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Compositional dependence of up-conversion process in Tm^{3+}–Yb^{3+} codoped oxyfluoride glasses and glass-ceramics

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Abstract

Up-conversion of infrared radiation to the visible and ultraviolet regions in PbF_2–GeO_2–Al_2O_3–Tm_2O_3–Yb_2O_3 oxyfluoride glasses and glass ceramics was obtained, exciting at 1.0 μm with a diode laser at room temperature. Transparent films and microspheres were prepared by a modified spin-coating technique. The effect of host composition on the up-conversion luminescence was studied in order to improve the ultraviolet radiation generation. In the glass samples, the Tm^{3+} blue (4786 Å) and red (6500 Å) visible emissions got more intense as the PbF_2 content was increased. The main Tm^{3+} blue emission (4786 Å, $^1G_4 \rightarrow {}^3H_6$), results from a three-photon process. A second blue emission (4500 Å, $^1D_2 \rightarrow {}^3F_4$), followed by a UV emission (3650 and 3850 Å, $^1D_2 \rightarrow {}^3H_6$) was observed in the ($2PbF_2/GeO_2$) glass ceramics, in a narrow range of Al_2O_3 concentration. The $^1D_2$ level of the Tm^{3+} ions is populated by a fourth photon from the cross-relaxation process given by ($^3F_4$,$^1G_4$)→($^3H_6$,$^1D_2$). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Amorphous materials; Electron–phonon interactions; Optical properties; Luminescence

1. Introduction

The study of luminescence and up-conversion in glass and glass ceramics is very interesting as regards conversion of infrared radiation into visible light. Up-conversion by APTE (addition de photons par transferts d'énergie) was first studied by Auzel et al. for IR→visible light in opaque glass ceramics [1]. It involves non-resonant transfers that depend highly on the phonon cut-off frequency, although the microstructure of the host itself has a very important role. Our group has been studying this process in rare-earth doped glassy materials for a long time [2–5].

Oxyfluoride glasses are one of the most attractive hosts, because they provide a low phonon energy environment for active rare-earth ions in a material very stable against spontaneous devitrification [6].

In this work we present an oxifluoride glass and glass ceramic doped with Yb^{3+} and Tm^{3+} ions. They were obtained in two different forms (films and microspheres) by a modified spin-coating technique [7], and the compositional dependence with the IR conversion to visible light and IR→UV conversion are reported.

2. Experimental methods

Vitreous samples were prepared using optical grade raw materials, consisting of 0.05 mol% of Tm_2O_3, 4.0 mol% of Yb_2O_3, 0 mol%$\leq Al_2O_3 \leq$5 mol% and PbF_2/GeO_2 in such an amount that $1.5 \leq (PbF_2/GeO_2) \leq 2.0$. Batches of 5 g were thoroughly mixed, put in a Pt:5%Au covered crucible and then melted in a resistive furnace at 950°C for 1.5 h. These samples were called the PGETYA series.

The melt was quenched on a soda-lime glass substrate plate coupled to a spin-on, rotating at 600–6000 rpm, using a modified spin-coating technique [8]. The glasses and glass ceramics were obtained as microspheres and transparent thick films between 30 and 150 μm thickness. The diameters and the areas of microspheres and thick films depends on the height of the melt drops and the rotation speed. They were annealed at the glass transition temperature (T_g) for 5 h to improve the mechanical properties.

The glass ceramics were obtained by annealing at the onset crystallisation temperature (T_x) for 1.0 h in order to grow microcrystallites. The thermoanalytical temperatures were obtained by DSC curves of 100–150 mesh powdered samples in hermetically closed pans under N_2 continuous flow. Heating rate was 10°C/min using a DSC DuPont 2010 TA instrument.

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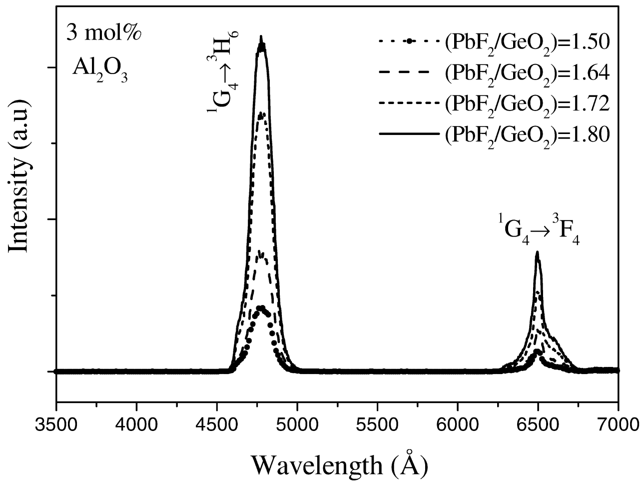

Fig. 1. Up-conversion emission spectra of Tm^{3+}–Yb^{3+} codoped PGETYA glasses, containing 3 mol% of Al_2O_3, as a function of PbF_2/GeO_2 ratio.

