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RESEARCH ARTICLE

Photonic properties of novel Yb^{3+} doped germanium-lead oxyfluoride glass-ceramics for laser cooling applications

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Abstract In recent years, our research group has developed and studied new rare-earth doped materials for the promising technology of solid-state laser cooling, which is based on anti-stokes fluorescence. To the best of our knowledge, our group is the only one in Canada leading the research into the properties of nanoparticles, glasses and glass-ceramics for optical refrigeration applications. In the present work, optical properties of $50GeO_2$-$30PbF_2$-18PbO-$2YbF_3$ glass-ceramics for laser cooling are presented and discussed as a function of crystallization temperature. Spectroscopic results show that samples have near infrared photoluminescence emission due to the $^2F_{5/2} - ^2F_{7/2}$ Yb^{3+} transition, centered at ~1016 nm with an excitation wavelength of 920 nm or 1011 nm, and the highest photoluminescence emission efficiency occurs for heat-treatment for 5 h at 350°C. The internal photoluminescence quantum yield varies between 99% and 80%, depending on the temperature of heat-treatment, being the most efficient under 1011 nm excitation. The $^2F_{5/2}$ lifetime increases from 1.472 to 1.970 ms for heat treatments at 330°C to 350°C, respectively, due to energy trapping and the low phonon energy of the nanocrystals. The sample temperature dependence was measured with a fiber Bragg grating sensor, as a function of input pump laser wavelength and processing temperature. These measurements show that the heating process approaches near zero for an excitation wavelength between 1020 and 1030 nm, which is an indication that phonons are removed effectivelly from the glass-ceramic materials, and they can be used for optical laser cooling applications. On the other hand, the temperature increase as a function of input laser power into samples remains constant between 920 and 980 nm wavelength excitation, a temperature variation of 36 K/W (temperature of 58°C/W) was attained under excitation at 950 nm, showing a possible use for biomedical applications to be explored.

Keywords optical refrigeration, oxyfluoride glass-ceramics, Yb^{3+} doping, quantum yield, infrared emission, lifetime

1 Introduction

The promising technology of solid state laser cooling which is based on anti-Stokes fluorescence is being explored for cooling of small devices and samples to low temperatures. In this process heat is removed through the annihilation of the lattice vibrations. Optical cooling is achieved when a coherent laser source of low-entropy light with narrow spectral bandwidth and high directionality is converted into a broadband, isotropic luminescence, increasing entropy of the system in the process, even in the presence of local cooling. This phenomenon was first proposed by Pringsheim in 1929 [1] and predicted with rare-earth dopants by Kastler in 1950 [2] and Yatsiv in 1961 [3], but was demonstrated only recently by Epstein et al. [4] in low phonon energy fluoride glasses. Since then, there has been extensive research to improve the efficiency of the phenomenon to allow commercial use of this cooling effect.

The cooling power, or the power which is extracted from a sample by optical means excluding blackbody radiation

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is given by the difference between the optical power which leaves the sample and the optical power that enters the sample, and can be expressed by Eq. (1) [5], without considering radiation trapping or reabsorption, or including these in the quantum efficiency.

$$P_{\mathrm{cool}}(\lambda_{\mathrm{P}}) = P_{\mathrm{abs}}(\lambda_{\mathrm{P}})\left(\eta\frac{\alpha_{\mathrm{r}}(\lambda_{\mathrm{P}})}{\alpha_{\mathrm{r}}(\lambda_{\mathrm{P}})+\alpha_{\mathrm{b}}}\frac{\lambda_{\mathrm{P}}}{\lambda_{\mathrm{f}}}-1\right), \quad (1)$$

where P_{abs}, α_{r}, η, α_{b}, λ_{p} and λ_{f} are respectively, the absorbed optical power, resonant absorption coefficient, quantum efficiency, background absorption coefficient, the pump wavelength and the emitted fluorescence wavelength.

To date, laser cooling has been observed in a wide variety of glass and crystalline hosts, doped with trivalent rare earth ions of Yb^{3+}, Tm^{3+} and Er^{3+} due to their suitable energy spacing and high fluorescence external quantum efficiency [6]. Semiconductors have also been investigated because of their potential to achieve lower temperatures ($<$ 20 K) with higher cooling capacity. However, research in this area is still at an early stage [7,8].

