ radiation: 1.54060 Å), in the range of $2\Theta = 5–80^\circ$. Morphological studies encompassing transmission electron microscopy (TEM), and selected area electron diffraction (SAED) measurements were performed using a Philips Transmission Electron Microscope CM-20 Super Twin with 0.24 nm resolution at 200 kV. Absorption spectra were recorded using a Varian 5 UV–vis–NIR spectrophotometer. Low-resolution emission spectra were performed by microspectrometer Ocean Optics Model USB 200. Upconversion spectra were excited by an Apollo Instruments diode laser emitting continuous wave (cw) radiation at 980 nm with a maximum power up to 3 W. Resulting luminescence was dispersed by an Optron DongWoo DM711 monochromator with 750-mm focal length and detected by a Hamamatsu R-955 photomultiplier in UV–vis and by PbS detector in NIR spectral range. Luminescence decay curves were recorded upon a pulsed excitation delivered by a Continuum Surelite optical parametric oscillator (OPO) pumped with the third harmonic of Nd:YAG laser. The decays were measured with Hamamatsu R-955 photomultiplier or a cooled InSb Janson J10D detector (depending on the spectral range) connected to a Tektronix Model TDS 3052 digital oscilloscope. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Morphological characteristics

Fig. 1 presents the X-ray diffractograms of samples single-doped with Ho^{3+} (0.5% of HoF_3) and Yb^{3+} (1% of YbF_3), and double-doped with Ho^{3+} and Yb^{3+} (0.5%HoF_3–4%YbF_3) that were heat-treated at temperatures from 610 to 630 °C. Sharp and intensive diffraction peaks are observed in the spectra of heat-treated glasses co-doped with Ho^{3+} and Yb^{3+} and single doped with Yb^{3+} ions whereas, the Ho^{3+}-doped glass not so easy undergoes structural modifications in the same thermal and temporal conditions regardless of holmium concentration (data not presented here). It seems that a tendency to crystallization may be controlled by ionic radii of lanthanide impurities. Ions from the beginning (Nd^{3+}, Pr^{3+}) and the end (Yb^{3+}) of lanthanide series were found as nucleating agents that promote evidently the crystallization of $NaYF_4$ phase in the systems [11,12]. The crystalline phase formed in the glass-ceramics has been

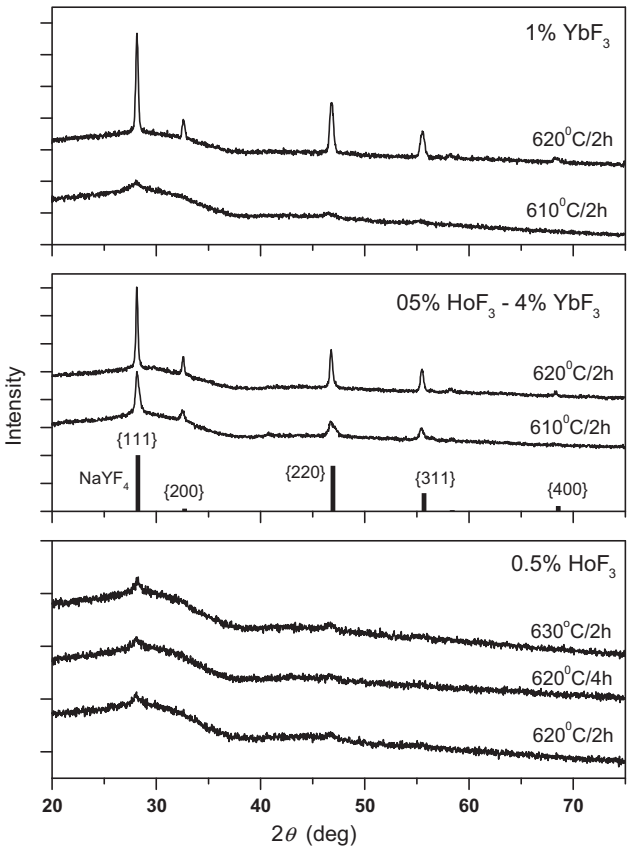

Fig. 1. X-ray diffraction patterns recorded for samples thermal treated at different temperatures. The cubic $NaYF_4$ pattern with 2Θ and $\{h\,k\,l\}$ values are presented for the comparison.

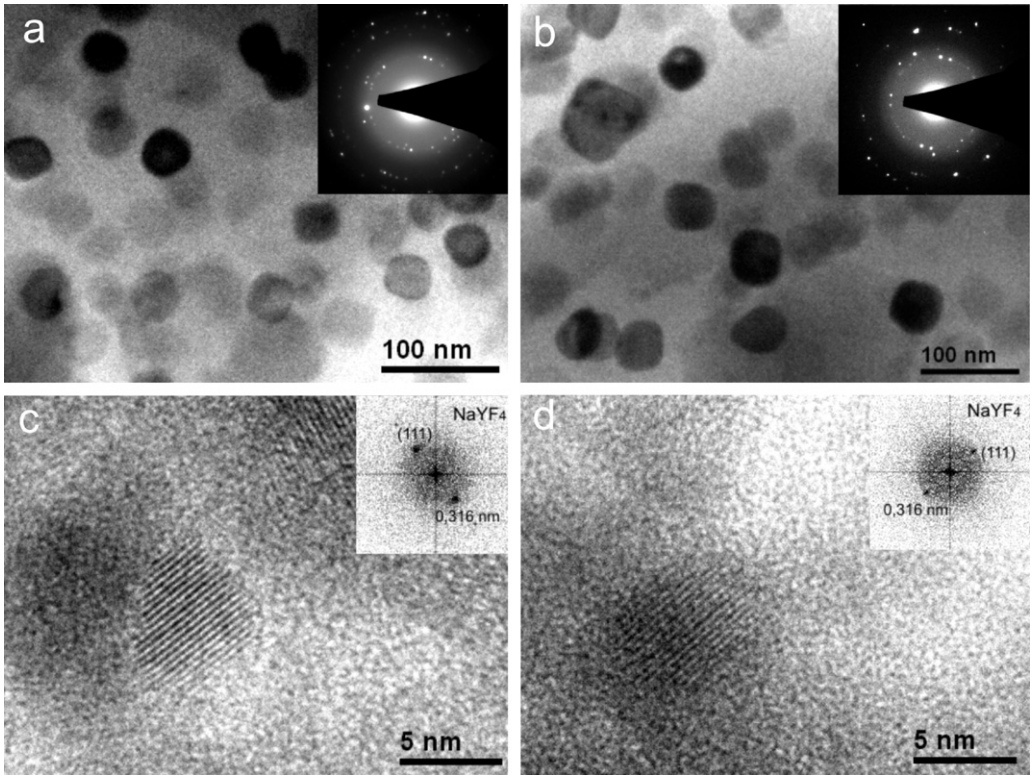

Fig. 2. TEM micrographs with corresponding SAED (insets) of glass-ceramics created at 620 °C and containing 1% of YbF_3 (a) and 0.5% of HoF_3–4% of YbF_3 (b). The HRTM images with corresponding fast Fourier transforms (FFT – insets) of the samples with 1%YbF_3 (c) and 0.5%HoF_3 (d) heat-treated at 610 °C and 620 °C, respectively.