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Red, green and blue light generation in fluoride glasses controlled by double excitation

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Abstract

A new multi-doped fluoroaluminate-based glass was developed to generate, with high accuracy, the three primary light colors simultaneously, allowing additive synthesis of light in the visible spectrum. The ions Er^{3+} and Tm^{3+} were used as red, green and blue narrow line emitters, by down-conversion and up-conversion processes. The Tm^{3+} and Er^{3+} concentrations in the glass were defined for simulation of the white emission, under double excitation in the infrared and ultraviolet region, allowing color tuning.

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

1. Introduction

Solid state materials allowing generation and control of primary light colors (red, green and blue) are required for image devices that need high spatial resolution with wide color gamut, and also for optoelectronic devices and high density optical storage engines. For these purposes, we have developed a glassy material doped with rare earth ions (Eu^{3+}, Tb^{3+} and Tm^{3+}), called FCG (full-color glass), which generates the three primary light colors by carefully selected 4f→4f transitions [1–3].

Since the 4f electrons of rare earth ions are shielded by the outer 5s and 5p electrons, the intra-$4f^n$ emission spectra of rare earth ions are characterized by narrow lines. Moreover, the positions of the 4f configuration energy levels are only slightly dependent on the host lattice, and are roughly the same as the free-ion levels. These properties are interesting for the development of new materials with the capability to produce visible light with narrow lines for RGB devices.

Fluoride glasses have been studied intensively as high performance new materials for infrared optical applications due to their high transparency and relatively low phonon energy in the heavy metal glass family [4]. The multicomponent AlF_3-based glasses are of special interest because they have high glass transition temperatures, higher than for the well-known ZBLAN (ZrF_4–BaF_2–LaF_3–AlF_3–NaF) fluorozirconate glass, for instance. In addition, the chemical and mechanical properties for this glass are improved, producing special interests in new technological applications for optical devices [5,6].

In this report, we will present the first results of a new FCG — a fluoroaluminate-based glass codoped with Er^{3+} and Tm^{3+}, called FCG2. The three primary colors light and the simulation of white light are obtained under simultaneous excitation with infrared and ultraviolet radiation, allowing color tuning.

2. Experimental

The glasses used in this study were prepared from highly purified fluorides as starting materials, in a dry box under a dynamic argon atmosphere. The batches were melted in carbon crucibles at 1000°C for 1 h, poured into a brass mold previously heated to 380°C, and slowly cooled to room temperature.

The general composition of the glass investigated in this work is

$$30.0AlF_3–20.0CaF_2–18.3YF_3–15BaF_2–9.2MgF_2–(7.5-a-b)YbF_3$$ (AYBCMYb host)

codoped with $a TmF_3$ and $b ErF_3$, where $a = 0.05–1$ mol% and $b = 0.1–1$ mol%.

The emission spectra were recorded at room temperature

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Table 1
Physical properties, transition temperatures and kinetic parameters from DTA measurements for the AYBCMYb glass

Optical transmission range	0.25 to 7.5 μm
Maximum phonon energy	630 cm^{-1}
Density	3.98 g/cm^3
Refractive index (medium)	1.4425
Glass transition temperature	436°C
Onset of crystallization temperature	501°C
Crystallization peak temperature	523°C
Onset of melt temperature	728°C
Apparent activation energy	86 kcal/mol

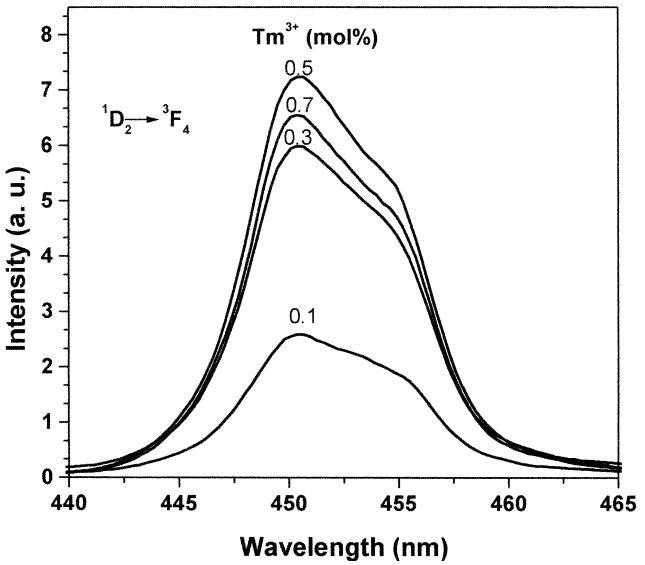

Fig. 1. Tm^{3+} emission intensity, under 355 nm excitation, as a function of concentration, showing the self-quenching regime.