The advanced photonics concepts laboratory (FABULAS Laboratory) at Ecole Polytechnique Montreal, is the only one in Canada currently working on laser cooling of solids. The use of a fiber Bragg grating (FBG) to measures the surface temperature of the cooled sample in air by contact for laser cooling measurements was originally proposed [9] and demonstrated [10] by our group. Recently a temperature drop of 8.8 K from the chamber temperature was observed in the Yb^{3+}:YAG crystal in air when pumped with 4.2 W at 1029 nm, close to 8.9 K observed in vacuum [11]. Also the laser cooling process with anti-Stokes fluorescence in Yb^{3+}:YAG samples with different ion concentrations, shapes and sizes ranging from centimeter to the nanometer scale were investigated [12]. From the simulations it was concluded that ion concentration influences the cooling process significantly. In 2012 theoretical schemes for laser cooling with nanoparticles was proposed [13]. It was shown that specially designed samples based on nanoparticles, for example colloidal PbSe quantum dots (QDs) doped in a glass host can be used to improve the process of laser cooling of solids. The discrete atomic-like energy levels of QDs permit us to consider QDs as artificiais atoms, which can be used for laser cooling. Anti-Stokes fluorescence which is a result of electron-hole recombination between the lowest electron state $1S_{\mathrm{e}}$ and hole state $1S_{\mathrm{h}}$ levels of a QD provided by the pump in the long wavelength tail of the absorption spectrum can remove energy from the sample.

Oxyfluoride glass-ceramics to be used for laser cooling were firstly proposed by Nemova and Kashyap [14], and glass-ceramics containing PbF_2 nanocrystals were also investigated experimentally by members of our group through measuring the temperature changes as a function of the pump wavelength [15]. The results showed that glass-ceramics have a higher cooling figure-of-merit than their glassy counterparts. The calorimetric results on the quantum efficiency of the samples are in line with the results obtained using an integrating sphere, showing an above 90% quantum efficiency for all the samples measured. It has also been shown for the first time, that an optically-cooled sample can be an accurate reference for quantum efficiency measurements. The low phonon energy of these materials, in addition to their low background absorption and high photoluminescence quantum yield (PLQY) makes them an ideal candidate for laser cooling applications [16]. The optical and photoluminescence properties of oxyfluoride glasses and ultra-transparent glass-ceramics (SiO_2-Al_2O_3-CdF_2-PbF_2-YbF_3) were investigated in 2016 [17]. All the samples showed the PLQY close to unity (100%). The detailed study on those samples with different Yb^{3+} concentrations showed that the 2 mol% Yb^{3+} doped oxyfluoride glass with its high PLQY, its low maximum phonon energy and low background absorption is the most promising candidate for laser cooling and solid-state laser applications besides serving as a reference to calibrate the instruments for PLQY measurements [18]. Pump power dependence studies have revealed a linear increase in the PLQY and a decrease in the lifetime with increasing pump power. Also a decrease in lifetime was observed for the Yb^{3+} excited level with increasing Yb^{3+} concentration. Taking advantage of both the ability of the lead-cadmium oxyfluoride glass system to form transparent and durable nano glass-ceramics with promising optical properties, a new fiber material for laser cooling applications was proposed [19]. Theoretical as well as experimental calculations showed that optical refrigeration would be achievable from these samples provided that 95% (segregation ratio) of Yb^{3+} ions are incorporated into the fluoride nanocrystals.

Highly purified rare earth doped glass ceramics are currently desirable, especially combining properties of glasses and crystals focusing on removing phonon energy under laser excitation to eliminate any vibrations and noise of traditional cooling systems. The current works are focused on obtaining higher purity SiO_2-Al_2O_3-CdF_2-PbF_2-YbF_3 glass-ceramics by the removal of contamination of other lanthanide ions which have up-conversion process and which compete with the cooling process. New high purity glass-ceramics samples are under development at the Centre of Optics, Photonique and Lasers at the Université of Laval; achieving cooling in these new glass should pave the way towards massive applications of optical refrigeration. Besides that, glasses and glass-ceramics of the GeO_2-PbF_2-PbO-YbF_3 system are under progress in our research group which can be used for optical refrigeration and biomedical applications depending on its structural and optical properties, Yb^{3+} doping levels, and heat-treatments. In the current paper, we present the latest results on optical properties of $50GeO_2$-$30PbF_2$-18PbO-$2YbF_3$ glass-ceramics, focusing on laser cooling applications. A fiber Bragg grating, which is an excellent sensor for contact temperature measurement in laser cooling experiments [10], is used to assess the potential of optical cooling of glass-ceramics samples by measuring the temperature changes as a function of pump wavelength. A best heat-treatment temperature and excitation wavelength were determined through this study.

2 Experimental

Yb^{3+}-doped glasses of nominal composition: $50GeO_2 + 30PbF_2 + 18PbO + 2YbF_3$ (named as GPFYb2.00), were prepared by the conventional melt-quenching process. High purity precursors were mixed thoroughly in an agate mortar and placed in a platinum crucible within a glove box with a controlled dry atmosphere. The powders were dried under a pure N_2 flow at 460°C for 12 h to eliminate hydroxyl groups, followed by melting at 900°C for 1 h in a resistive furnace integrated in the glove box, under N_2 flow. The liquid was cooled in a stainless-steel mold preheated near the glass-transition temperature (T_g, onset is ~ 336°C), and annealed at the same temperature (360°C) for 3 hours to remove residual internal stress and/or strain in the glasses. The glasses were cooled down, samples were cut and polished optically, and heated to a temperature high enough to stimulate crystals to nucleate througout the glass. All of the glass-ceramic (GC) samples were thus obtained by heat-treatment at 330°C, 350°C and 370°C for 5 hours, in which nanocrystals were formed in the glasses.

