Ceramics International 42 (2016) 13990–13995

Contents lists available at ScienceDirect

Ceramics International

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

Up-conversion luminescence and optical thermometry properties of transparent glass ceramics containing CaF_2:Yb^{3+}/Er^{3+} nanocrystals

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ARTICLE INFO

Article history:
Received 7 May 2016
Received in revised form
31 May 2016
Accepted 1 June 2016
Available online 2 June 2016

Keywords:
Caf_2:Yb^{3+}/Er^{3+} glass ceramics
Energy transfer process
Power dependence
Tunable emission
Optical thermometry

ABSTRACT

A series of Yb^{3+}/Er^{3+} codoped transparent oxyfluoride glass ceramics with various amounts of Yb^{3+} have been successfully fabricated and characterized. Under 980 nm laser prompting, the samples produce intense red, green and blue up-conversion emissions, and the emission intensities increase with Yb^{3+} concentration and heat treatment temperature. Before losing good transparency in the visible region, optimum emission intensities are obtained for the sample with 25 mol% of Yb^{3+} at a heat treatment temperature of 680 °C. A possible up-conversion mechanism is proposed from the dependence of emission intensities on pumping power. The fluorescence intensity ratio between the two thermally coupled levels $^2H_{11/2}$ versus $^4S_{3/2}$ was measured with the laser output power of 57 mW to avoid the possible laser induced heating effect. The fluorescence intensity ratio values in the temperature range from 295 K to 723 K can be well fitted with the equation: $A\exp(-\Delta E/k_BT)$, where $A = 6.79$ and $\Delta E = 876\ \text{cm}^{-1}$. The relative temperature sensitivity at 300 K was evaluated to be 1.4% K^{-1}. All the results suggest that the Yb^{3+}/Er^{3+} codoped CaF_2 glass ceramics is an efficient up-conversion material with potential in optical fiber temperature sensing.

1. Introduction

Recently, trivalent rare-earth (RE) ions doped up-conversion (UC) glass-ceramics (GC) have attracted significant interests in view of their potential application in fiber amplifiers, spectral conversion, temperature sensors, biological imaging, drug delivery carriers, DNA detection and solar cells [1–7]. In particular, transparent oxyfluoride GC have received considerable attention, as they have not only comparatively low phonon energies related to fluorides, but also high durability and mechanical stability ascribed to oxides [8,9]. The optical properties of the active ions will be controlled by their fluoride crystal host, and the nanocrystals will be protected by the oxide glass matrix. CaF_2 is a promising candidate for desired host materials with high solubility of both sensitizer and activator RE ions and high transparence in the wavelength range from 0.13 to 9.5 μm [10]. Yb^{3+} ion was usually chosen as sensitizer for its large absorption cross section around 980 nm and can efficiently transfer its absorption energy to adjacent Er^{3+} ions. The coefficient of $Yb^{3+}\rightarrow Er^{3+}$ energy transfer was evaluated to be about 3.5 times higher than that of $Er^{3+}\rightarrow Yb^{3+}$ energy back transfer [11], which significantly enhances the UC luminescence efficiency.

Among many reported RE ions doped materials for temperature sensing based on the change of fluorescence intensity ratio (FIR) of two thermally-coupled energy levels (TCELs) with temperature [3,12–19], Eu^{3+}, Ho^{3+} and Tm^{3+} have TCELs with energy differences over 1500 cm^{-1}, which could lead to thermal decoupling at low temperature. While the energy differences of TCELs of Yb^{3+} and Pr^{3+} are too small, which go against high temperature sensitivity. Er^{3+} has two sets of TCELs, one set ($^2H_{11/2}$, $^4S_{3/2}$) with a gap of ca. 780 cm^{-1} and the other set ($^4G_{11/2}$, $^2H_{9/2}$) with a gap of ca. 1530 cm^{-1} [19], as depicted in Fig. 1. By making use of both sets of levels, Er^{3+} could be suitable for optical thermometry from very low to very high temperature with excellent sensitivity [3]. Plus the GC sample's low phonon energy and high thermal stability, an improved measurement accuracy and extended operating temperature range can be achieved with the GC sample, suggesting that transparent GC containing CaF_2:Yb^{3+}/Er^{3+} nanocrystals has potential application in optical fiber temperature sensing.

