
Luminescence of Nd³⁺-doped LaF₃ glass-ceramics enhanced with Ag nanoparticles

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Abstract

Rare earths (RE) doped transparent oxyfluoride glass-ceramics (GCs) have demonstrated to be promising materials for applications in different fields, such as solid-state laser, down and up conversion phosphors or optical amplifiers. These materials combine the low phonon energy (300- 500 cm⁻¹) of fluoride nanocrystals, which are known to be efficient host for RE ions; with the good mechanical, chemical, and thermal properties of the oxide glasses (1-4). The majority of applications using the luminescence of RE ions involve electronic transitions of RE ions between states within a *4f* configuration and the corresponding emission lines cover the entire optical spectrum, from UV (ultra-violet) to NIR (near-infrared). Despite the excellent and encouraging results obtained so far, the intrinsically forbidden-nature of the *4f-4f* transitions is reflected in quite low absorption and emission cross sections and this is an important and fundamental problem still unsolved. Several ways to increase the luminescence efficiency of RE-doped materials for different applications have been summarized recently (5-7). A promising alternative is the use of metallic nanoparticles, such as Ag and Au, to increase the local field strength around the RE ions through the surface plasmon resonance (SPR) produced at the surface of the metallic nanoparticles when excited by light (8,9). Some authors reported an improvement of the photoluminescence of almost 300% in RE-doped glass-ceramics after introducing noble metal nanoparticles (10).

Nd³⁺-doped, LaF₃-based, transparent oxyfluoride glass-ceramics (GCs) containing Ag nanoparticles (NPs) have been prepared by a melt-quenching method. Different Ag-containing precursors were employed being AgNO₃ the most suitable for obtaining Ag NPs segregated in the glassy matrix. Transmission electron microscopy and X-ray absorption spectroscopy determined the presence of Ag⁰ NPs, with higher concentrations in glass-ceramics produced in an inert atmosphere (N2).

The spectral features of emission and excitation spectra, in addition to the different lifetimes of the 4F_{3/2} state in the co-doped samples with Ag NPs, demonstrate the incorporation of Nd³⁺ ions into the LaF₃ nanocrystals. The relative contribution to the emission from Nd³⁺

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in the nanocrystals depends on the Ag concentration and atmosphere. The glass-ceramic co-doped with 0.2 wt.% Ag, thermally treated in N₂, exhibits the highest contribution of emissions attributable to Nd³⁺ ions in the crystalline phase. The crystalline fraction is similar to that of an Ag-free sample synthesized under analogous conditions. This increase of the luminescence is, therefore, attributable to the enhancement of the local electric field of the LaF₃ nanocrystals due to the presence of Ag₀ NPs.

References

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