Ultraviolet-visible-near-infrared (UV-Vis-NIR) transmission spectra were recorded on a Cary 5000 (Varian) double-beam spectrophotometer on ~2.5 mm-thick samples, using a resolution of 2.0 nm.

The linear refractive index of the samples was measured by using the M-lines prism-coupling technique (Metricon 2010) at 632.8 and 1308.2 nm wavelengths.

The photoluminescence emission (PL) and quantum yield (QY) of the samples, with dimensions of ~10 mm × 2 mm × 2 mm, were measured by pumping at 920 and 1011 nm with a Ti: Sapphire laser (Spectra-Physics 3900S, pumped by Millennia 5SJSPG with 5 W), collecting the emitted light from an integrating sphere (2″) (Thorlabs IS200-4) coupled to a multimode optical fiber (ThorLabs M75L01, 200 μm, 0.39 NA) to an Ando AQ6317B optical spectrum analyzer (OSA) operating in the wavelength range of 800 – 1600 nm.

QY studies were performed by exciting the samples at 920 and 1011 nm wavelengths from a Ti: Sapphire laser. The excitation beam was focused at the entrance port of the integrating sphere and directed to the center of the sphere. The sample was placed inside of the sphere in a position which received excitation reflected by the internal walls of integrating sphere (Indirect excitation). The diffused light from the sphere walls was collected by a 200 μm diameter multimode fiber and detected by the OSA with resolution of 0.1 nm for PL emission spectra. All the measurements were performed at room temperature.

PL decay curves were recorded with a resolution of 10 μs by using a photodiode (Thorlabs SM05PD1B). The signal was amplified by a bench top transimpedance amplifier (Thorlabs PDA200C) and read with a digital storage oscilloscope (Tektronix TDS2012C 100 MHz 2 GS/s). The excitation signal was modulated mechanically by a chopper (ThorLabs MC100A) with two slot blades and at a frequency of 20.0 Hz. An edge filter was used to block the light at the pump wavelength. No fluorencence was detected from the edge filter. The detected PL decay signal was thus only from our samples.

Finally, temperature measurements were performed using a direct contact FBG technique, as reported in previous works [11,15]. To this, we used a fiber laser operating at 1536 nm and the reflected signal was detected and analyzed by an OBR4600 instrument (Luna Technologies).

3 Results and discussion

Firstly, the glass transition (T_g, onset of ~330°C) and crystallization temperatures (T_x, of ~506°C) and thermal stability against crystallization of the GPFYb2.00 glass were previously determined by thermal analysis using differential scanning calorimetric (DSC) measurements [20]. The thermal stability against crystallization parameter (K_{ts}) of the glass which was monitored from the semiempirical formula proposed by Hruby, which $K_{st} = T_x - T_g$, ~176°C showing high stability of the investigated matrix. Based on this, all samples were annealed at 330°C, 350°C and 370°C for 5 hours to obtain transparent glass-ceramics.

The UV-Vis-NIR transmission spectra were collected from 300 to 1200 nm to evaluate the optical quality of the glass-ceramic samples, as presented in Fig. 1(a). From 300 to 350 nm a high absorption was observed in all samples due to bandgap absorption. Different transmittance values were noted between 350 and 800 nm, which were related to optical inhomogeneity of the glass: *striae* in the glasses leading to local variations in the refractive index, and crystallization process forming nanocrystals that scatter visible light mainly for the GC-370°C/5 h sample. An intense absorption band was observed from 900 to 1025 nm due to the Yb^{3+} $^2F_{7/2} - {}^2F_{5/2}$ transition, that reduces slightly by increasing the heat-treatment temperature.

Figure 1(b) shows the absorption coefficient for all samples which changes with increasing heat-treatment temperature. The spectral shape shows significant changes at GC-350°C/5 h when compared to GC-330°C/5 h, probably due to the crystallization process occurring more effectively at GC-350°C/5 h and the increased quantity of nanocrystals affecting the absorption band of Yb^{3+} ions, illustrating a different local structure around Yb^{3+} ions.

