Synthesis and optical properties of luminescent molybdate glass-ceramics

V.P. Chornii [1,2,*], S.G. Nedilko [1], K.V. Terebilenko [1], M.S. Slobodyanik [1], P.O. Teselko [1], V.V. Boyko[2], O.P. Pan'ko[2]

1 Taras Shevchenko National University of Kyiv. Volodymyrska st., 64/13, Kyiv-01601, Ukraine
2 National University of Life and Environmental Sciences of Ukraine. Geroiv Oborony st., 15, Kyiv-03041, Ukraine
**corresponding author e-mail: vchornii@gmail.com*

Motivation

The transparent glass-ceramics (GC) attract great attention due to necessity to substitute silicone-based phosphor converters for manufacturing of high-power white light emitting diodes. This kind of composite materials possesses the host property like glass and retains the optical performance of micro/nanocrystaline phosphors. The latter ones are actively elaborated on the base of doped with rare-earth ions molybdate and phosphate compounds. It can be assumed that the glass and crystalline constitutes should have similar refractive indices in case of their similar chemical composition. Consequently, the GC should have higher optical homogeneity and possess small internal light scattering when both components have similar chemical nature. Moreover, this light scattering can be lower when the nanosized phosphors are used in GC. This work deals with synthesis and optical characterization of transparent luminescent phosphate-molybdate glass and glass-ceramics.

Samples and methods

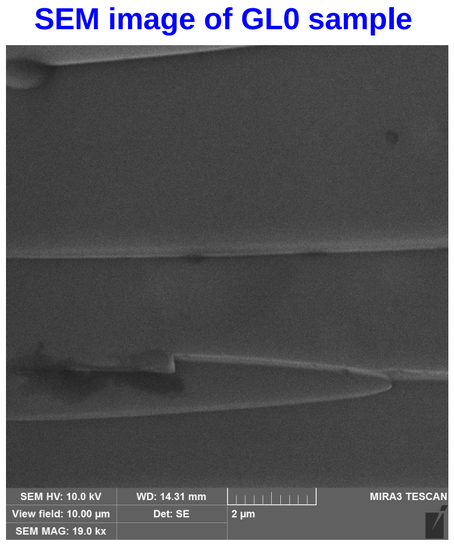
The sets of pure and Eu^{3+}-doped glasses of $37.09K_2O$-$31.79P_2O_5$-$25.43MoO_3$-$5.69Bi_2O_3$ composition have been prepared by conventional melt quenching technique. The glass-ceramic samples consisting of abovementioned glass and micro/nanophosphor were prepared by adding of low amount of oxide into melt. The samples were abbreviated as :

1) GL0 – starting glass of abovementioned composition;
2) GLxEu = ($37.09K_2O$-$31.79P_2O_5$-$25.43MoO_3$-$5.69Bi_2O_3$):x% Eu
3) GCxPrKBM = GL0 + x % KBi0.99Pr0.01(MoO4)2
4) GCxEuKBM =GL0 + x % KBi0.99Eu0.01(MoO4)2

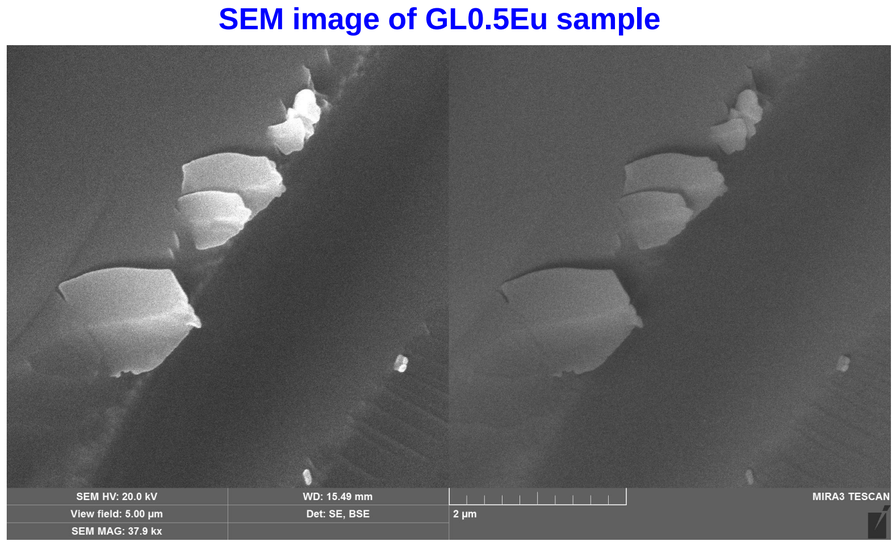
The samples have been characterized by means of scanning electronic microscopy (SEM), X-ray powder diffraction (XRD), differential thermal (DTA) and thermogravimetric analysis (TG), and photoluminescence (PL) spectroscopy.