For fluorescence measurements, 100–150 mesh powdered glasses and glass ceramics were homogeneously spread on an inactive Scotch tape substrate. The excited areas were 3.0 cm^2. The IR→UV up-conversion emission spectra were measured with a Jobin-Yvon Ramanor U-1000 double monochromator spectrophotometer, by exciting the samples with a continuous 1.0-μm infrared diode laser at room temperature. The signals were detected by an RCA C31034-RF photomultiplier.

3. Results and discussion

Fig. 1 shows the up-conversion emission spectra (1.0 μm excitation) of PGETYA glasses as a function of PbF_2/GeO_2 concentration ratio. For that, we have fixed the Al_2O_3 concentration at 3 mol%, an intermediate value between the ranges used in this work. We observed that by increasing the PbF_2 content, the intensity of blue ($^1G_4 \rightarrow {}^3H_6$) and red ($^1G_4 \rightarrow {}^3F_4$) visible luminescence of the Tm^{3+} ions is improved. The increase of this ratio is limited to the glassy domain of the material, to avoid the development of the single β-PbF_2 phase, as identified in a previous work [8]. In the present case, transparent glass ceramics may be obtained from the starting glass, with a controlled thermal treatment, leading to a crystalline phase with microcrystals smaller than 1/10 of the wavelength