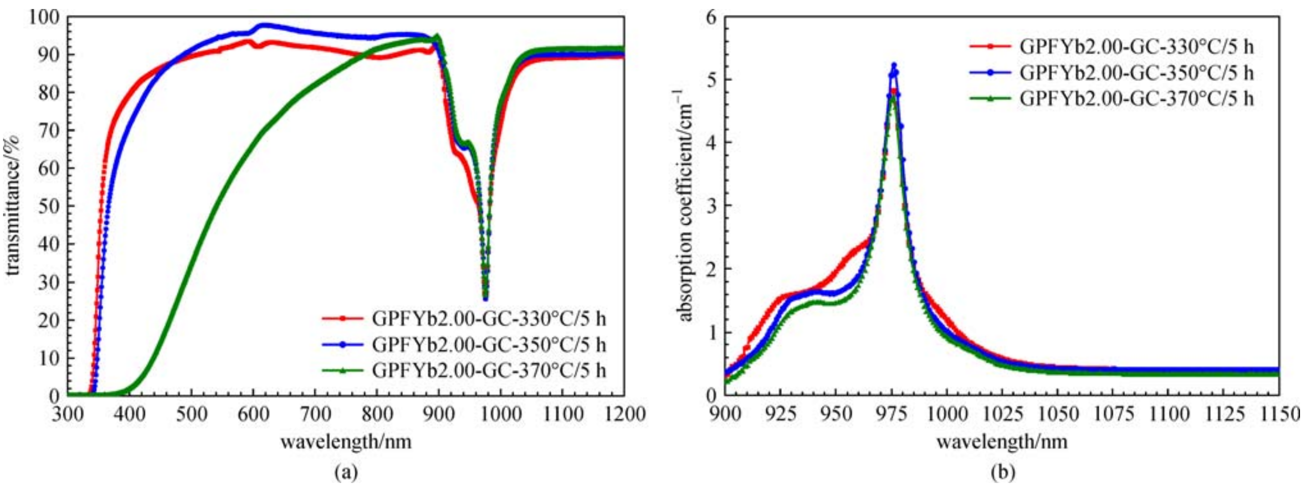

Fig. 1 (a) Transmission spectra in the UV-Vis-NIR regions, and (b) absorption coefficient from 900 to 1150 nm of all glass-ceramics with different heat-treatment temperature. The length of samples was 2.5 mm

Note in Fig. 1(a) that the sample heat treated at 330°C exhibits a spectrum with higher transmittance between 350 and 450 nm than the other samples. Increasing heat-treatment to 350°C reduces the transmission slightly in this region, but the greatest transmission reduction occurs for heat-treatment at 370°C most probably due to the nanocrystal growth. Previous studies on the influence of the annealing temperature on the glass-ceramics characteristics of the composition GeO_2–PbO–PbF_2: ErF shows that for a heat treatment over 365°C for 10 h, all of the PbF_2 has crystallized and all the Er^{3+} ions were incorporated into the crystallites [21].

Based on the results illustrated in Fig. 1, we can suppose that heat-treatment at 350°C will be the best to have a glass-ceramic containing Yb^{3+} embedded in nanocrystals while maintaining high transparency in the visible region with high optical quality. The transparency of these glass-ceramics is due to the smallness of the crystallites with respect to the wavelength of visible light [22].

Another important parameter is the refractive index and the results obtained by m-lines spectroscopy at 632.8 nm and at 1308.2 nm wavelengths, are presented in Table 1 for all samples.

As expected, the refractive index values at 632.8 nm increase with increasing heat-treatment because the crystallization process becomes faster at higher temperatures. The values vary from 1.9768 for heat-treatment at 330°C to 1.9959 for heat-treatment at 370°C (TE mode). On the other hand, the refractive index measured at 1308.2 nm are lower, but also increase from 1.9066 to 1.9323 (TE mode) when heat-treatment is increased. The birefringence can be considered to be low. We observed that refractive index variation between TE and TM modes was between 0.0013 and 0.0018 for 632.8 nm wavelength and between 0.0031 and 0.0083 for 1308.2 nm wavelength. It appears that heat-treatment did not influence significantly the Δn values at each wavelength. Finally, we could observe guiding modes on all the glass-ceramic surfaces. M-lines spectroscopy technique can determine the refractive index in a small area only on the material's surface, and cannot provide a mean refractive value for each sample neither the variation between surface and the center of the sample, and a detailed future work will be required to well characterize these waveguiding modes.

Figures 2(a) and 2(b) shows the PL emission spectra of glass-ceramics heat-treated at different temperatures under excitation at 920 and 1011 nm wavelengths, respectively. These spectra were collected using an integrating sphere to compare their intensity and determine the quantum yield. The laser power inside of integrating sphere was 525($\pm$10) mW at 920 nm (Fig. 2(a)) and 273($\pm$5) mW at 1011 nm (Fig. 2(b)).