In this work, the optimal Yb^{3+} content in Yb^{3+}/Er^{3+} codoped CaF_2 transparent GC and applicable thermal treatment temperature for enhancing the UC luminescence were investigated, and then the quadratic pump power dependence of the red and green emission intensities and the three photon conversion process were

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http://dx.doi.org/10.1016/j.ceramint.2016.06.002
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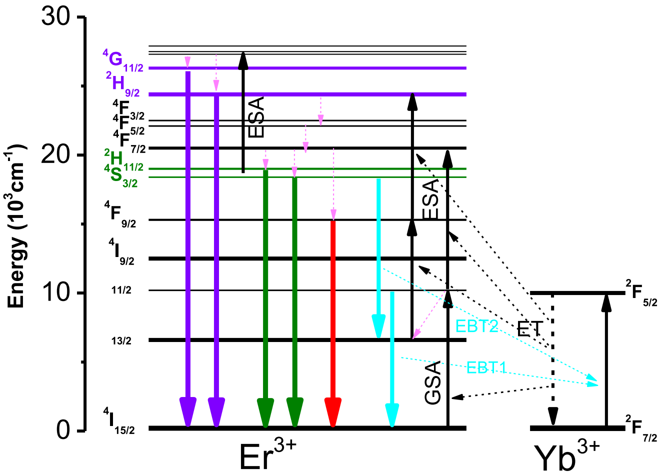

Fig. 1. Schematic diagram of the energy levels of Er^{3+} and Yb^{3+} ions, with the possible energy transfer processes between them and the optical transitions of interest.

discussed. Furthermore, we measured the dependence of UC emission properties on temperature and evaluated the temperature sensing properties for FIR technique.

2. Experimental

2.1. Materials

The samples were prepared with nominal composition $45SiO_2$–$20Al_2O_3$–$10CaCO_3$–25 (CaF_2:x% YbF_3+2% ErF_3), x=15, 20, 25, 30 and 35. For each group, 0.2 mol sample was fabricated in air by melt-quenching technique. High purity RE fluorides YbF_3 (99.99%) and ErF_3 (99.99%) were purchased from AnSheng Inorganic Materials Co., Ltd. SiO_2, Al_2O_3, $CaCO_3$ and CaF_2 were purchased from the Alfa Aesar Chemical Company.

2.2. Preparation

The starting materials were mixed with the desired stoichiometric ratio. Then well-mixed batches were melted in alumina crucibles at 1400 °C for half an hour. The melts were firstly poured onto a preheated brass plate and pressed swiftly by another plate to form precursor glass (PG) and then annealed at 450 °C for 10 h to relinquish the inner stress. The obtained samples were subsequently cut into 1 cm × 1 cm slices and then thermally treated respectively at 650 °C, 660 °C, 680 °C (determined by differential thermal analysis measurements) for 2 h to form the glass ceramics GC650, GC660 and GC680.

2.3. Characterization

The crystal-phases of 25% Yb^{3+}/2% Er^{3+} codoped oxyfluoride PG, GC650 and GC680 were characterized by an X-ray diffractometer (MAC Science Co., Ltd., MXP18AHF) using nickel-filtered Cu Kα radiation (λ=0.15418 nm) in the 2θ range from 10° to 70°. The morphology was analyzed by a high-resolution transmission electron microscopy (HRTEM, Model JEM-2010; JEOL Ltd., Tokyo, Japan). Transmittance spectra were measured by a SOLID 3700 spectrometer (Shimadzu Ltd., Kyoto, Japan). The samples were excited by a 980 nm diode laser to record emission spectra. Their visible emissions were dispersed by a Jobin-Yvon HRD1 double monochromator (Jobin Yvon HRD1, Paris, France) and detected by a Hamamatsu R928 photomultiplier (Hamamastsu, Japan). For the measurements of temperature dependent properties, the samples were loaded on a copper post, whose temperature was controlled by a temperature controller (OMRON E5CC-800) with a type-K thermocouple and a heating tube.

