

Optical investigation of $\text{Eu}^{3+}:\text{PbF}_2$ ceramics and transparent glass–ceramics

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ARTICLE INFO

Article history:

Received 25 January 2010

Received in revised form 9 December 2010

Accepted 30 December 2010

Available online 1 February 2011

Keywords:

Oxyfluoride glasses

Glass–ceramic

Eu^{3+} ions

Fluorescence

Thermal analysis

Crystallization

ABSTRACT

This paper reports an optical investigation of glass–ceramics formed by annealing glasses with compositions $50 \text{GeO}_2\text{--}40 \text{PbO}\text{--}10 \text{PbF}_2\text{--}x \text{EuF}_3$, $x = [0.5; 1; 1.5; 2]$ and polycrystalline ceramics with composition $100 \text{PbF}_2, y \text{EuF}_3$, with $y = 5, 10, 15$ and 20 . For each material, the photoluminescence spectrum and the photoluminescence lifetimes of the ${}^5\text{D}_0$, ${}^5\text{D}_1$ and ${}^5\text{D}_2$ Eu^{3+} levels are measured. Occurrence of $\text{Eu}^{3+}:\beta\text{-PbF}_2$ nanocrystallites in the glass–ceramics is confirmed and total ceramisation requires more than 10% of EuF_3 with respect to PbF_2 in the starting glass.

In the $\text{Eu}^{3+}:\beta\text{-PbF}_2$ ceramics and glass–ceramics, Eu^{3+} ions replace Pb^{2+} in their regular cubic site, but they interact together to form dimers and higher nuclearity clusters. These two species are easily distinguished according to their photoluminescence decay rate. For the EuF_3 rates investigated here, there are no isolated Eu^{3+} ions in the PbF_2 lattice.

A preliminary investigation of the optical properties of co-doped $\text{Gd}^{3+}:\text{Eu}^{3+}:\beta\text{-PbF}_2$ ceramics was also performed. It shows that mixed $\text{Gd}^{3+}\text{--}\text{Eu}^{3+}$ dimers and clusters are formed, and that efficient $\text{Gd}^{3+} \rightarrow \text{Eu}^{3+}$ energy transfer occurs in these ceramics. The Pb^{2+} ions of the lattice may also be involved in the energy transfer process.

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1. Introduction

Studied from tens of years [1], the transparent glass–ceramic systems have been identified more recently to be promising materials for optical amplification in compact optical communications setup [2,3]. Obtained with standard glass technology followed by controlled devitrification induced by glass annealing, glass–ceramics doped with lanthanide ions offer narrower emission linewidths and higher emission cross-section than their parent's glasses thanks to simultaneous crystallization of a phase and segregation of the lanthanide inside this crystal phase [4,5]. Therefore, they combine easy processing ability of glasses and outstanding optical properties of the crystals. For about 10 years, we are investigating lanthanides-activated transparent oxyfluoride glass–ceramics in which the doping ions are confined in $\beta\text{-PbF}_2$ nanocrystals embedded in an oxide glassy matrix [5–9].

The present investigation was performed in order to gain a better knowledge of the local environment of the lanthanide ion in the glass–ceramic. As lanthanide ion in this study, we used Eu^{3+} , introduced in the parent glass composition as EuF_3 . The optical properties of this ion are very sensitive to its environment [10] and this explains why the Eu^{3+} ion in solids has frequently been used as a luminescent structural probe [11].

Several studies [12–19] have already been devoted to the thermal and photoluminescence properties of transparent glass–ceramic containing $\text{Eu}^{3+}:\text{PbF}_2$ nanocrystals, using EuF_3 -doped lead–cadmium or lead fluorosilicate or fluorogermanate as parent glasses.

We are reporting here the optical properties of various Eu^{3+} -doped fluorogermanate glass–ceramics obtained by devitrification of EuF_3 -doped lead fluorogermanate glasses whose properties have been reported in a previous paper [20].

With respect to the already published studies, the present one includes an investigation of the $\text{Eu}^{3+}:\text{PbF}_2$ ceramics with the same europium content than the transparent glass–ceramics in a broad composition range. We also present a detailed study of the fluorescence dynamics of the $\text{Eu}^{3+} {}^5\text{D}_2$ and ${}^5\text{D}_1$ levels, which allows concluding that, in the composition range studied: 5–20% Eu/Pb ratio, all the Eu^{3+} ions lie in clusters of various nuclearities.

