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Erbium doped glass–ceramics: concentration effect on crystal structure and energy transfer between active ions

M. Mortier*, P. Goldner, C. Chateau, M. Genotelle

CNRS-UPR211, 1, place A. Briand, 92195 Meudon cedex, France

Abstract

Transparent glass–ceramics have been obtained by nucleation and growth of βPbF_2 crystallites around erbium impurities in a germanate glass. Different doping levels have been used to monitor the nucleation process. The segregation of the rare earth ions in the crystalline phase and then the resulting high local doping level induces a modification of the lattice parameter of PbF_2 evidenced on the X-ray diffraction spectra and explained with a structural model. The decay profile of the 2.7 μm transition of the erbium ions is strongly affected by the surrounding changes induced by the ceramming process. Due to the high doping level of the crystallites, a model taking into account the energy transfers is necessary to fit the decays. Polycrystalline samples of erbium doped PbF_2 have been synthesised in order to compare with the observation in the glass–ceramics. The variations occurring in the transients are compared with the structural modifications accompanying the local concentration changes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Glass–ceramic; Erbium; X-ray analysis; Lifetime; Energy transfer

1. Introduction

Transparent glass–ceramics, improving the optical properties of the rare earth (RE) ions in comparison with the starting glass, have been obtained by heterogeneous nucleation of βPbF_2 around erbium ions in a germanate glass of composition ($50GeO_2$,$40PbO$,$10PbF_2$). Many different doping levels have been used in order to monitor the nucleation and growth [1]. Indeed, a weak erbium ion content (≤2 mol% in excess) corresponds to 20 nm sized particles; while a higher doping level (≥4 mol%) will generate more numerous but smaller particles of 8 nm size.

After nucleation and growth, the optical properties of the erbium doped samples are crystal like with a strong reduction of the inhomogeneous linewidth of the absorption and emission spectra due to the segregation of the rare earth in the crystal phase [2]. The lifetime of the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition centred around 2.7 μm, and which is one of the most sensitive to non radiative de-excitations, is estimated at 360 μs for the 3% erbium doped as-melted glass and at 3 ms for the reheated one [2]. This difference of lifetime is assumed to be due to the change of the RE sites induced by the reheating treatment. In the as-melted glass, the RE is surrounded by an oxide glass of phonon cut-off frequency equal to about 1000 cm^{-1}; in the glass–ceramic, the surrounding is a fluoride crystal of phonon cut-off frequency equal to 336 cm^{-1} [1].

Here, we will describe the effects induced by the strong segregation of the RE ions in the crystal phase and then the resulting high local doping level.

2. Experimental

Glass samples were melted from commercial (3 N) raw materials in a platinum crucible at 1000°C in normal atmosphere. The liquid was poured on a copper plate and quenched with another plate. The 2 mm thick glassy sample was then annealed around the glass transition temperature [1]. Glasses with different molar compositions were prepared: ($50GeO_2 50-x PbO x PbF_2 + y ErF_3$) with ($x$; y)=(10; 2,2.5,3,4), (15; 1,2). These glasses were reheated for 10 h at 360°C to obtain the complete precipitation of PbF_2 [1] giving the glass–ceramic.

Polycrystalline PbF_2 was elaborated, in an argon purified glove box, by very slow cooling of a melt from 875°C to room temperature with different ErF_3 doping level, i.e. 1, 9 and 16.6 mol%. For these three samples, the local RE concentration is equal to the doping level in the melt.

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*Corresponding author. Tel.: +33-1-45-075-300; fax: +33-1-45-075-107.

E-mail address: mortier@cnrs-bellevue.fr (M. Mortier).