with a Jobin-Yvon Ramanor U1000 spectrometer, using either a 150 W Xe lamp with a Jobin-Yvon H10-UV monochromator or a infrared diode laser (GaAs:Si, 1 μm CW) as excitation source. The detector was a RCA C31034 photomultiplier tube.

The temperature characteristics were determined using a DTA-50 Shimadzu, with heating rates between 5 and 10°C/min. The apparent activation energy was obtained by the Ozawa method. The refractive index was measured using an Abbe refractometer Model 2WA, and the density by the Archimedean method.

3. Results and discussion

Table 1 shows the physical properties, transition temperatures and kinetic parameters obtained from DTA measurements for the glass matrix AYBCMYb used throughout this work. The glass transition temperature (T_g), at 436°C, for this material is greater than the T_g of the ZBLAN glass, at 280°C [7], broadening the range of specific technological applications. In addition, the glass shows a high stability against spontaneous devitrification, even with an apparent activation energy of 86 kcal/mol. The phonon cutoff frequency of this glass, at 630 cm^{-1}, is appropriate for improving the energy transfer between Er and Tm ions, allowing us to obtain a narrow-line emission in regions of special interest with color tuning by selective excitation.

The electronic transitions that generate the primary colors in rare earth-doped materials are: $^1D_2 \rightarrow {}^3F_4$ for Tm^{3+} at 453 nm (blue), $^4S_{3/2} \rightarrow {}^4I_{15/2}$ for Er^{3+} at 550 nm (green) and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ for Er^{3+} at 655 nm (red). These

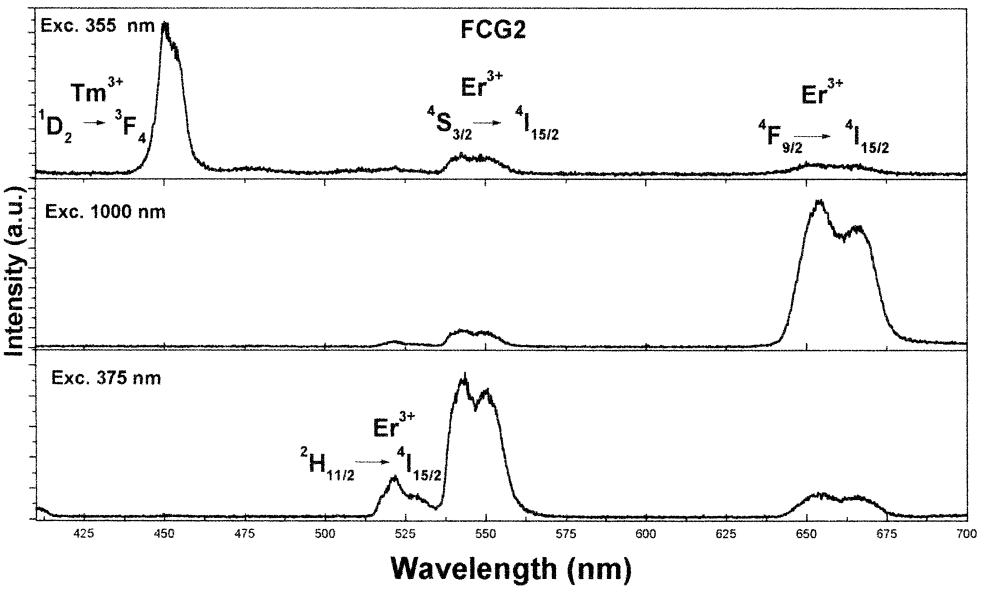

Fig. 2. Luminescence spectra of FCG2 blue, green and red generation under different excitation conditions.