Additionally, efficient $\text{Gd}^{3+}\text{--}\text{Eu}^{3+}$ energy transfer was recently demonstrated in a variety of compounds [21–23] and, based on these materials, photon-cutting phosphors with quantum efficiency reaching almost 200% were proposed [24–27]. Such materials are needed for mercury-free fluorescent lamps and plasma display panels [28,29] which are excited by xenon discharge in the VUV. For such application, fluorides, with their large band-gaps leading to optical transparency in the VUV, are the best choice. Furthermore, it has been shown recently that Pb^{2+} , in a fluoride compound, can be used as a sensitizer of the $\text{Gd}^{3+}\text{--}\text{Eu}^{3+}$ pair [30]. This

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suggests that transparent glass–ceramics containing $\text{Gd}^{3+}:\text{Eu}^{3+}:\beta\text{-PbF}_2$ nanocrystals may be promising as photon-cutting phosphors. A preliminary optical study of a $\text{Gd}^{3+}\text{-Eu}^{3+}$ co-doped $\beta\text{-PbF}_2$ polycrystalline sample will be presented here. It shows that energy transfer from Gd^{3+} to Eu^{3+} ions does occur in this system.

2. Experimental

2.1. Sample preparation

The reagents used in the synthesis of the materials were: GeO_2 (5N, Preussag); PbO (2N, Alpha Aesar); PbF_2 (4N, Alpha Aesar); EuF_3 and GdF_3 (4N, REacton).

2.1.1. $\text{Eu}^{3+}:\text{PbF}_2$ containing glass–ceramics

At first, a family of EuF_3 -doped lead fluorogermanate glasses having the following molar compositions: $50 \text{ GeO}_2\text{-}40 \text{ PbO}\text{-}10 \text{ PbF}_2\text{-}x \text{ EuF}_3$, $x = [0.5; 1; 1.5; 2]$ was prepared as described in a previous paper [20]. Then, the glasses were heated at 390°C for 10 h. Since it has been shown that this devitrification process lead to a glass–ceramic made of $\text{Eu}^{3+}:\beta\text{-PbF}_2$ nanocrystals embedded in a glassy oxide matrix [12,17–20], the glass–ceramics will be labelled GC10x, assuming a total segregation of europium in the $\text{Eu}^{3+}:\text{PbF}_2$ nanocrystals.

2.1.2. $\text{Eu}^{3+}:\text{PbF}_2$ ceramics

$\text{Eu}^{3+}:\text{PbF}_2$ ceramics of the compositions 100 PbF_2 , $y \text{ EuF}_3$, with $y = 5, 10, 15$ and 20 (hereafter labelled Cy) were prepared by crushing together in an agate mortar oven-dried commercial PbF_2 and EuF_3 in appropriate amounts. The mixture was then heated at 550°C for 3 h. It appeared essential to avoid partial oxidation of PbF_2 into lead oxyfluoride at the reaction temperature. This can be achieved by conducting the heat treatment under vacuum. X-ray diffraction was used to check the purity of the as prepared Cy materials.

Two mixed $\text{Eu}^{3+}\text{-Gd}^{3+}$ polycrystalline ceramics having the following compositions: $\text{PbF}_2\text{-}0.05 \text{ GdF}_3\text{-}0.1 \text{ EuF}_3$ and $\text{PbF}_2\text{-}0.1 \text{ GdF}_3\text{-}0.05 \text{ EuF}_3$ were also prepared in a similar manner than for the $\text{Eu}^{3+}:\text{PbF}_2$ ceramics.

2.2. Optical measurements

The photoluminescence spectra were recorded at room temperature under excitation at 467 nm , in the $\text{Eu}^{3+} \text{ } ^5\text{D}_2$ level. The spectra were obtained with a computer-monitored system associating a pulsed source (OPO pumped by the 3rd harmonic of a Q-switched Nd:YAG laser), a 25 cm monochromator and a CCD camera which allows recording the fluorescence spectrum for different gate width (GW) and delay (PD) after the laser excitation pulse. This setup was used to obtain the time-resolved luminescence spectra, luminescence decay profiles and to measure the room temperature fluorescence lifetime (τ_{5D_j}) of the $^5\text{D}_0$, $^5\text{D}_1$ and $^5\text{D}_2$ Eu^{3+} energy levels in the different glass–ceramics and ceramics.

