Sol–gel preparation and white up-conversion luminescence in rare-earth doped PbF_2 nanocrystals dissolved in silica glass

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Abstract $89.5(\text{SiO}_2)10(\text{PbF}_2)0.5(\text{REF}_3)$ silicate glasses have been prepared using *room temperature* sol–gel processing of $\text{Si}(\text{OCH}_2\text{CH}_3)_4$, $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, $\text{RE}(\text{CH}_3\text{COO})_3 \cdot n\text{H}_2\text{O}$ and trifluoroacetic acid as a fluorinating agent, where RE stands for rare-earth ions, such as Yb^{3+} , Er^{3+} , Ho^{3+} , Tm^{3+} , or combinations of those ions. On heat treatment of these glasses at about 300–400 °C, the rare-earth doped spherical PbF_2 nanocrystals precipitate within SiO_2 glass matrix providing *transparent nano-structured glass-ceramics*, while the diameter of the nanocrystals can be set in the range from 5 to 25 nm by varying time and temperature of the heat treatment. The structural and photoluminescence studies confirm the incorporation of rare-earth ions into the PbF_2 nanocrystals and white and tuneable colour up-conversion luminescence has been detected in case of Yb^{3+} - Er^{3+} - Tm^{3+} and Yb^{3+} - Ho^{3+} - Tm^{3+} co-doped nanocrystals by varying dopant ratio and pump power.

Keywords Sol–gel materials · Glass–ceramics · Rare-earth ions · Up-conversion luminescence

1 Introduction

RE-doped transparent nano-structured oxyfluoride glass–ceramics (NGC) have been attracted recently a substantial interest for several nano-photonics applications, such as efficient infrared and up-conversion luminescence, nano-sensors, nanolabels, nanoheaters, e.g. [1–14 and ref therein]. The NGC combine the low phonon energy fluoride-based host for RE dopants [3, 11], in particular lead fluoride nanocrystals [3–5], and robustness of silica oxide glass [2–14], because the dopants are incorporated in the PbF_2 -based fluoride nanocrystals, while the nanocrystals are embedded in silica based glass network. Normally, the NGC are prepared by glass melting technique with subsequent heat treatment [2–12] or laser irradiation [13, 14] of precursor oxyfluoride glass for precipitation of rare-earth doped fluoride nanocrystals.

However, in some cases, the NGC has to be prepared as a thin layer or even thin film, especially when the large area surfaces should be covered with NGC, i.e. for display applications. Pulsed laser deposition of precursor glass film has been reported in [15]; however, this method is complex, expensive and hardly can be used for production of large amounts and large surface area NGC layers and films. Therefore, an alternative and technically simpler *sol–gel* method has been explored in this work, which can be further used for preparation of large surface area layers and films of NGC. To date, to our knowledge, only few works have been reported where sol–gel method was involved in preparation procedure of *bulk* $(\text{SiO}_2):(\text{PbF}_2)$ [16] and $(\text{SiO}_2):(\text{LaF}_3)$ [17–19] oxyfluoride glass–ceramics. In this work, we have used sol–gel process to prepare nano-structured glass–ceramics $89.5(\text{SiO}_2)10(\text{PbF}_2)0.5(\text{REF}_3)$, where RE stands for rare-earth ions, such as Yb^{3+} , Er^{3+} , Ho^{3+} , Tm^{3+} , or combinations of those ions.

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2 Experimental

2.1 Preparation of precursor glass

Oxyfluoride glasses with compositions of 89.5(SiO₂)10 (PbF₂):0.5(RE), mol% as batched, have been prepared, where RE stands for Yb³⁺, Er³⁺, Ho³⁺ and Tm³⁺ and their combinations. Particularly, the ratios Yb³⁺/Er³⁺/Tm³⁺ = 0.3/0.1/0.1 and Yb³⁺/Ho³⁺/Tm³⁺ = 0.3/0.1/0.1 have been chosen, hereafter referred as YET and YHT samples, respectively.

