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CRYSTALLIZATION PROCESS IN OXYFLUORIDE NANO-GLASS-CERAMICS DOPED WITH NEODYMIUM IONS

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Oxyfluoride nano-glass-ceramics doped with neodymium ions have been developed and synthesized. The precipitation of crystalline phase in neodymium nano-glass-ceramics after heat treatment has been experimentally investigated. The neodymium ions are incorporated into the nanosize crystalline phase of $PbY_{(1-x)}Nd_{(x)}OF_3$.

Keywords: x-ray diffraction, crystalline phase, glassceramics.

1. Introduction

Transparent nano-glass-ceramics doped with rare earth ions (Er, Eu, Tm, Nd, and Pr) are of the great interest for photonics. They occupy an intermediate state between glasses and crystals. The thermal and mechanical properties of glass-ceramics are superior to those of the parent glass while having spectral and luminescence characteristics that are similar to crystal analogues [1, 2]. Rare-earth ions (REI) in a fluoride environment have lower phonon energies, especially in the case of heavy metal fluoride glasses (HMFG). REI in this type of oxygen-free environment have a lower probability of non-radiative excitation relaxation, thus leading to an increase in the luminescence quantum yield in comparison with the case of the oxygen environment [3]. Therefore the transparent fluorine-containing nano-glass-ceramics doped with rare-earth ions are promising media for up-conversion lasers and broadband optical amplifiers.

2. Results and Discussion

Included in this report are studies of the precipitation of crystalline phases in oxyfluoride nano-glass-ceramics and a survey of their spectral and luminescence properties.

2.1. Sample Preparation

Samples of parent glasses were prepared with the following composition: $30SiO_2$–$15AlO_{3/2}$–$29CdF_2$–$18PbF_2$–$5ZnF_2$–$x$$NdF_3$–$(3-x)YF_3$, where x varied from 0 to 3.0 mol%. The parent glass was synthesized in an alumina cup at 1050 °C under an argon atmosphere. Tg was determined using simultaneous thermal analysis (Netzsch STA 449). To obtain transparent nano-glass-ceramics the glass samples were heated in an electric muffle furnace at 500 °C for 120 minutes. Experimental diffraction patterns were obtained using the wavelength of CuKα = 1.5418 Å(X-ray diffractometer Rigaku Ultima IV).

2.2. X-ray and Spectroscopic Investigations

The heat treatment resulted in the precipitation of crystalline phase in the glass matrix. X-ray diffraction (XRD) and simultaneous thermal analysis (DSC) observation of nano-glass-ceramics doped with 3 mol% yttrium revealed the precipitation of $PbYOF_3$ crystallites [4]. The volume crystallization was accomplished after 120 minutes of thermal treatment. The size of the crystals was determined by Sherrer's equation:

$$l = \frac{K^* \lambda}{\beta^* \cos\theta}.$$

The precipitated crystals were approximately 20 nm in size. The lattice constant was equal to 5.74 Å.

The introduction of neodymium ions qualitatively changes the character of glass crystallization. The XRD analysis of nano-glass-ceramics doped with NdF3 in concentration from 0.1 to 2.9 mol% revealed that the crystalline phase was of the composition $PbYOF_3$ (fig. 1). Thus, the secondary heat treatment of the parent glass resulted in the growth of a crystalline phase of the same chemical composition, which was independent from the dopant concentration.

