Downconversion in Pr$^{3+}$–Yb$^{3+}$ co-doped ZBLA fluoride glasses

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OUTLINE

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- THERMAL PROPERTIES
- OPTICAL PROPERTIES
- ENERGY TRANSFER EFFICIENCIES
- CONCLUSIONS AND PERSPECTIVES
Pr$^{3+}$-Yb$^{3+}$ activated ZBLA GLASS FABRICATION (1/2)

RE doping of the base ZBLA glass

$57\text{ZrF}_4 - 34\text{BaF}_2 - 5\text{LaF}_3 - 4\text{AlF}_3$

is achieved by substitution of $\text{LaF}_3$ by $\text{REF}_3$ and by addition of $\text{REF}_3$ for total doping higher than 5 mol%.

Two series of glasses were fabricated by the melt-quenching technique with the following mol% compositions:

series 1:

$57 \text{ ZrF}_4 - 34 \text{ BaF}_2 - (5-x) \text{ LaF}_3 - 4\text{AlF}_3 - 0.5 \text{PrF}_3 - x \text{YbF}_3$

($x = 0, 1, 2, 3$ and $4.5$)

series 2:

$57 \text{ ZrF}_4 - 34 \text{ BaF}_2 - 4\text{AlF}_3 - 0.5 \text{PrF}_3 - x \text{YbF}_3$

($x = 6, 8$ and $10$).
The fluoride components (purity > 99.9%) for a total of 5g were mixed and melted at 875°C for 10 min in a dry glove box (H₂O = 1 ppm) under inert atmosphere (argon). The temperature was shortly taken to 900°C (5 min) in order to minimize the losses of ZrF₄, the melt was then poured onto a preheated (220°C) brass mold.
### Thermal properties (1/3)

Thermal and optical data for co-doped 0.5Pr$^{3+}$-xYb$^{3+}$ ZBLA glasses: glass transition temperature ($T_g$), crystallization temperature ($T_x$), stability criteria ($\Delta T = T_x - T_g$) and refractive index $n$ at 633 nm. The accuracy is ±1°C for the temperatures and ±0.0005 for $n$.

<table>
<thead>
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<th>$x$ (mol%)</th>
<th>$T_g$ (°C)</th>
<th>$T_x$ (°C)</th>
<th>$\Delta T$ (°C)</th>
<th>$n_{@633\text{nm}}$</th>
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<td>397</td>
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<td>10</td>
<td>335</td>
<td>399</td>
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Vitreous transition temperature Tg and refractive index n @ 633 nm as function of Yb$^{3+}$ concentration for 0.5Pr$^{3+}$-xYb$^{3+}$ co-doped glasses. The dots lines represent visual guides.
Thermal properties (3/3)

- The thermal stability ($\Delta T$) decreases with the Yb$^{3+}$ concentration.

- No crystallization was detected even for high RE doping.

- $T_g$ increases for $x \geq \sim 5$ mol% of Yb$^{3+}$ while it remains nearly the same at lower concentration.

*The decrease in the series 1 is due to the lower refractive index of YbF$_3$ compared with that of LaF$_3$ 1.5238 and 1.5346 respectively at 633 nm.*
Absorption spectrum for the 0.5Pr\(^{3+}\)-1Yb\(^{3+}\) co-doped ZBLA glass and terrestrial solar spectrum (AM1.5); Evolution of the Yb\(^{3+}\): \(^2\)F\(_{7/2}\) \(\rightarrow\) \(^2\)F\(_{5/2}\) absorption coefficient \(\alpha\) as function of the Yb\(^{3+}\) concentration: the slope gives the absorption cross section of Yb\(^{3+}\): \(\alpha_{\text{abs}} = 1.06 \pm 0.02 \times 10^{-20} \text{ cm}^{-2}\).
Energy transfer efficiencies - Down conversion (1/6)

