Spectroscopic study of femtosecond laser irradiated GeO_2–PbO–PbF_2 glass doped with Pr^{3+} and Yb^{3+}

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The influence of femtosecond laser irradiation on the photoluminescence and vibrational spectra of oxyfluoride glasses doped with lanthanides were studied. The examined glasses were made of germanium oxide GeO_2 (99,998%), lead oxide PbO (99,99%), lead fluoride PbF_2 (99,997%) and anhydrous fluoride of rare earth ions (1% Pr^{3+} and 5% Yb^{3+}). Substrates were mixed and then melted in platinum crucible at 1000° C for 15 min in normal atmosphere. The liquefied glass mixture was poured into preheated copper form where the samples were finally shaped. The reference sample was left unchanged, while the other was irradiated with 300nm femtosecond laser.

Both micro-Raman and photoluminescence measurements were performed at room temperature with the help of the T64000 Jobin-Yvon spectrometer configured in backscattering geometry and the single mode of operation equipped with a multichannel CCD camera (illuminated spot ~1μm). The samples were excited by an Ar^{2+} laser working at a wavelength of 514.5 nm. Raman spectra were measured within the range of 50-1500cm^{-1} whereas the emission spectra from 515nm to 900nm.

Raman spectra of irradiated glass sample exhibit sharp and narrow peaks at 491cm^{-1} and 709cm^{-1} whereas those of reference sample show broad maxima. According to [1], these peaks were assigned to one of the crystalline forms of the PbO-GeO_2 system. A small peak at 190cm^{-1}, which originates from crystallization process as well, was also observed.

The photoluminescence spectra of the irradiated samples show noticeable difference with respect to the reference sample within the wavelength range of 530-620nm. Sharp peaks related to the $^3P_0 \rightarrow {}^3H_5$ (530-565nm), $^3P_0 \rightarrow {}^3H_6$ (600-610nm) and $^1D_2 \rightarrow {}^3H_4$ (598nm) transitions emerged.

Femtosecond laser irradiation induced changes in the glassy structure of GeO_2-PbO-PbF_2 system doped with rare-earth ions. In particular, it led to the local crystallization of the amorphous structure, thereby offering a way to provide sophisticated materials for a wide range of applications, including waveguides, 3D optical data storage and optical switches.

[1] V.N. Sigaev, I. Gregora, P. Pernice, B. Champagnon, E.N. Smelyanskaya, A. Aronne, P.D. Sarkisov *Journal of Non-Crystalline Solids* **279** 136-144 (2001).