In Fig. 2(a), the emission intensity increases with increasing heat-treatment from 330°C to 350°C, and decrease for 370°C. We can assume that re-absorption take place, due to Yb^{3+}-Yb^{3+} interaction and phonon

Table 1 Refractive index values for all glass-ceramic samples at 632.8 and 1308.2 nm

heat-treatment/°C	refractive index (n) at 632.8 nm ($\pm$0.0005)		$\Delta n = n_{TE} - n_{TM}$ at 632.8 nm	refractive index (n) at 1308.2 nm ($\pm$0.0005)		$\Delta n = n_{TE} - n_{TM}$ at 1308.2 nm
	TE mode	TM mode		TE mode	TM mode	
GC-330°C/5 h	1.9768	1.9755	0.0013	1.9066	1.9035	0.0083
GC-350°C/5 h	1.9837	1.9819	0.0018	1.9260	1.9177	0.0031
GC-370°C/5 h	1.9959	1.9946	0.0013	1.9323	1.9286	0.0037

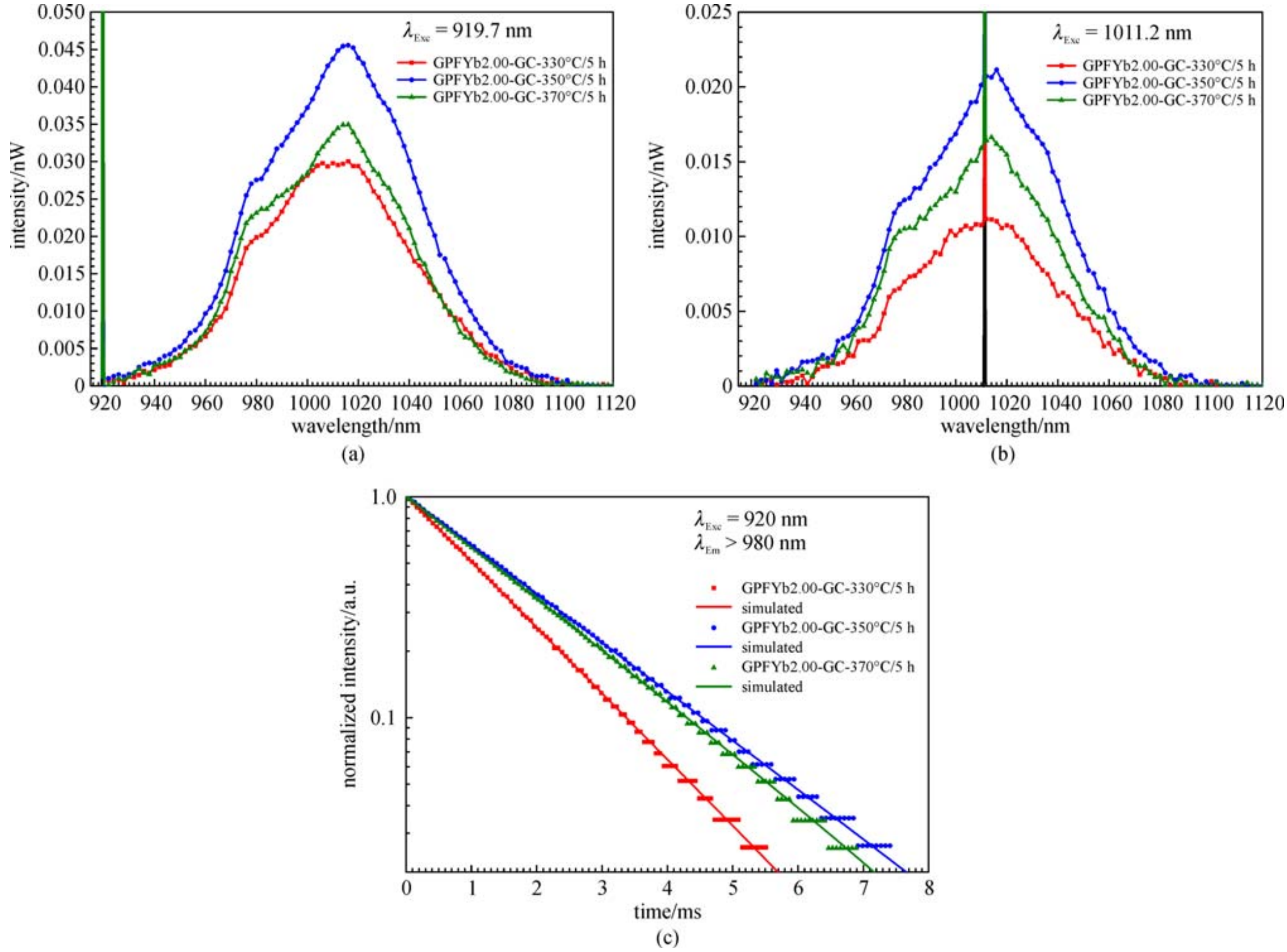

Fig. 2 Emission PL spectra for all glass-ceramic samples under excitation at (a) 920 nm and (b)1011 nm. (c) Emission PL decay curves of Yb^{3+} $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition for all samples under excitation at 920 nm (Symbols are experimental values and solid lines are the fitted curves)