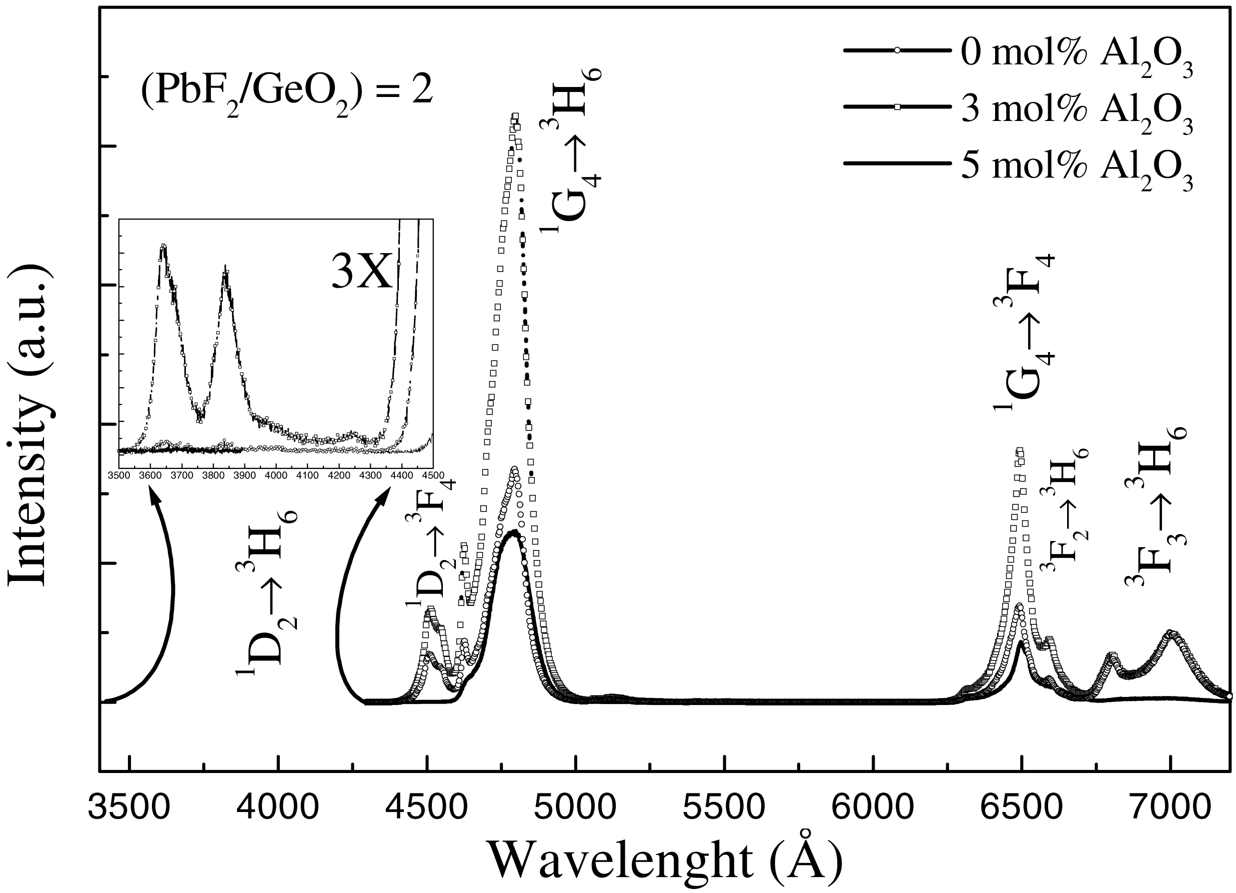

Fig. 2. Up-conversion emission of PGETYA glass ceramics as a function of the Al_2O_3 contents, noting the UV region (zoomed 3× in the 3500–4500-Å range).

[9]. It is not possible to control this crystallisation for values of PbF_2/GeO_2 ratio greater than 2.

The up-conversion emission of Yb^{3+}–Tm^{3+} PGETYA glass-ceramics is shown in Fig. 2 as a function of the Al_2O_3 content. The greatest possible $2PbF_2/GeO_2$ ratio was used to control the glass devitrification.

We can observed the blue Tm^{3+} emissions at 4786 Å ($^1G_4 \rightarrow ^3H_6$) and 4500 Å ($^1D_2 \rightarrow ^3F_4$), the intensities of which depend directly on Al_2O_3 content. We are interested in monitoring the $^1D_2 \rightarrow ^3F_4$ transition intensity, because the UV emission comes from the same $^1D_2$ level ($^1D_2 \rightarrow ^3H_6$ transition).

The up-conversion process was optimised in PGETYA glass ceramics containing 3 mol% of Al_2O_3, the UV emission of which is 24 times more intense than in the absence of Al_2O_3. When the content of Al_2O_3 was increased to 5 mol%, the UV emission was completely suppressed. This fact indicates that UV emission is much affected by the Al_2O_3 content, since the energy transfer involves many non-resonant steps, and the phonon cut-off frequency of the host becomes very important, which may explain the role of the Al^{3+} ions.

The same figure shows the emission up-conversion spectra marking the transition $^1D_2 \rightarrow ^3H_6$ zoomed 3× in the UV region (3650–3850 Å) as a function of the Al_2O_3 content.

It is clear that these significant changes in the intensities of blue, red and UV transitions depend strongly on the phonon cut-off frequency of these materials since the energy transfer process between the Yb^{3+} and Tm^{3+} ions is not completely resonant. The transitions involved in the up-conversion IR→Vis and IR→UV are shown in Fig. 3.

According to Tm^{3+}–Yb^{3+} level diagrams, the blue emission of Tm^{3+} ($^1G_4 \rightarrow ^3H_6$, 4786 Å) occurs by APTE by a three-photon process, as shown in Fig. 3. The transition at 4500 Å depends on the population of $^1D_2$ (transition $^1D_2 \rightarrow ^3F_4$). The emission $^1D_2$ to the ground state ($^3H_6$) is assigned to the UV (3650 and 3850 Å) emission. For these transitions the $^1D_2$ level may be populated via a fourth photon from the $^1G_4$ level provided by the cross-relaxation process by another Tm^{3+} ion ($^3F_4 \rightarrow ^3H_6$). In this case, the $^3F_4$ level is populated after the $^1G_4 \rightarrow ^3F_4$ transition (red emission) whose intensity is in agreement with the UV emission intensity, as shown in Fig. 2. This process justifies the sixth-order dependency over the entire pump intensity range, since the fourth photon produced in this way has a cubic dependency on the excitation power (Fig. 4).

The $^1D_2$ level could also be populated by a $(^1G_4,^1G_4) \rightarrow (^3F_2,^1D_2)$ cross-relaxation process, but this process seems not to be in agreement with the $^3F_3 \rightarrow ^3H_6$ transition intensity behavior, as shown in Fig. 2. We have analysed the $^3F_3 \rightarrow ^3H_6$ transition, since the $^3F_2 \rightarrow ^3F_3$ non-radiative transition probability is very high, and the $^3F_2 \rightarrow ^3H_6$ transition is overlapped by the $^1G_4 \rightarrow ^3F_4$ transition, as shown in the same figure.