The sol–gel preparation procedure included the following: Tetraethoxysilane (TEOS) Si(OCH₂CH₃)₄, used as a source of SiO₂, was hydrolyzed for 1 h at room temperature with a mixed solution of ethanol and H₂O, using acetic acid as a catalyst. The molar ratio of TEOS:ethanol:H₂O:CH₃COOH was 1:4:10:0.5. As a source of Pb, Pb(CH₃COO)₂·3H₂O was used. The required quantities of Pb(CH₃COO)₂·3H₂O, Yb(CH₃COO)₃·nH₂O, Er(CH₃COO)₃·nH₂O and Tm(CH₃COO)₃·nH₂O or Ho(CH₃COO)₃·nH₂O were dissolved in CF₃COOH and H₂O solution, which was slowly mixed with the initial solution. The molar ratio of metal ions to CF₃COOH was 1:4. In order to obtain an homogeneous solution, the resultant one was stirred vigorously for 1 h at room temperature. A highly transparent gel was obtained by leaving the resultant homogeneous solution in a sealed container at 35 °C for several days. Then, the gels were dried by slow evaporation of residual water and solvent.

2.2 Preparation of nano-structured glass–ceramics (NGC)

After obtaining these xerogels, they were heat treated in air atmosphere at different temperatures ranging from 300 to 400 °C, in order to achieve a stiff glass network and precipitate PbF₂ nanocrystallites with controlled sizes giving rise to transparent glass–ceramics. The GCs samples are cut into pieces of 7 × 5 × 2 mm³.

3 Results and discussion

3.1 Structural characterisation of NGC by HRTEM, EDS and XRD

HRTEM images and EDS spectra were obtained using JEOL 3010F microscope operated at 300 kV. This microscope is equipped with a Field Emission Gun, which allowed us to achieve a point-to-point resolution of 0.17 nm. Specimens were prepared by dispersing the fine powder obtained by grinding the bulk sample, using a mortar and pestle, in acetone with ultrasonic agitation, and then, a droplet of the suspension was put on a copper holey carbon grid.

Nanocrystal phases can be identified by HRTEM image. Furthermore, the presence of lead fluoride in the nanocrystalline environment can be confirmed by EDS measurements. Figure 1a shows HRTEM image of a crystalline PbF₂ nanoparticle in the bulk glass–ceramic as a dark spot

Fig. 1 a High resolution TEM bright field image of sol–gel glass–ceramic containing a PbF₂ nanocrystal and EDS spectrum of **b** an individual nanocrystal revealing the presence of lead fluoride and **c** the glassy matrix

in the silica matrix. Moreover EDS spectra of the individual nanocrystal and the glassy matrix are presented in Fig. 1b, c, respectively. Intense lead peaks are clearly detected in the EDS spectrum from the single nanoparticle. The glassy matrix environment of the nanoparticle gives rise to weak Si and O signals. On the other hand the EDS spectrum of the amorphous environment shows only Si and O peaks. This confirms the effective partition of the PbF_2 nanocrystals embedded in the silica network. Copper peaks are present due to the carbon grid used.

X-ray powder diffraction (XRD) patterns of the samples were recorded with a Philips X'Pert Pro diffractometer equipped with a primary monochromator, $\text{Cu K}_{\alpha 1,2}$ radiation, and an X'Celerator detector. The XRD patterns were collected with a step of 0.016° in the 2θ angular range 15° – 90° and acquisition time of 2 h. Furthermore, the patterns were corrected by using LaB_6 .

XRD patterns in Fig. 2 show the dependence of the nanocrystals precipitation in YET and YHT samples on heat treatment temperature and time. These patterns show only broad diffraction peaks, characteristics of the amorphous state, after heat treated at low temperatures, about 250°C . However, when the heat treatment temperature was increased to 300 – 400°C , reflections peaks corresponding to cubic lead fluoride crystalline phase (JCPDS 89-5516) are observed, confirming the precipitation of these nanocrystals during thermal treatment process. Nanocrystals mean diameters were calculated from XRD patterns by using Scherrer's equation, $D = 0.9\lambda/\beta\cos\theta$, where D is the crystal diameter, λ the X-ray wavelength, θ the diffraction angle and β the full-width at half-maximum (FWHM) of the diffraction peak. The obtained values for YET and YHT samples are shown in Table 1, presenting values in the range from 6 to 25 nm. An enlargement of the mean size with temperature and time of heat-treatment is observed which indicates that both, the average nanocrystal size and the volume fraction crystallized, are found to increase, as can be seen from Fig. 2. In previous work we obtained similar mean size values for single Er^{3+} (i.e. 21.2 nm) and Yb^{3+} - Er^{3+} (i.e. 19.0 nm) co-doped samples heat treated at 400°C [20]. Thus, we concluded that the hindering of the growth of the PbF_2 was related to the increase of dopant concentration. This can be due to the accumulation of the RE ions at the PbF_2 crystallite surface, which provides an additional barrier for atomic diffusion of crystal growth [16].