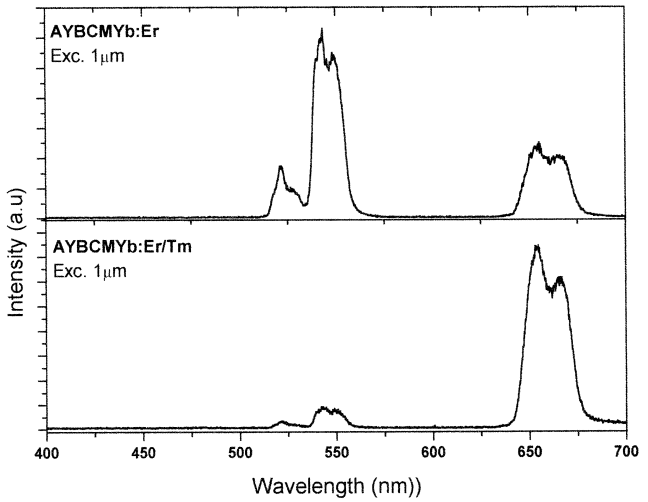

Fig. 3. Up-conversion spectra from the Er^{3+} singly doped glass, compared with the emission in the codoped glass (Er^{3+}–Tm^{3+}). In the second case the red emission is dominant.

transitions appear in strategic positions in the CIE chromaticity diagram, allowing perfect generation of color light for RGB devices.

The maximum concentration of Tm^{3+} must be carefully monitored, in order to avoid self-quenching due to cross-relaxation processes. In this way, the concentration of Er^{3+} is determined after a defined maximum concentration of Tm^{3+}, in order to attain the maximum Tm^{3+} quantum yield, since the Er^{3+} emission is less sensitive to self-quenching processes by cross-relaxation. Fig. 1 shows the self-quenching effect of the Tm^{3+} emission. In this case, the optimal Tm^{3+} concentration is 0.5 mol%. The Tm^{3+} and Er^{3+} concentrations in the AYBCMYb host, for the generation of the primary light and white emission, are 0.5 mol% of Tm and 0.5 mol% of Er. The sample with this composition was named FCG2.

Fig. 2 presents the emission spectrum of the FCG2 glass. The blue color predominates under 355 nm UV excitation, while the green color prevails for 375 nm excitation. The well-know green and blue generation by up-conversion in Er–Yb and Tm–Yb pairs does not takes place in the FCG2 samples. When the sample is excited in the infrared region (1 μm), the generation of red is possible due to the efficient energy transfer process involving Er^{3+} and Tm^{3+} resulting in the suppression of the $^2H_{11/2}\rightarrow{}^4I_{15/2}$ and $^4S_{3/2}\rightarrow{}^4I_{15/2}$ (Er^{3+}) transitions (Fig. 2 (middle) and Fig. 3). A possible mechanism for the dominant energy transfer process is (process 1):

$$^4F_{7/2}(Er),\ ^3H_6(Tm)\rightarrow{}^4F_{9/2}(Er),\ ^3F_4(Tm),\ \Delta E\cong 625\ cm^{-1}$$

(Fig. 4, hollow arrow). This energy gap is quite close to the corresponding phonon frequency associated with the host glass, at 630 cm^{-1}. For this reason, it is necessary only for one phonon to promote the energy transfer between the two ions, allowing this process to take place.

Another quenching mechanism that may be present is represented by the striped arrow in Fig. 4, related to the process (process 2):

$$^4S_{3/2}(Er),\ ^3H_6(Tm)\rightarrow{}^4I_{9/2}(Er),\ ^3F_4(Tm)$$

Although this resonant process could be more efficient, and results in the green luminescence quenching, as the process 1, the process 2 is followed by the red luminescence quenching, while the process 1 (Fig. 4, hollow arrow), increases the population of the $^4F_{9/2}$(Er) level and