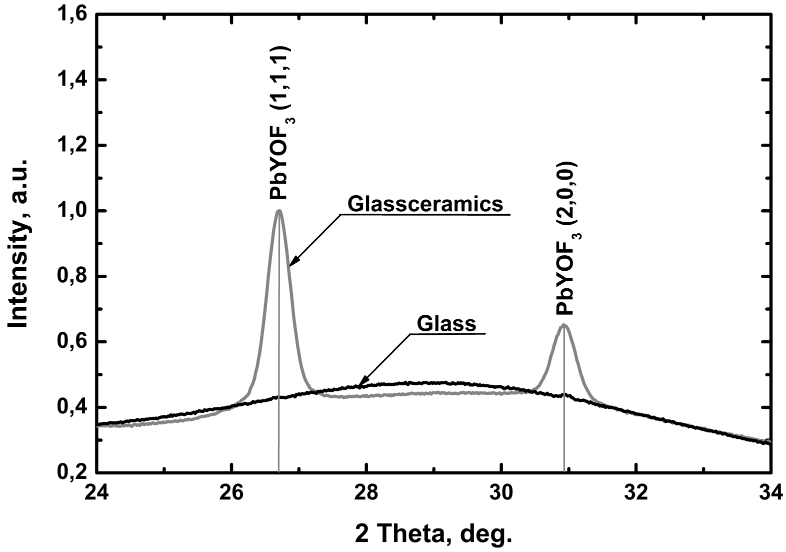

FIG. 1. X-ray diffraction patterns of virgin glass and glassceramics doped NdF_3 of 0.5 mol% after thermal treatment for 120 minutes

The increasing the heating time did not lead to a meaningful increase in the nanocrystalline phase size. These small sizes appreciably reduced the level of light scattering in heterogeneous nano-glass-ceramics. The high transmittance of nano-glass-ceramics and its homogeneity make it a good candidate for use in optical applications.

Nano-glass-ceramics doped with 3 mol% NdF_3 revealed the precipitation of ca. 25 nm NdF_3 crystallites (fig. 2). Increasing the neodymium concentration resulted in an increase of the lattice constant from 5.74 up to 5.84 Å(fig. 3).

The lattice constant depended on the concentration of neodymium ions because of the yttrium and neodymium ratio in the crystalline phase. Two different linear parts of the lattice constant dependence are explained by the precipitation ratio of $PbY_{(1-x)}Nd_{(x)}OF_3$ and $PbYOF_3$ crystalline phases.

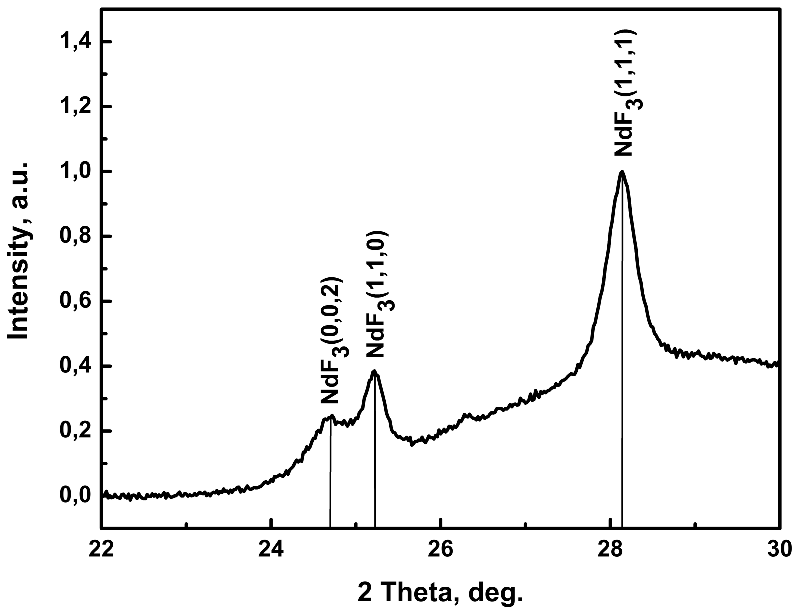

FIG. 2. X-ray diffraction patterns of virgin glass and glass-ceramics doped with 3 mol% NdF_3 after 120 mins thermal treatment