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Table 1
Parameter cell, erbium concentration and decay parameters for polycrystalline PbF_2

ErF_3 (mol%)	a (Å)	n (cm^{-3})	τ $^4I_{11/2}$ (ms)	$1/\tau$ (s^{-1})	W_{NR} (s^{-1})	c (s^{-1})
1	5.94	$1.89 \cdot 10^{20}$	8.8	114	0	79
9.1	5.895	$1.79 \cdot 10^{21}$	7.3	137	23.5	181
16.6	5.875	$3.33 \cdot 10^{21}$	3.9	256	143	391

Table 2
Parameter cell, erbium concentration in glass and in crystallites after treatment and decay parameters for glass–ceramics ($50GeO_240PbO10PbF_2$)

ErF_3 (mol%)	ErF_3 in PbF_2 (mol%)	a (Å)	n (cm^{-3})	τ $^4I_{11/2}$ (ms)	$1/\tau$ (s^{-1})	W_{NR} (s^{-1})	c (s^{-1})
2	20	5.83	$4.04 \cdot 10^{21}$	4.75	211	97	(1089–1400)
3	30	5.81	$6.12 \cdot 10^{21}$	3.3	303	189	
4	40	5.81	$8.16 \cdot 10^{21}$	2.4	417	303	3108

X-ray analysis was done with a powder diffractometer between $2\theta=10°$ and $2\theta=80°$ in steps of 0.02° and with a resolution better than 0.05° using a Cu radiation.

The X-ray peak widths analysed with the Scherrer formula indicated mean crystal sizes between 8 and 30 nm depending on the PbF_2 and ErF_3 content [1]. In Tables 1–3, the local erbium concentration in the crystal phase is reported for the different samples assuming a complete segregation of the RE in the crystal phase and the complete crystallisation of PbF_2 without any losses during the melting phase of the glass preparation. We can notice that a very high doping level is supposed to be reached in the crystallites through the segregation effect, up to 40 mol% (Table 2).

The emission spectrum around 2.7 μm has been recorded with a PbS detector placed at the exit slit of a HRD Jobin Yvon monochromator after excitation by the 514.5 nm line of an argon laser. The resolution was better than 10 nm.

Lifetime measurements around 2.7 μm were made with a cooled InAs detector after excitation at 970 nm by a pulsed Ti:Sapphire laser.

3. X-ray analysis

The X-ray diffraction (XRD) spectrum of the glass ceramic ($50GeO_2$, 35PbO, $15PbF_2$, $2ErF_3$) is reported between $2\theta=10°$ and $2\theta=50°$ on Fig. 1. The XRD spectrum shows both the typical halo of the glassy phase and the characteristic peaks of the β-PbF_2 cubic phase $O_h^5 - Fm3m$ with $a=5.94$ Å. The {111}, {200} and {220} plane families are calculated respectively at $2\theta=25.99$, 30.09 and 43.07° with $\lambda_{RX}=1.5418$ Å for the ideal structure.

Table 3
Parameter cell, erbium concentration for glass–ceramics ($50GeO_235PbO15PbF_2$)

ErF_3 (mol%)	ErF_3 in PbF_2 (mol%)	a (Å)	n (cm^{-3})
1	6.67	5.89	$1.3037 \cdot 10^{21}$
2	13.33	5.84	$2.6770 \cdot 10^{21}$

In Fig. 2 and Tables 1–3, we report the value of the PbF_2 lattice parameter deduced from the angular position of the eight main diffraction peaks using a U-Fit software vs. the local erbium content in the crystal phase. For the glass–ceramic samples, the uncertainty on the parameter cell is 0.01° and 0.005° for the polycrystalline PbF_2. The uncertainty on the erbium concentration can be estimated to 10%.

The high doping level induces a modification of the lattice parameter of PbF_2 in the glass–ceramic shown in Fig. 2. For the glass–ceramic and the polycrystalline