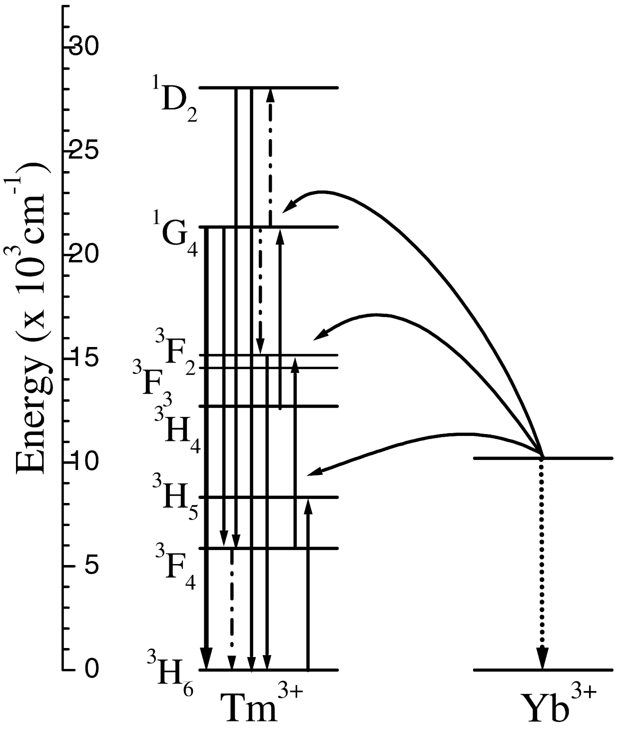

Fig. 3. Energy level diagram of Tm^{3+} and Yb^{3+} ions and the proposed up-conversion mechanism to the UV radiation generation in the 3 mol% Al_2O_3 PGETYA glass ceramic.

The intensity of the blue up-conversion emission bands at 4786 and 4500 Å from codoped glass ceramics as a function of the intensity of the IR excitation, shown in Fig. 4, is in agreement with the proposed mechanism. The experimental data fitted straight lines. The blue emission at 4786 Å shows an approximately cubic dependence and the blue at 4500 Å had approximately a sixth-order dependency on excitation light intensity.

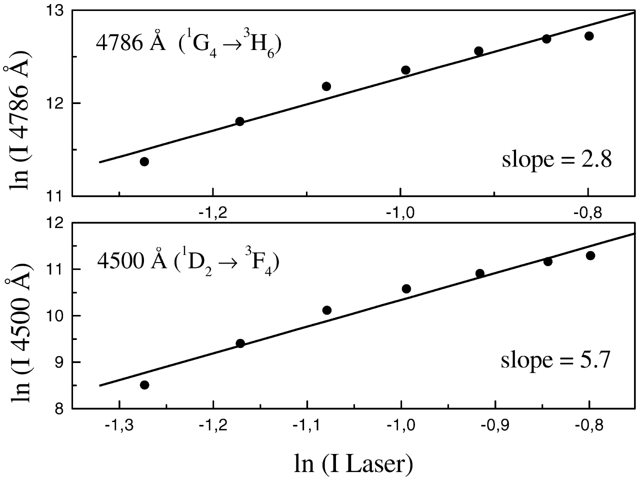

Fig. 4. Up-convertion intensities as a function of the excitation power at 1.0 μm. Solid lines correspond to the fit to linear dependence.

4. Conclusions

We observed infrared up-conversion to the visible and near ultraviolet region, in PbF_2–GeO_2–Al_2O_3–Tm_2O_3–Yb_2O_3 glasses and glass ceramics, using a 1.0 μm excitation diode laser. The material was prepared in two different forms, resulting in transparent films and microspheres, prepared by a modified spin-coating technique.

The effect of compositional dependence of the host on the up-conversion luminescence was studied, in order to improve the ultraviolet radiation generation under infrared excitation. We observed that by increasing the PbF_2 content, the intensity of blue and red visible luminescence was improved in the oxyfluoride glass samples, but the UV emission was observed only in oxyfluoride glass ceramics in a narrow range of Al_2O_3 concentration, in addition to the blue emission coming from the $^1D_2$ level. In this way, the optical material was optimised to increase the UV signal.

Although the main blue emission of Tm^{3+} (4786 Å, $^1G_4 \rightarrow ^3H_6$) results from a three-photon process, a secondary four-photon blue emission appears (4500 Å, $^1D_2 \rightarrow ^3F_4$) in the glass ceramics ((2PbF_2/GeO_2)–3 mol%Al_2O_3) followed by the ultraviolet emission at 3650 and 3850 Å from the $^1D_2$ level to the ground state $^3H_6$. The $^1D_2$ level is populated by a fourth photon from the cross-relaxation $(^3F_4, ^1G_4) \rightarrow (^3H_6, ^1D_2)$.

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