Table 2 QY determined values for all samples under excitation at 920 nm and at 1011 nm as a functions of heat treatment

heat-treatment/°C	λ_{Exc}/nm	iQY (±5%)	eQY (±5%)	power/mW
GC-330°C/5 h	920	89	7	525±10
GC-350°C/5 h	920	80	11	525±10
GC-370°C/5 h	920	92	8	525±10
GC-330°C/5 h	1011	99	5	273±5
GC-350°C/5 h	1011	95	10	273±5
GC-370°C/5 h	1011	99	7	273±5

activation of the host at 370°C. Note that the maximum peak is around 1016 nm and a small change was observed from 330°C to 370°C, but the spectral shape under 920 nm excitation changed with heat-treatment temperature becoming well-defined for 350°C and 370°C in comparison to 330°C. This clearly demonstrates that the chemical environment around Yb^{3+} ions is changing as a function of crystallization, being a similar behavior for absorption coefficient (Fig. 1(b)). However, similar emission PL spectra shape were recorded under excitation at 1011 nm, with a maximum intensity emission for heat-treatment at 350°C. Probably, longer wavelengths (of 1011 nm) excite only Yb^{3+} ions embedded in nanocrystals, all of them within a similar environment, in which the high crystallinity induce re-absorption effects reducing emission intensity for sample heat-treatment at 370°C.

The internal and external quantum yields (iQY and eQY, respectively) values for all samples are listed in Table 2 with an error bar estimated be ±5%. For excitation at 920 nm, the iQY changes between 80% and 92%, from 350°C to 370°C respectively.

The concentration of some defects in crystals is expected to become low with increase in the crystallite size, since the specific surface area of the crystal decreases with increasing size diameter. This may result in an increase in QY. In addition, since Mie scattering is the main cause for the scatter-loss in the glass-ceramic, it decreases with increasing particle size. This may also contribute to the increase in QY [23]. However, the eQYs have a maximum of 11% for heat-treatment at 350°C, decreasing to 8% for heat-treatment at 370°C. The iQY was calculated by the relation between number of photons emitted and number of photons absorbed, and eQY by the relation between number of photons emitted and number of exciting photons (laser signal onto samples) [24,25].

Similarly, under excitation at 1011 nm, the maximum iQY of 10% is for heat-treatment at 350°C. For the iQY, it has values close to unity (99%) for heat-treatment at 330°C and 370°C, but is 95% for heat-treatment at 350°C, confirming our previous assumption that longer wavelengths excite well protected Yb^{3+} and no quenching effect is observed. Considering the error bars, all of the iQY values are similar and close to 100%, leading us to propose that these glass-ceramics are promising for laser cooling applications. Furthermore, the differences between iQY under excitation at 920 and 1011 nm, as can be seen in Table 2, are related to activation of different channels and ions dependent on the excitation energy. For laser refrigeration applications, solid-state materials need to have high iQY values, close to unity (or 100%), low defects concentration and low parasitic elements absorbing at the excitation wavelength. Defect creation can be induced during the crystallization process of β-PbF_2 and can also explain the reduction in iQY for 350°C sample. The radiation trapping and β-PbF_2 nanocrystals size and quantity could lead to the change the iQY and eQY behaviors, which is depend on the excitation wavelength, then this leads to the higher eQY value for 350°C sample.

Figure 2(c) shows the experimental values of PL decay from Yb^{3+} $^2F_{5/2}$ level for all samples, under excitation at 920 nm and monitoring emissions above 980 nm wavelength. They can be simulated by considering an exponential function:

$$I(t) = A\mathrm{e}^{-t/\tau}, \tag{2}$$

where A is a constant equal to unity for normalized curves and τ is the lifetime. All lifetime values are listed in Table 3, with the adjusted R-square values higher than 0.999 showing a high quality for the fittings.

The lifetime under exctation at 920 nm increases from (1.470±0.002) ms for heat-treatment at 330°C to (1.970±0.002) ms for heat-treatment at 350°C, and a small reduction to (1.900±0.002) for heat-treatment at 370°C in our glass-ceramic samples. These results are an indication that radiation trapping occurs in these glass-ceramics, especially those with heat-treatment at 350°C and 370°C.

Similar lifetime values and behaviour were found for excitations at 980, 1011 and 1030 nm. All these features lead us to conclude that radiation trapping increases the lifetime and gives a lower iQY for heat-treatment at 350°C when compared to heat-treatment at 330°C and 370°C samples.

Similar behavior was observed previously by Sumida and Fan [26] for Yb^{3+} doped YAG crystals and by Dai et al. [27] for Yb^{3+} doped phosphate glasses. They observed that at low Yb^{3+} concentration, radiation trapping takes place. Sumida and Fan [26] noted this effect for doping levels between 1.1 at.% (0.94 ms) and 10 at.% (0.98 ms), at higher concentrations quenching occurs and the lifetime is reduced (0.78 ms for 25 at.%). In the case of phosphate glasses, Dai et al. [27] observed an increase in lifetime from ~0.94 ms for 0.2 mol% to 1.53 ms for 6 mol% of Yb^{3+}.