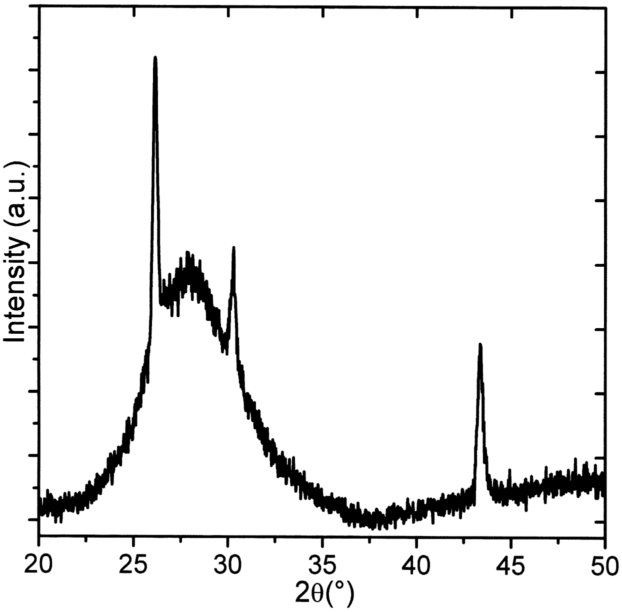

Fig. 1. XRD spectrum of a glass ($50GeO_235PbO15PbF_2+2ErF_3$) after heating for 10 h at 360°C.

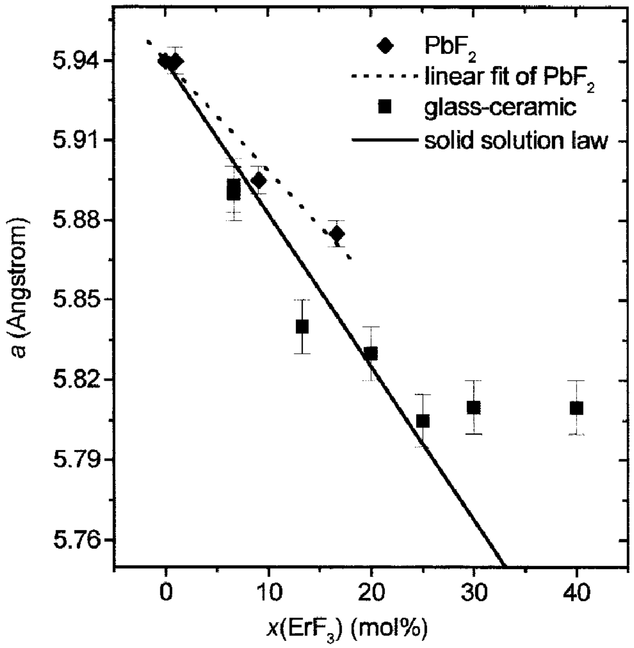

Fig. 2. Evolution of the parameter cell vs. ErF_3 content in PbF_2 crystal phase.

samples, the parameter cell decreases when the erbium concentration increases due to the small size of Er^{3+} ion (1.03 Å) with regard to Pb^{2+} (1.32 Å). Polycrystalline samples of erbium doped PbF_2 have been synthesised in order to compare the lattice changes with the observation in the glass–ceramics. The parameter cell of polycrystalline PbF_2 follows a linear law vs. its RE content which differs from the comportment observed with the glass–ceramic samples. Indeed, the polycrystalline PbF_2 is supposed to be free of oxygen ions because of its synthesis inside a purified glove box. In isotype compounds (CaF_2, BaF_2, ...) [3], the RE^{3+} ion occupies the M^{2+} position with an interstitial F^- ion located in the neighbouring sites. On the other hand, the starting glass of the glass-ceramic is an oxy-fluoride medium. In such a case, a solid solution of ErOF in PbF_2 insuring the charge compensation can explain the evolution of the parameter cell vs. the RE content.

The ErOF structure can be described in the hexagonal or in the rhombohedral system; in this last case with $a=6.639$ Å and $\alpha=33.10°$ which is not very different from $\alpha=33.22°$ for a cubic lattice. The volume of this cell is $V=231.77$ Å^3 with $Z=6$. So, the volume of one ErOF unit is equal to $V/6$. In the fluorine structure (PbF_2), $Z=4$. In a such structure, the cubic cell with ErOF would give the volume: $4V/6=154.51$ Å^3 and then a parameter cell of 5.366 Å. We then consider a solid solution $(1-\delta)PbF_2$ $\delta ErOF$ with a parameter cell: $a=(1-\delta)5.94+\delta 5.366$. This law is represented by a bold solid line in the Fig. 2, and gives a good representation of the lattice parameter of the glass–ceramic up to 25 mol% ErF_3. However, the 30 and 40 mol% samples are strongly out of this law and their parameter stays equal to the 25 mol% parameter. With a doping level of 25 mol%, one erbium ion is located in each cell ($Z=4$) and the erbium–erbium distance is equal to the parameter cell a. With more erbium ions, two ions must share the same cell and then the minimal Er–Er distance goes down to $a\sqrt{2}/2$ instead of a, increasing strongly the energy transfer processes between erbium ions. However, the lack of parameter cell variation in the more concentrated samples has not been explained.