3.2 Up-conversion luminescence in NGC

Luminescence measurements were obtained by exciting the samples with light from a laser diode at 980 nm with pump power up to 200 mW, focused with a $4\times$ microscope objective lens, and detected through a 0.25 m

Fig. 2 X-ray diffraction patterns of bulk nano-glass-ceramics comprising Yb^{3+} - Er^{3+} - Tm^{3+} (YET) and Yb^{3+} - Ho^{3+} - Tm^{3+} (YHT) co-doped PbF_2 nanocrystals heat treated at indicated temperatures

Table 1 Nanocrystals sizes calculated by Scherrer equation

	YET D (nm)	YHT D (nm)
300°C	6.6	6.2
350°C	6.8	7.8
400°C	17.8	19.2
400°C 4 h	24.4	21.8

monochromator equipped with a photomultiplier. All spectra were collected at room temperature and corrected by the instrumental response.

Up-conversion emission spectra of YET and YHT NGC, heat treated at 400°C during 4 h, under infrared laser excitation at 980 nm at 200 mW, are shown in Fig. 3. In both samples, blue, green and red simultaneous emissions can be seen by the naked eye with main emission peaks at around 410–475, 520–550 and 625–700 nm, respectively,

Fig. 3 Up-conversion emission spectra of bulk nano-glass-ceramics comprising Yb^{3+} - Er^{3+} - Tm^{3+} (YET) and Yb^{3+} - Ho^{3+} - Tm^{3+} (YHT) co-doped PbF_2 nanocrystals heat treated at 400 °C during 4 h pumping at 980 nm and 200 mW

together with UV emissions from upper lying levels at around 360 nm. The sharp and well resolved Stark structure of the emission peaks indicates the incorporation of RE ions into the precipitated nanocrystals during ceramming process, taking to a high effective doping level inside these nanocrystals. Thus, the shortening of the mean distance among RE ions favours the energy transfer processes. These luminescence peaks have been assigned to transitions of Er^{3+} , Tm^{3+} and Ho^{3+} ions in YET and YHT samples in agreement with the energy level diagrams presented in Fig. 4. It is worth mentioning that the RE luminescence observed came mainly from those ions residing inside the nanocrystals and therefore shielded from OH groups located in the remaining glassy matrix or near the nanocrystals.

As it is well known, the 980 nm pump mainly excites Yb^{3+} ions due to their high absorption cross section at this wavelength. Subsequently, energy transfer processes to Er^{3+} , Ho^{3+} and Tm^{3+} ions take place, giving rise to the observed UV–visible emissions via different up-conversion mechanisms, depicted in Fig. 4 [21, 22]. It is noticeable that the presence of high energy UV and blue emissions, at around 360, 410 and 475 nm, is indicative of very low phonon energy environments (about 250 cm^{-1}) that prevent non-radiative de-excitation [23] in the precipitated PbF_2 nanocrystals.

In YET samples there are also energy transfer processes among Tm^{3+} and Er^{3+} ions via cross-relaxation channels [23, 24], indicated by the dot lines (1) and (2) in Fig. 4. In this sense, the red emission at 660 nm, mainly due to the $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ of Er^{3+} ions, is enhanced by energy transfer processes from Tm^{3+} ions, see Fig. 4.

Fig. 4 Energy level diagrams of Yb^{3+} - Er^{3+} - Tm^{3+} and Yb^{3+} - Ho^{3+} - Tm^{3+} . Main up-conversion emissions are indicated by solid arrows and energy transfer mechanisms by dashed arrows

In YHT samples, blue emission is enhanced with respect to the green and red ones, as compared with YET samples. This will result in overall emission closer to white light, as it will be discussed further. Different energy transfer processes between Tm^{3+} and Ho^{3+} ions, see dot lines labelled by (3) and (4) in Fig. 4, enhance the red emission at 650 nm.

