Functional Materials

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Spatial distribution of Thulium in Tm^{3+}-doped oxyfluoride glasses and glass-ceramics

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The synthesis of rare-earth (RE) ion-doped oxyfluoride glass-ceramics is a promising way to obtain crystalline phases with very low phonon energies, like LaF_3,[1] $NaLaF_4$,[2] and $NaYF_4$,[3] embedded in a glassy matrix. In such transparent materials, the latter crystal phases act as hosts for the RE ions, thus enhancing radiative optical-emission processes, like up- and down-conversion emissions [4], yet still keeping the good mechanical properties of silicate matrices.

Until now, the verification of the incorporation of RE ions in nanocrystalline phases in glass-ceramics is mainly based on optical techniques, such as luminescence spectroscopy and luminescence decay curves. However, the possibility to perform elemental distribution mappings of RE elements would allow to directly localizing RE ions in the glass and glass-ceramics. Thus, the aim of this work is to complete our previous studies [1], adding unexcelled spatial resolution by using Transmission Electron Microscopy techniques (TEM) and Energy Dispersive X-Ray Spectroscopy (EDXS).

In this work, a glass of composition 55 SiO_2–20 Al_2O_3–15 Na_2O–10 LaF_3 (mol %), doped with 1 mol % Tm_2O_3, and the corresponding glass-ceramic were structurally characterized through TEM, STEM and EDXS (Figure 1). Tm^{3+} ions provide interesting optical properties to the glass, like blue up-conversion emission from the excitation in the near infrared range.

Based on previous works, the elucidation of the LaF_3 nano-crystallisation mechanism in Tm_2O_3 doped-oxyfluoride glass-ceramic has been improved by the application of TEM techniques described in this contribution. The parent glass contains amorphous La- and F-enriched phase separation droplets of ca. 30 nm diameter, also containing Si, Al, and O. The doping ion Tm^{3+} is partly incorporated in the phase-separation regions. Al is present, likely as Al_2O_3, in a thin shell surrounding the droplets. Upon annealing, growth of 10-20 nm LaF_3:Tm crystallites within these phase separation droplets takes place (Figure 1a,c), which are trapped in a volume determined by the size of the preceding phase-separation droplets. The LaF_3 nano-crystals act as host for part of the Tm^{3+} ions (Figure 1c). The remaining volume not occupied by the crystals is filled with Al, while silicon relocates itself towards the periphery (Figure 1b). In this final stage, further crystal growth is inhibited, due to the increase of viscosity in the periphery of the crystals (Figure 2). The possibility to actually being able to map the distribution of Tm in a radiation sensitive sample is well worth mentioning, since it is only made possible through a combination of proper sample preparation, cutting-edge analytical transmission electron microscopy at 80 kV acceleration voltage and, particularly, the application of a dedicated EDXS detector system (FEI Super X). Moreover, thanks to the advance STEM/EDSX analysis it was possible to discern between a thin aluminum layer around the crystals, and a second shell of Si, which inhibit further crystal growth, enabling the nano-crystal size. The verification of the inclusion of Tm^{3+} ions into the LaF_3 structure through EDX elemental mappings is a great advance in the development of rare earth doped glass-ceramics, since it is the key feature of these materials for their application in optical devices.