It appears in Fig. 2 that the polycrystalline PbF_2 samples can give a good simulation of the crystallites in the glass–ceramic. Their parameter cell decreases when the erbium concentration increases and is not strongly different from those of the corresponding glass–ceramic (at the same doping level) even if the charge compensation mechanism differs. The tendency to a decrease of the parameter cell with the concentration increase enhances this last increase. The values of lattice parameters deduced from the XRD data allows to calculate the chemical concentration in the crystal phase (Tables 1–3).

4. Decay profile analysis

The emission corresponding to the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition is presented in the Fig. 3 for an as-melted and treated glass. The emission spectrum of the glass–ceramic presents two bands narrower than the as-melted glass. The reduction of inhomogeneous linewidth is weaker than with transitions involving $^4S_{3/2}$ level. The effect of reduction of inhomogeneous linewidth seems to be compensated by the accidental coincidence between the numerous Stark components of the initial and final multiplets $^4I_{11/2}$ and $^4I_{13/2}$ [4].

In Fig. 4, five different decay curves are shown for different samples. The decay curve (A) of the non treated

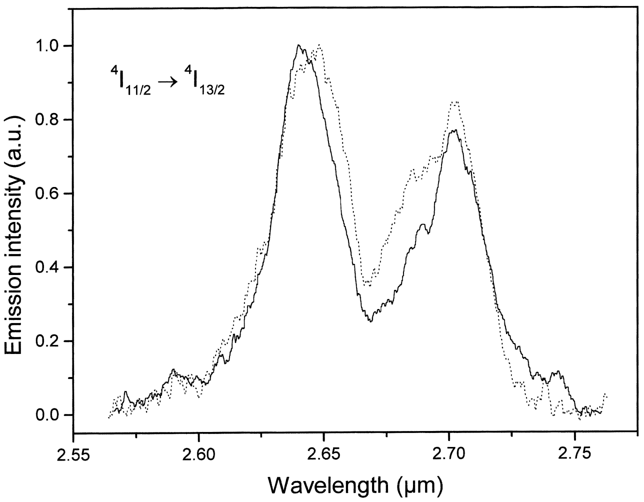

Fig. 3. Emission spectrum of the as-melted and treated glass after excitation at 514.5 nm.

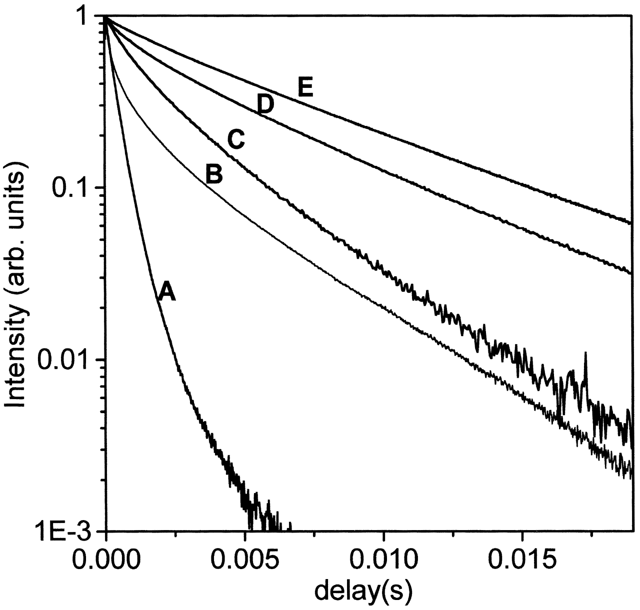

Fig. 4. Decay profile of the ${}^4I_{11/2}\rightarrow{}^4I_{13/2}$ emission for different samples: glass ($50GeO_2 40PbO 10PbF_2 + 2ErF_3$), (A) as-melted; (B) after treatment polycrystalline PbF_2; (C) 16.6 mol% ErF_3; (D) 9.1 mol% ErF_3; and (E) 1 mol% ErF_3.