On the other hand, Fig. 5 shows up-conversion emissions by varying pump power, from 25 to 200 mW in YET and YHT NGC. In both samples, emission coming from upper lying levels show strong dependence on pump power, giving rise to an appreciable change in the relative intensities among up-conversion bands. In this sense, UV and blue emissions associated to three photon processes (see energy level diagram in Fig. 4) are enhanced stronger than two-photon up-conversion emissions in the green and red range of the spectrum. These well-known pump power dependences have been already evidenced in some of our previous works [25–28] revealing the number of photons involved in the processes. In this sense, insets of Fig. 5 show log–log plots of intensity versus pump power of blue

Fig. 5 Up-conversion emission spectra of bulk nano-glass-ceramics comprising $\text{Yb}^{3+}\text{-Er}^{3+}\text{-Tm}^{3+}$ (YET) and $\text{Yb}^{3+}\text{-Ho}^{3+}\text{-Tm}^{3+}$ (YHT) co-doped PbF_2 nanocrystals heat treated at 400 °C during 4 h pumping at 980 nm from 25 to 200 mW. Spectra have been normalized to the maximum of the 660 nm emission band. Insets show log–log plots of up-conversion intensity versus pump power

and green up-conversion emissions of Tm^{3+} , Er^{3+} and Ho^{3+} , respectively. From these plots, the green up-conversion emissions at around 540 nm present slopes of 1.8 while for the blue up-conversion emission a slope of 2.2 is obtained. It should be mentioned that the dependence of the up-conversion emission intensity on the pump power is often expected to be $I_{\text{up}} \propto P^n$, where n is the number of photons involved; this behaviour corresponds to low pump power density. Deviations of this behaviour have been observed under high pump power density, when the depopulation of the excited levels by up-conversion processes is comparable to the radiative decay rate. In these conditions the observed behaviour can be fitted by considering powers lower than n [29–31].

Moreover, the green to red ratio is also varied due to different population mechanisms of the emitting levels [32,

Fig. 6 CIE standard chromaticity diagram showing the up-conversion emissions of YET (circles) and YHT (squares) NGC heat treated at 400 °C during 4 h under excitation at 980 nm for different pump power. Black symbols correspond to maximum excitation pump power (200 mW)

33]. As a consequence of these different dependences, the overall emitting colour can be tuned as a function of pump power. This change will be useful for colour tuneable up-conversion phosphor and will be analyzed below.

All chromaticity visible to the human eye after correction to sensitivity of blue, green and red receptors of the eye can be represented by the respective point in the CIE (Comision Internationale d'Eclairage) standard chromaticity diagram [34]. In this diagram the edge corresponds to monochromatic light while white light appears in the centre. Thus, the emitting colour is characterized by two coordinates (x ; y), corresponding to a point in the CIE diagram, which are the respective projective coordinates of the total visible luminescence. In this sense, the colour coordinates obtained from overall up-conversion emitted by YET and YHT NGC heat treated at 400 °C during 4 h are presented in Fig. 6. It can be seen how colour gradually changes in YET and YHT samples with increasing pump power from 25 to 200 mW, showing up the tuneability of emission colour from the reddish part to the centre of the diagram. Corresponding x and y coordinates are (0.36; 0.46) and (0.33; 0.37) for YET and YHT samples at 200 mW, respectively. It is important to notice that the tuneability in both samples is achieved only by varying pump power, which changes the up-conversion emission ratios, without modifying the composition of the samples.

4 Conclusions

$\text{Yb}^{3+}\text{-Er}^{3+}\text{-Tm}^{3+}$, $\text{Yb}^{3+}\text{-Ho}^{3+}\text{-Tm}^{3+}$ co-doped PbF_2 spherical nanocrystals dissolved in silica glass have been

prepared using room temperature sol–gel processing of precursor glass, and subsequent drying and heat-treatment steps. High resolution TEM, EDS and XRD studies confirm the precipitation of nanocrystals. Moreover the high Stark splitting in up-conversion luminescence spectra indicate that most of co-dopants ions are partitioned into the nanocrystals, taking to high effective doping level inside these nanocrystals and therefore efficient energy transfer processes. Combining the blue emission band of Tm^{3+} , green emission bands of Er^{3+} or Ho^{3+} , and red emission bands of Er^{3+} or Tm^{3+} , respectively, colour tuneability of up-conversion luminescence has been achieved by varying pump power and ratio between co-dopants, and in particular white up-conversion luminescence has been generated.

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