Luminescence excitation spectra between 250 and 600 nm at room temperature were obtained using a Cary Eclipse UV–Visible spectrophotometer. Usually, the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition at 612 nm was monitored. The photoluminescence spectra of co-doped $\text{Gd}^{3+}:\text{Eu}^{3+}:\beta\text{-PbF}_2$ ceramics excited at 312 nm were also recorded with this spectrometer.

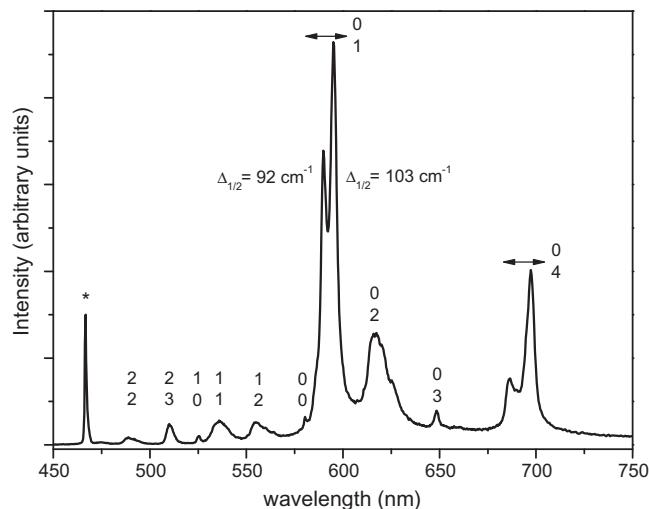


Fig. 1. Room temperature photoluminescence spectrum of the GC15 glass–ceramic recorded with PD = 50 ns and GW = 50 μs . The excitation wavelength was 467 nm , corresponding to the $^7\text{F}_0 \rightarrow ^5\text{D}_2$ transition. The observed transition $^5\text{D}_j \rightarrow ^7\text{F}_{j'}$ are labelled according to their j (above) and j' (below) values. $\Delta_{1/2}$ is the linewidth at half maximum of the two $^5\text{D}_0 \rightarrow ^7\text{F}_1$ components. *: Trace of the excitation laser pulse.

3. Results

3.1. Photoluminescence of the $\text{Eu}^{3+}:\text{PbF}_2$ glass–ceramics and ceramics

Fig. 1 display the photoluminescence spectrum of GC15 obtained with PD = 50 ns and GW = 50 μs , under excitation at 467 nm into the $\text{Eu}^{3+} \text{ } ^5\text{D}_2$ level. Such parameters emphasize the contribution of the short lived $^5\text{D}_2$ and $^5\text{D}_1$ Eu^{3+} emissions with respect to the long lived $^5\text{D}_0$ one (see Section 3.2.2), so that the emission from the three emitting ^5D levels can be displayed on one single scale. In all the ceramics and glass–ceramics studied, transitions arising from the $^5\text{D}_2$, $^5\text{D}_1$ and $^5\text{D}_0$ levels are observed.

The photoluminescence spectra of the GC15 glass precursor, GC15 glass–ceramic and C15 ceramic recorded with PD = 50 ns and GW = 1 ms are gathered in Fig. 2. With such parameters, which

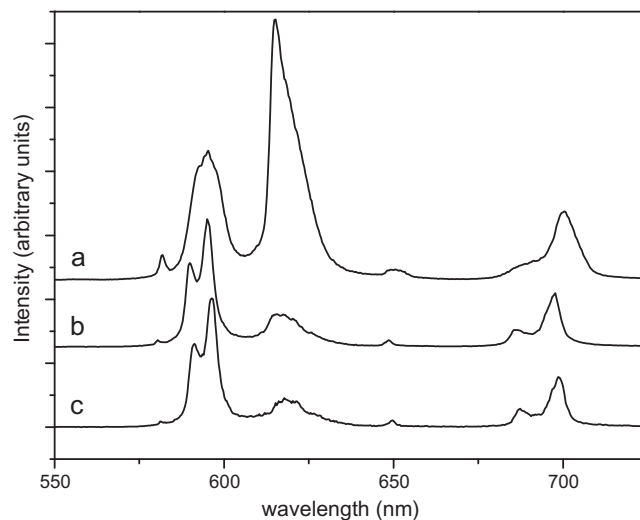


Fig. 2. Room temperature photoluminescence spectrum of the GC15 glass precursor (a trace), GC15 glass–ceramic (b trace) and C15 ceramic (c trace) recorded with PD = 50 ns and GW = 1 ms. The three spectra have been normalized on the strongest peak of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition.

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