glass (10Pb, 2Er) corresponds to a decay time of 250 μs and the associated glass ceramic (B) to a longer lifetime but with a non single exponential decay. It is quite obvious that a strong enhancement of the lifetime is caused by the ceramming process. The decay curve of PbF_2 polycrystalline samples are also shown for different doping level (E: 1, D: 9 and C: 16.6 mol% of ErF_3). The decay curve of the 2 mol% Er doped glass–ceramic (B) appears quite similar to the one of the (C) 16.6 mol% erbium doped polycrystalline PbF_2 confirming the high doping level of the crystallites embedded in the glassy matrix.

The decay curves of the PbF_2 and glass–ceramic samples are clearly non exponential at the short delay. This behaviour can be linked to limited diffusion [5] or up conversion processes. The limited diffusion has not been considered because of the high doping level reached in our samples. However, the following law accounting for $({}^4I_{11/2}, {}^4I_{11/2})\rightarrow({}^4I_{15/2}, {}^4F_{7/2})$ up conversion process has been used to fit the decay curves:

$$N(t) = \frac{e^{-t/\tau}}{1 + \tau c(1 - e^{-t/\tau})}$$

with τ (s) the decay time of the level and c (s^{-1}) the probability of energy transfer. The fitting results for polycrystalline PbF_2 (Fig. 5) are reported in Table 1. The same law has been used for the glass–ceramics (Table 2).

In order to compare these different results and check the validity of this model, the chemical concentration n (cm^{-3}) has been calculated in the polycrystalline PbF_2 samples and estimated in the crystallites of the glass-ceramics. In Fig. 6, we report the c coefficient vs. n^2. The energy transfer coefficient is found to vary linearly with n^2 and could reflect a quenching under ultrarapid migration conditions along erbium ions [6].

The transfer probability evolves with the RE concentration as shown by the non exponential contribution at the beginning of the decay curves. The lifetime is also affected by the RE concentration. The non radiative contribution has been estimated considering the lifetime of the 1 mol% erbium doped polycrystalline PbF_2 as purely radiative. The probability of non radiative transition is plotted vs. the chemical concentration of RE, n, in Fig. 7. This probability increases linearly with the chemical concentration.

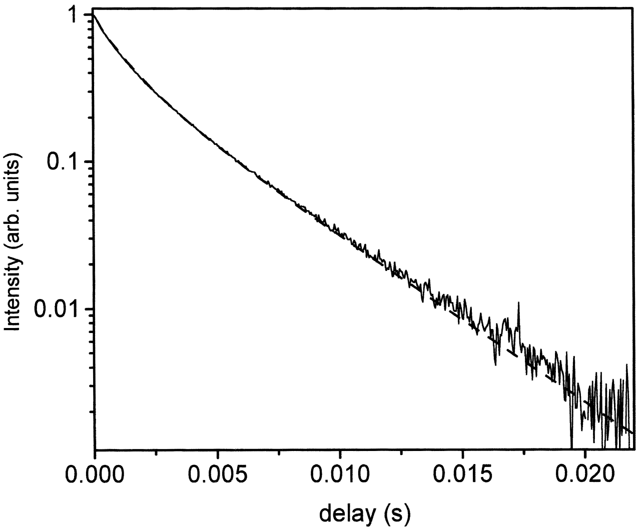

Fig. 5. Decay profile of a PbF_2 polycrystalline sample doped with 16.6 mol% ErF_3. In dashed line, fit with the law defined in paragraph 4 with τ=3.9 ms and c=391 s^{-1}.