Comparing our lifetime results with a previous work [18] for oxyfluoride glasses from the $30SiO_2$-$15Al_2O_3$-$(29-x)CdF_2$-$22PbF_2$-$4YF_3$-$x$$YbF_3$ system doped with 2, 5, 8, 12, 16 and 20 mol% of Yb^{3+} ions, similar values were measured for 2 mol%; they measured ~1.57 ms and in the present work we report 1.470 ms for heat-treatment at 330°C with a lower nanocrystal concentration than heat-treatment at 370°C with lifetime of 1.900 ms. Krishnaiah et al. [18] mentioned that the dominant mechanisms for lifetime quenching are the energy transfer among the Yb^{3+} ions and multi-phonon relaxation, especially for concentrations higher than 5 mol% of Yb^{3+}. Here, in GPFYb samples, multi-phonon relaxation is probably not because the Yb^{3+} concentration is low (2 mol%) and the matrix has

Table 3 Lifetime values of Yb^{3+} $^2F_{5/2}$ level and adjusted R-square values by monoexponential function fitting, obtained under different excitation wavelengths

heat-treatment/°C	λ_{Exc} = 920 nm		λ_{Exc} = 980 nm		λ_{Exc} = 1011 nm		λ_{Exc} = 1030 nm	
	lifetime/ms	adj. R^2	lifetime/ms	adj. R^2	lifetime/ms	adj. R^2	lifetime/ms	adj. R^2
GC-330°C/5 h	1.470±0.002	0.9998	1.417±0.001	0.9997	1.404±0.001	0.9999	1.468±0.001	0.9997
GC-350°C/5 h	1.970±0.002	0.9999	1.960±0.002	0.9996	1.974±0.001	0.9999	1.947±0.001	0.9998
GC-370°C/5 h	1.900±0.002	0.9998	1.842±0.001	0.9999	1.863±0.001	0.9998	1.953±0.001	0.9998
input power into samples/mW	436±10		278±5		207±5		171±5	

a low phonon energy.

Longer lifetime is not an obstacle for laser cooling, but it is not desirable, since it can slow down the cooling process [18], however, it is necessary to have high iQY values, close to unity (or 100%). In fact, these radiation trapping effects change the iQY and eQY behavior, dependent on the excitation wavelength, which leads us to propose that $50GeO_2$-$30PbF_2$-18PbO-$2YbF_3$ samples are probably good candidates for laser cooling applications.

With laser cooling applications in mind, similar experiments using the direct FBG contact technique as reported earlier [15,17], were performed. Optical quality samples were cut to dimensions of 10 mm-long and 2 mm × 2 mm cross-section and polished with parallel facets and pumped with different wavelengths from 920 to 1030 nm from a continuous wave Ti: Sapphire laser.

Figure 3(a) shows the temperature variations (ΔT in Kelvin) normalized by the input laser pump power (in Watt) delivered to the sample surface as a function of wavelength for all glass-ceramic samples; and the values in Fig. 3(b) were normalized by the absorption coefficient (presented in Fig. 1(b)) at each wavelength for all samples.

Figures 3(a) and 3(b) illustrate two main behaviors in all samples, one for excitations between 920 and 980 nm (called HZ = heating zone), and another one from 990 to 1030 nm (called CZ = cooling zone).

Regarding the results in Fig. 3(a), the region HZ presents a constant temperature variation per Watt per absorption unit (almost no dependence on the excitation wavelength), but this plateau reduces by increasing heat-treatment temperature to 350°C, lowest values; however, for region CZ the heating effect depends on the excitation wavelength almost linearly decreases by increasing wavelength, while heating process becomes lower for samples heat-treatment at 350°C, which has a minimum between 1020 and 1030 nm.

It is noteworthy to mention each domain is well correlated with iQY variation measured under excitation at 920 and 1011 nm (Table 2), or a higher iQY leads to lower heating effects. Also, the longer lifetime value of heat-treatment at 350°C (Table 3) appears to contribute to lower heating effect.

To better understand these behaviors, we considered the absorption coefficient as plotted in Fig. 3(b). Here both behaviors are also visible, with the limit between 980 and 990 nm having the highest absorption coefficient. Note a strong temperature reduction at 1030 nm excitation wavelength for heat-treatment at 350°C sample. Also the maximum phonon energy of this germanate-oxyfluoride glass matrix which correponds to ~900 cm^{-1}, as previously determined by Refs. [28,29], and it plays a crucial role for eliminating heat from the system during laser irradiation, but optical cooling effect can be influenced by β-PbF_2 crystals having a phonon energy of ~260 cm^{-1} [30]. Certainly, a net cooling could be achieved at an excitation wavelength around 1030 nm. Since radiation trapping is present, and other effects such as: an inhomogeneous pumping (only the center of sample received the most portion of excitation photons), laser power limitations and heat-transfer from sample to cooled air of the room atmosphere, it prevents the observation of net-cooling.