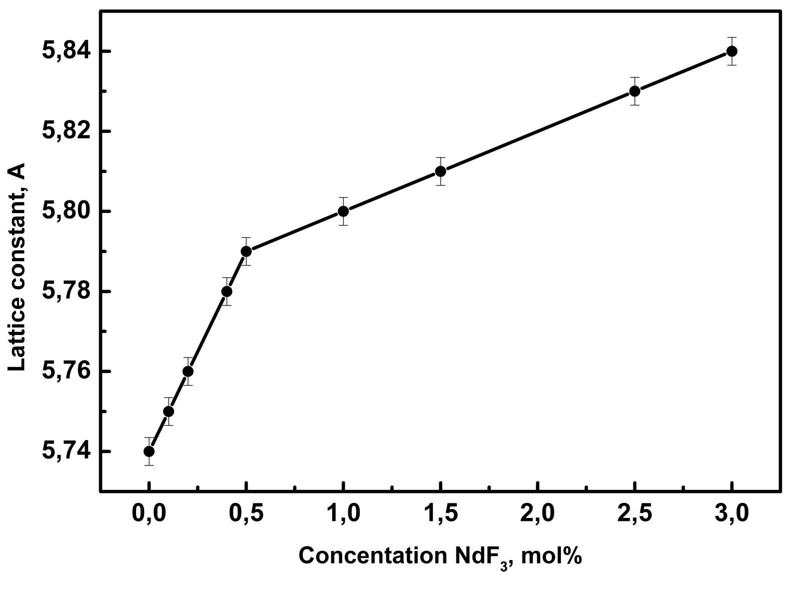

FIG. 3. Relationship between lattice constant and neodymium ions concentration

Thermal treatment results in the appearance of the fine Stark structure in luminescence spectra (fig. 4). The combination of spectral and fluorescent measurements with the XRD and DSC analysis allowed us to conclude that neodymium ions are incorporated into the crystalline phase of $PbY_{(1-x)}Nd_{(x)}OF_3$.

3. Conclusion

The oxyfluoride nano-glass-ceramics doped with neodymium ions have been developed and synthesized. The precipitation of crystalline phases of $PbY_{(1-x)}Nd_{(x)}OF_3$ and $PbYOF_3$ in

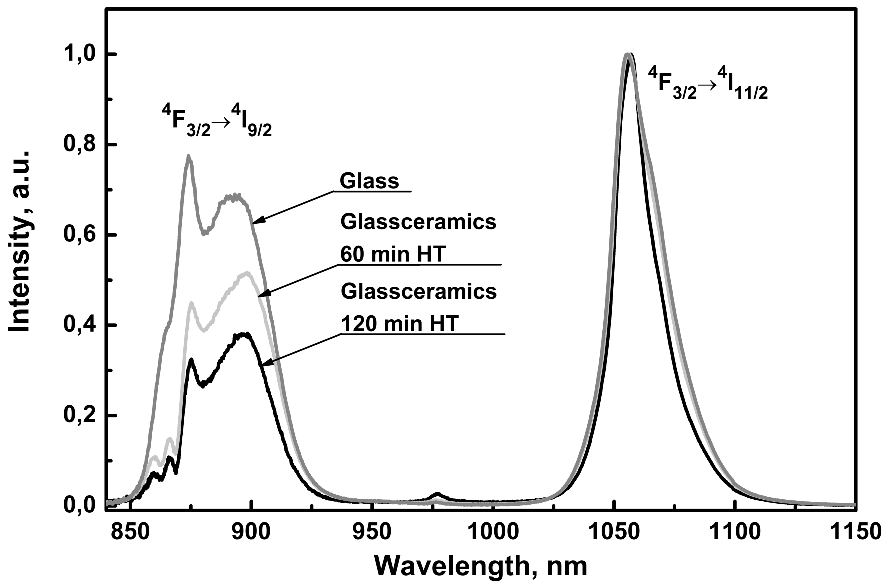

FIG. 4. Luminescence spectra of parent glass and glassceramics after heat treatment

the glass host after heat treatment has been experimentally investigated. The neodymium ions are incorporated into the nanosize crystalline phase of $PbY_{(1-x)}Nd_{(x)}OF_3$. The size of crystalline phase achieves to 30 nm. The lattice constants of nanocrystals were shown to be dependent upon the concentration of neodymium ions.

Acknowledgments

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