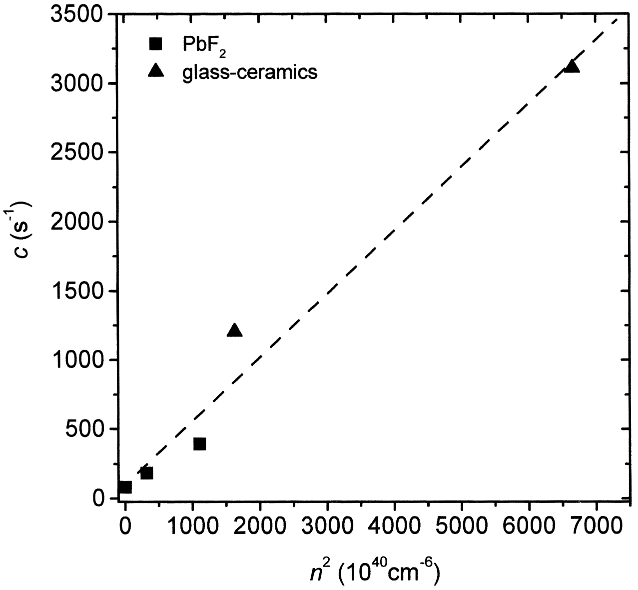

Fig. 6. Energy transfer constant c (s^{-1}) vs. n^2 square of the chemical concentration. The dashed line indicates a linear law.

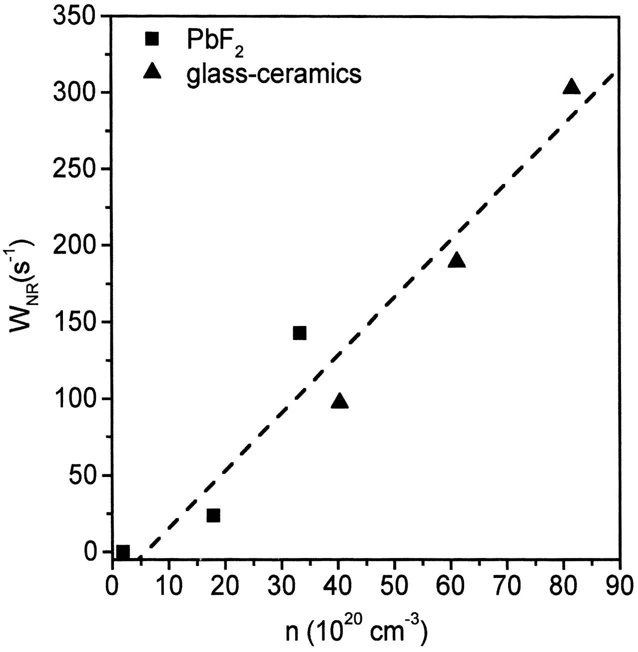

Fig. 7. Non radiative transition probability vs. the chemical concentration for different samples. The dashed line indicates a linear law.

So, the ceramming process increases the lifetime of the erbium ions mainly through a strong reduction of the non radiative contribution induced by the environment change but limited by the energy transfers induced by the segregation of the RE ions.

5. Conclusion

Transparent glass–ceramics, improving the optical properties of the RE ions in comparison with the starting glass, have been obtained by heterogeneous nucleation of βPbF_2 around erbium impurities in a germanate glass of composition ($50GeO_2$, 40PbO, $10PbF_2$). Different doping levels have been used to monitor the nucleation and give various sizes of crystallised particles between 8 and 20 nm.

After nucleation and growth, the optical properties of the erbium doped samples are crystal like with a strong reduction of the inhomogeneous linewidth of the absorption and emission spectra due to the complete segregation of the RE in the crystal phase.

The high doping level due to the segregation of the RE induces a modification of the lattice parameter of PbF_2 evidenced by an angular shift of the X-ray diffraction peaks and explained with a structural model. Polycrystalline samples of erbium doped PbF_2 have been synthesised in order to compare the lattice changes with the observation in the glass–ceramics. The lifetime of the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition centred around 2.7 μm and which is very sensitive to non radiative de-excitations is strongly increased by the ceramming process due to the induced changes in the surrounding and concentration of erbium ions. The decay profile is fitted by a single exponential at very low concentration level, but a model taking into account up conversion energy transfers is necessarily used to fit higher doping level decays. The non radiative processes, strongly reduced in the glass–ceramic compared to the starting glass, are also weakly enhanced by the concentration increase and is proportional to the concentration. The chemical concentration calculated from XRD data gives a very reliable result as verified with the linearity of the variation of c and W_{NR}, respectively vs. n^2 or n.

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