Schematic energy level diagram of Pr$^{3+}$ and Yb$^{3+}$ ions explaining the energy transfer process between the dopants. Two IR photons can be obtained upon absorption of one blue photon via two sequential resonant ET steps from Pr$^{3+}$ to Yb$^{3+}$: Pr$^{3+}$ ($^3P_1 \otimes ^1G_4$); Yb$^{3+}$ ($^2F_{7/2} \rightarrow ^2F_{5/2}$) and Pr$^{3+}$ ($^1G_4 \otimes ^3H_4$); Yb$^{3+}$ ($^2F_{7/2} \rightarrow ^2F_{5/2}$).
Photoluminescence spectra under 440 nm excitation of 0.5Pr$^{3+}$- xYb$^{3+}$ co-doped ZBLA glasses as function of Yb$^{3+}$ content. No effects related to Yb$^{3+}$ content are observed.
The intensity of the emission band of Pr$^{3+}$ at 910 nm decreases down to zero when Yb$^{3+}$ reaches 6 mol%: effective ET from Pr$^{3+}$ to Yb$^{3+}$: Pr$^{3+}$ ($^3P_1 \rightarrow ^1G_4$) ; Yb$^{3+}$ ($^2F_{7/2} \rightarrow ^2F_{5/2}$).

For low Yb$^{3+}$ concentrations, there is a competition between the radiative desexcitation of $^3P_0$ level and ET.

Photoluminescence spectra in the NIR for glasses ZBLA: 0.5Pr$^{3+}$ - xYb$^{3+}$ under 440 nm excitation. The dashed spectrum corresponds to a ZBLA: 0.5 Pr$^{3+}$ glass sample which is not polluted by Er$^{3+}$ impurities. The spectra of the co-doped glasses are normalized to illustrate the effect of photon reabsorption.
Decay curves corresponding to the $^3P_0$ state of Pr$^{3+}$ ions monitored at 478 nm under 440 nm excitation for different Yb$^{3+}$ concentrations. The inset shows the dependence of the average decay time $\tau$ as a function of the Yb$^{3+}$ concentration.

$$E_{TE} = 1 - \frac{\tau_{Pr - xYb}}{\tau_{Pr}}$$
Energy transfer efficiencies - Down conversion (5/6)

Comparison of energy transfer efficiencies with Yb\(^{3+}\) concentration for different 0.5Pr\(^{3+}\)-xYb\(^{3+}\) co-doped hosts: ZBLA, ZLAG and ISBZ fluoride glasses, crystalline CaF\(_2\), K\(_3\)YF\(_{10}\) and YF\(_3\).
Luminescence decay of the Yb$^{3+}$: $^2$F$_{5/2}$ $\rightarrow$ $^2$F$_{7/2}$ emission at 978 nm in Pr$^{3+}$-x Yb$^{3+}$ co-doped ZBLA glasses excited at 440 nm. The non single exponential decay at low Yb$^{3+}$ content is due to the presence of Er$^{3+}$ impurities. The inset shows the dependence of the decay times as function of Yb$^{3+}$ concentration.
Conclusions and Perspectives

- 0.5Pr³⁺-xYb³⁺ ZBLA glasses were prepared with x from 0 to 10 mol%.

- The PL emission in the visible and NIR, decay time of the Pr³⁺: ³P₀ ® ³H₄ and Yb³⁺: ²F₅/₂ ® ²F₇/₂ transitions were measured under blue excitation at 440 nm as a function of the Yb³⁺ concentration.

- Energy transfer from Pr³⁺ to Yb³⁺ was demonstrated in the ZBLA glass and the maximum efficiency for the first step of DC process was estimated to be 86% for 10 mol% of Yb³⁺.

- However the process was found less efficient than in other fluoride hosts (lanthanum fluorozirconate and fluoroidate glasses, KY₃F₁₀ single crystal) although RE dopants are supposed to be randomly distributed.

GLASS CERAMIC SHOULD BE THE SUITABLE ROUTE TO MANAGE ENERGY TRANSFER EVEN AT HIGH RE CONTENT
Acknowledgments

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