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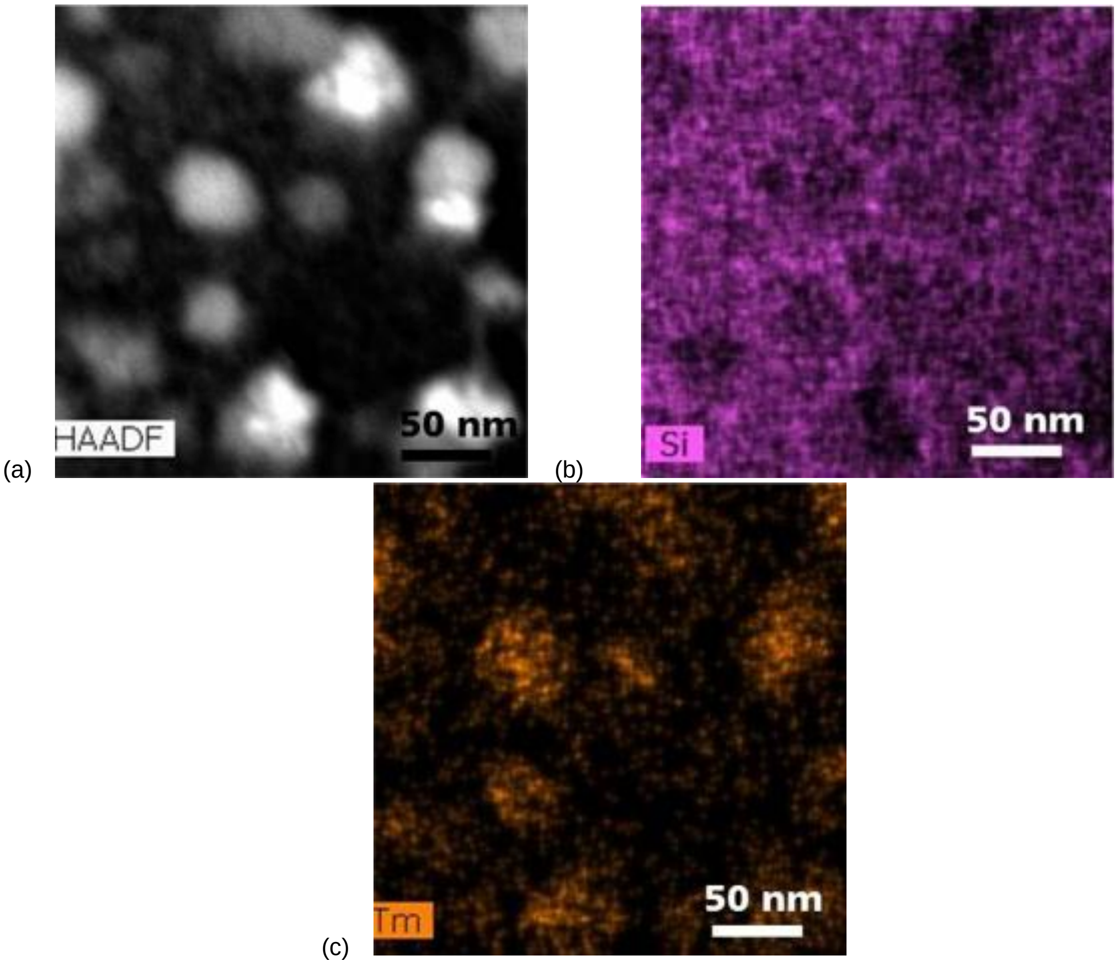

Figure 1. (a) HAADF micrographs taken in STEM mode of the glass-ceramic after annealing at 640 °C for 40 h and the corresponding EDXS mappings of (b) Si, (c) Tm.

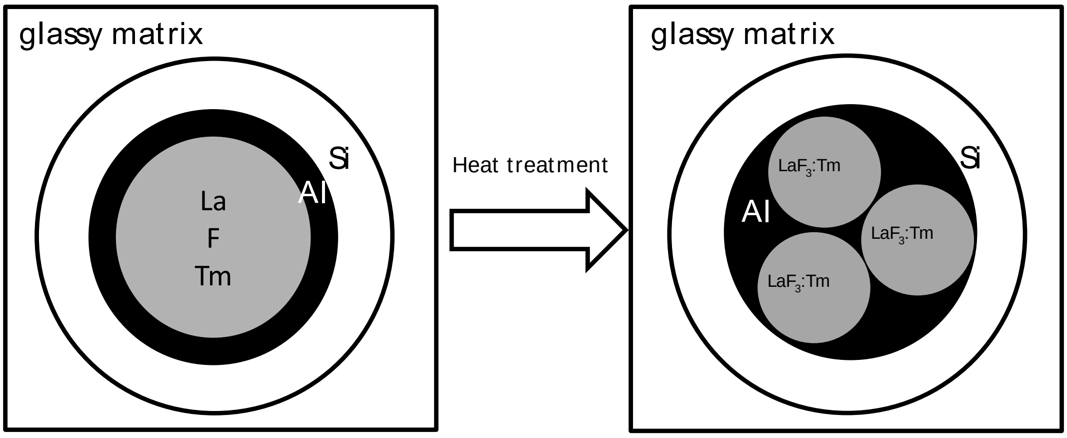

Figure 2. Scheme of the nano-crystallisation mechanism in the studied Tm^{3+} doped glass