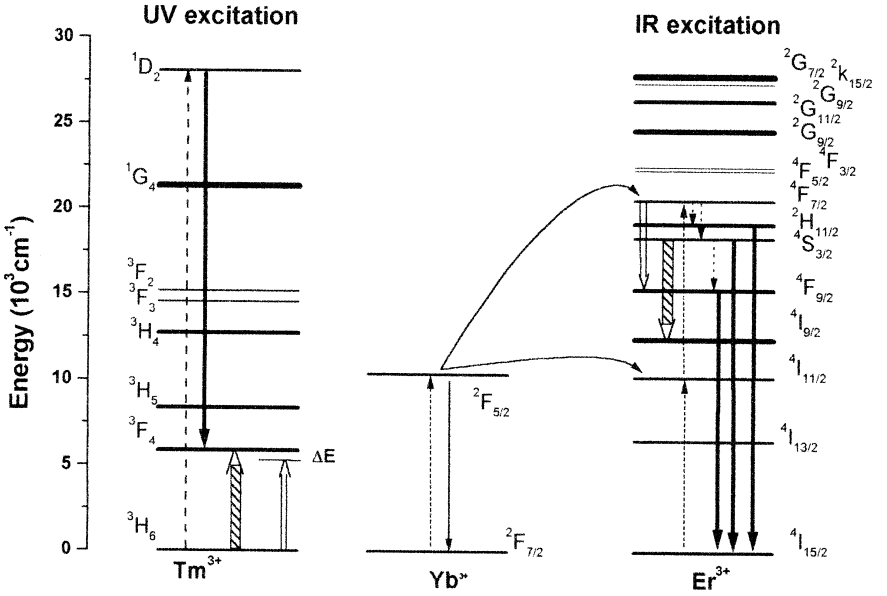

Fig. 4. Schematic diagram of the energy levels of Tm^{3+}, Er^{3+} and Yb^{3+} with the main transitions for RGB generation.

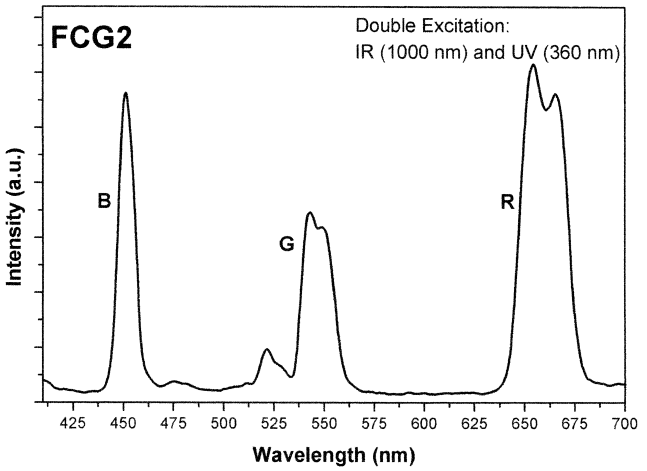

Fig. 5. Luminescence spectra of FCG2. White light simulation is produced when the sample is doubly excited in the ultraviolet and infrared regions.

the red luminescence, in accordance with the results shown in Fig. 2 (middle).

A schematic energy level diagram for Tm^{3+}, Er^{3+} and Yb^{3+} with the main transitions for the RGB generation is shown in Fig. 4.

The white light of the FCG2 glass is obtained by the simultaneous combination of the down-conversion (UV excitation at 360 nm) and up-conversion (IR excitation at 1000 nm) processes. Fig. 5 shows the emission spectrum of the glass which simulates the white emission.

4. Conclusion

The emission spectra obtained for the studied samples are very simplified, presenting well-defined transitions for the red, green and blue emissions and narrow spectral lines.

The three primary light colors generated by the presented glass are in convenient chromatic coordinate for possible applications in high color and spatial resolution devices, and simultaneous excitation with infrared and ultraviolet radiation allows light color tuning without interference in the resulting chromaticity.

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References

[1] J.E.C. Silva, O.L. Malta, G.F. de Sá, P.A. Santa Cruz, J. Lumin. 72/73 (1997).
[2] J.E.C. Silva, O.L. Malta, G.F. de Sá, P.A. Santa Cruz, Química Nova 21 (3) (1998) 372.
[3] J.E.C. Silva, O.L. Malta, G.F. de Sá, P.A. Santa Cruz, in: Proceedings of an International Conference on Science and Technology for Display Phosphors, SID, California, 1997, p. 163.
[4] F. Auzel, Mater. Sci. Forum 67/68 (1991) 489.
[5] D. Dakui, Ma Fundig, J. Non-Cryst. Solids 168 (1994) 275.
[6] A.V. Cardoso, P. Korgul, A.B. Seddon, J. Non-Cryst. Solids 161 (1993) 56.
[7] L.J. Moore, D.R. MacFarlane, P.J. Newmam, J. Non-Cryst. Solids 140 (1993) 159.