Glasses and glass-ceramics based on TeO_2 for potential luminescent applications

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Tellurite glasses TeO_2-ZnO-Na_2O-RE_2O_3 (RE= La, Gd, Y) (where RE= Y, La, Gd) as well as glass-ceramics, doped with lanthanide and Ni^{2+} ions are the subject of this dissertation. The goal of the doctoral dissertation was to explain relaxation of excited states and energy transfer mechanisms in tellurite glasses and glass-ceramics. These materials have been tested for potential luminescent applications such as: visible light phosphors, lasers, shortwave radiation converters, optical temperature and pressure sensors, luminescent materials for converting sunlight into electricity.

The title glasses were prepared by the melt-quenching technique. Subsequently, as a result of crystallization process, transparent glass-ceramics containing $ZnTeO_3$ and $La_2Te_4O_{11}$ nanocrystals were obtained for the first time. The crystallization process was controlled by thermal analysis techniques (TGA-DTA), transmission electron microscopy (TEM) and powder X-ray diffraction (XRD). There are significant differences in the luminescent properties of the glass-ceramic compared to the amorphous material.

The Judd-Ofelt theory has been applied to absorption spectra analysis and the quantitative determination of the $4f \rightarrow 4f$ transition intensities. From the evaluated Judd-Ofelt parameters Ω_λ (λ= 2,4,6), the radiative transition probabilities (A_R), luminescence branching ratios (β_R) and radiative lifetimes (τ_R) were calculated. The calculated luminescent parameters were used as a basis of interpretation of emission spectra, relaxation of excited states and energy transfer mechanisms. The spectroscopic parameters have been shown that title glasses fulfil requirements for laser materials.

The CIE chromaticity coordinates and colour purities (*CRI*) were determined based on visible emission spectra of glasses and glass-ceramics. The emission colour of Pr^{3+}- doped glasses is dependent on activator concentration. The emission colour of Tm^{3+}- doped glasses is dependent on excitation wavelength.

The concentration quenching processes have been characterized based on the results of kinetic measurements. The luminescence decay curves have been analysed using Inokuti-Hirayama and Yokoto-Tanimoto models. The energy transfer microparameters: donor–acceptor (C_{DA}) and donor–donor (C_{DD}) interactions and critical distance (R_0) have been determined. The obtained results indicate that the depopulation of Ln^{3+} excited states is based on the cross-relaxation and energy migration. The relaxation mechanisms of excitation energy from the first excited states of Ln^{3+} (Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}) have been determined. It has been shown that self-quenching and reabsorption processes play a fundamental role in the population of these electronic states.

The presented materials have been successfully tested to convert UV-Vis light to NIR radiation. The quantum cutting process and rarely reported emission from the $^1G_4$ level in oxide materials have been demonstrated in Pr^{3+}-doped glasses. The energy transfer $Ni^{2+} \rightarrow Yb^{3+}$ was observed for the first time, which has not been reported in the literature. The luminescence and excitation spectra of glasses revealed the presence of bands arising from electronic transitions of Te^{4+}. Glasses and glass-ceramics doped with Pr^{3+}, Yb^{3+} and glassed doped with Ni^{2+}, Yb^{3+} have been indicated as materials, improving sunlight-to-electricity conversion efficiency.

The effect of temperature on relaxation processes of excited states of glasses and glass-ceramics has been described. The anomaly changes in lifetimes of the $^1D_2$ level as a function of temperature were noticed for Pr^{3+}- doped glasses in the temperature range of the glass transition. Glasses and glass-ceramics doped with Nd^{3+} and Er^{3+} can be regarded as potential optical temperature sensors. Thermal quenching of luminescence of $^4F_{9/2}$ level was observed for Dy^{3+}- doped tellurite glass. This phenomenon has been explained by quenching mechanism caused by electronic states of matrix.

The linear relationship between luminescence intensity and pressure was observed for the first time in Pr^{3+}- doped glasses. Preliminary results of spectroscopic studies of Pr^{3+}- doped glasses show that they can be attractive materials for applications as vacuum gauges.