Finally, all these results lead us to propose that $50GeO_2$-$30PbF_2$-18PbO-$2YbF_3$ samples are good candidates for laser cooling applications, but improvement in sample purity is necesssary, because a green-bluish emission was observed due to Tm^{3+} or Er^{3+} impurities of the YbF_3 precursor, and it possibly influences the cooling process efficiency.

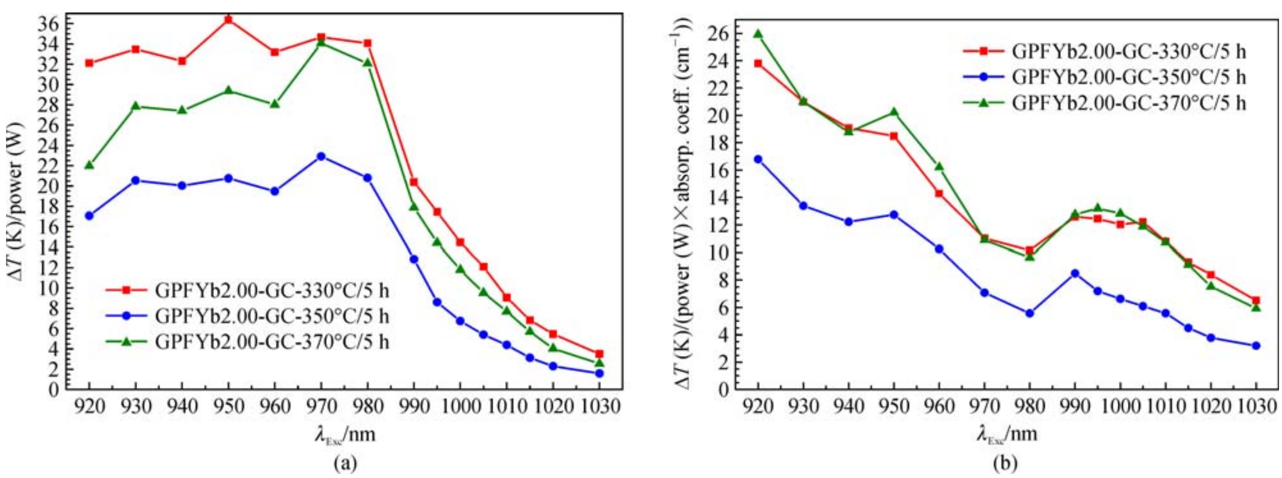

Fig. 3 (a) Temperature changes normalized by input pump power delivered onto samples as a function of wavelength for all glass-ceramic samples; (b) values of Fig. 2(a) normalized by the absorption coefficient from Fig. 1(b). The curves indicate that the minimum temperature was achieved for heat-treatment at 350°C sample, that net cooling could be probably be achieved at an excitation wavelength of 1030 nm, prevented by radiation trapping and inhomogeneous pumping. The minimum between 970 and 980 nm in Fig. 3(b) is around the higher absorption coefficient with the peak at 976 nm, as we can see in Fig. 1(b), for instance we have not an explanation on this behaviour and more studies should be performed, especially measurements as a function of excitation power

4 Conclusions

Yb^{3+}-doped germanium lead oxyfluoride glass-ceramics with high transparency (higher than 80% in the visible region) were synthesized with heat-treatments at 330°C, and 350°C, and optical as well as photoluminescence properties of all samples were characterized. The refractive index values increase with increasing heat-treatment temperature, as expected and varies from 1.9768 to 1.9959 at 632.8, and 1.9060 to 1.9323 at 1308.2 nm. Spectroscopic measurements showed near infrared photoluminescence emission due to the $^2F_{5/2}-^2F_{7/2}$ Yb^{3+} transition, with its intensity dependent on the crystallization process, and with the highest PL emission for samples heat-treated at 350°C under excitation at 920 nm and at 1011 nm. Also, the PL internal quantum yield varies between 80% and 99%, depending on the heat-treatment and excitation wavelength, being most efficient for those excited at 1011 nm with iQY between 95% and 99%. Our temperature monitoring experiments as a function of excitation wavelength showed that samples heat-treated at 350°C have a net heating close to zero under excitation around 1030 nm, indicating their potential for laser cooling applications. However, samples heat-treated at 330°C presented the highest heating of 36 K/W superior to room temperature (a temperature of 58°C/W can be reached) under 950 nm excitation (in the biological tissue window range), and this glass-ceramic could be explored for biomedical applications, but further experiments should be performed.

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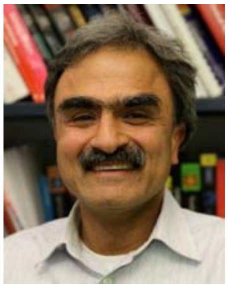

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