Formation of nanostructures in Eu3+ doped glass–ceramics: an XAS study

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Lead-aluminosilicate oxyfluoride transparent glass–ceramics doped with RE3+ ions have been revealed to be unique in the field of optical material engineering. This kind of material consists of a beta-PbF2 fluoride nanocrystalline phase in an aluminosilicate glassy amorphous phase. In this way, the macroscopic properties of this material are characteristic of aluminosilicate glass, whereas the spectroscopic properties of the RE3+ ions remain those of low-phonon-energy fluoride crystals. The optical properties of the RE3+ ions, and therefore their interest for photonic applications, depend on the final environment of these ions in a host matrix. Exploration of the local structure of the Eu3+ ions as well as characterization of the amorphous matrix demands structural techniques that do not rely on long range order. Given the complexity of the system under study, chemical selectivity is also required. In this work [1], we describe the results of x-ray absorption experiments carried out to deduce structural and chemical information in Eu3+ doped, transparent, oxyfluoride glass and nanostructured glass–ceramic samples. The spectra were measured at the Pb and Eu-LIII edges. The Eu environment in the glass samples is observed to be similar to that of EuF3. Complementary x-ray diffraction experiments show that thermal annealing creates beta-PbF2 type nanocrystals. X-ray absorption indicates that Eu ions act as seeds in the nanocrystal formation. There is evidence of interstitial fluorine atoms around Eu ions as well as Eu dimers. X-ray absorption at the Pb-LIII edge shows that after the thermal treatment most lead atoms form a PbO amorphous phase and that only 10% of the lead atoms remain available to form beta-PbF2 type nanocrystals. Both x-ray diffraction and absorption point to a high Eu content in the nanocrystals. Our study suggests new approaches to the oxyfluoride glass–ceramic synthesis in order to further improve their properties.


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