3. Results and discussion

3.1. Crystallization behavior and structure

XRD patterns of 25% Yb^{3+} /2% Er^{3+} codoped oxyfluoride PG, GC650 and GC680 are shown in Fig. 2. The XRD curves for both GC650 and GC680 contain intense diffraction peaks corresponding to cubic CaF_2 crystal (JCPDS No. 35–816), indicating that GCs with well-crystallized CaF_2 nanocrystals encapsulated by glass were successfully obtained. XRD lines were fitted with Gaussian profile shape functions. The sizes (D) of the nanoparticles are calculated using the Scherrer formula [20]:

$$D = k\lambda/\beta cos(\theta) \quad (1)$$

where k=0.89, λ is the diffractometer wavelength (λ=0.15418 nm), 2θ is the peak position, and β is the peak-width at half maximum. The mean crystallite sizes of the GC650 and GC680 are estimated to be about 15 nm and 25 nm respectively, increasing monotonically with heat treatment temperature.

To investigate the morphology and particle size of the obtained samples, the representative TEM and HRTEM images of the 25% Yb^{3+}/2% Er^{3+} codoped GC680 are shown in Fig. 3(a) and (b). The homogeneously distributed black spots in Fig. 3(a) and the lattice fringes in Fig. 3(b) are identified as CaF_2 nanocrystals with narrowly distributed size, which is consistent with the size estimated by Scherer's equation. The HRTEM of nanoparticle (Fig. 3(b)) shows an interplanar spacing of 0.316 nm, which can be attributed to the (111) lattice plane of the CaF_2 (d111=0.323 nm) with cubic phase.

3.2. Transmittance spectra

Transmittance is an important property for GC samples. The average nanocrystal sizes of GC are much smaller than the wavelength of visible and near-infrared light, so the scattering remains weak and the GCs are highly transparent [21]. As depicted in Fig. 4, the transmittance spectra of 25% Yb^{3+}/2% Er^{3+} codoped PG, GC660 and GC680 were recorded in the wavelength range of 350–750 nm at room temperature. The GCs possess good transparency in the visible region, indicating that the sizes of the CaF_2

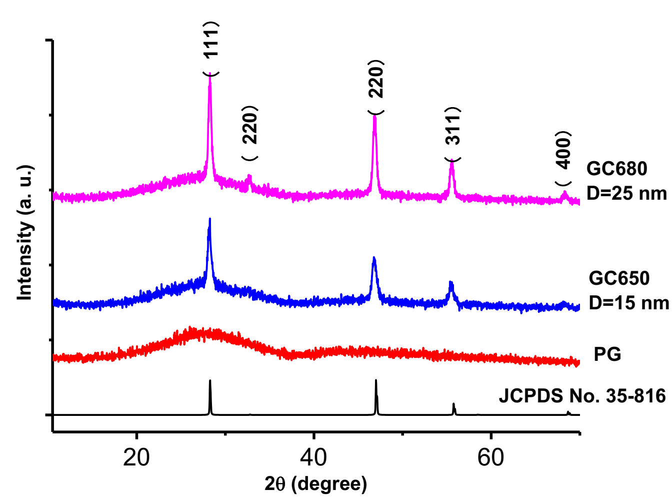

Fig. 2. XRD patterns of 25% Yb^{3+}/2% Er^{3+} codoped PG, GC650 and GC680, and the reference data of JCPDS card (No. 35–816) for cubic CaF_2.