Experimental results

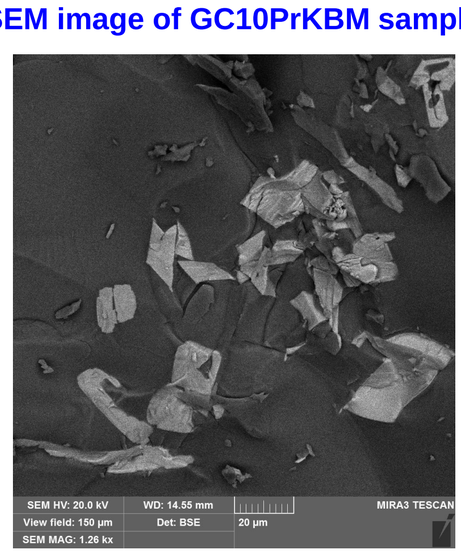
SEM image of GL0 sample



SEM image of GL0.5Eu sample

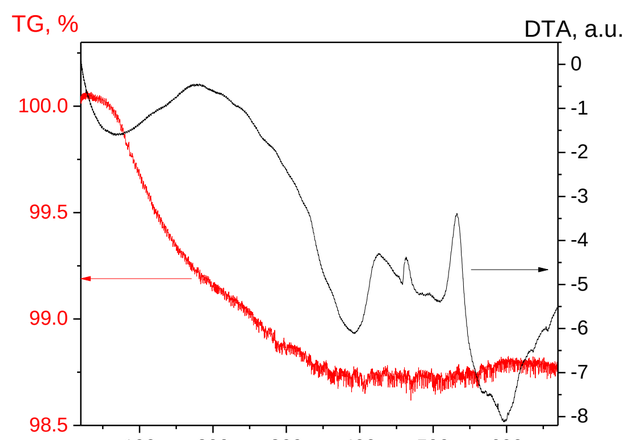


SEM image of GC10PrKBM sample



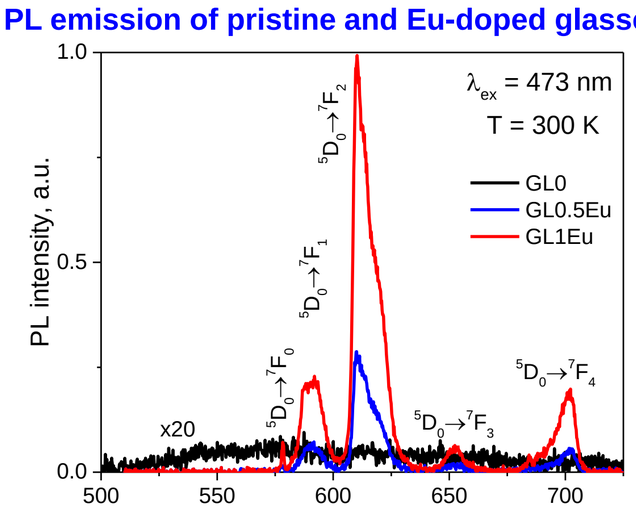
1) Homogeneous regions correspond to amorphous (glass) phase. 2) Wave-like formations and crests are chipped region of glass. 3) Inclusions in GC1PrKBM sample correspond to phosphor component

TG and DTA measurements for GL0 sample



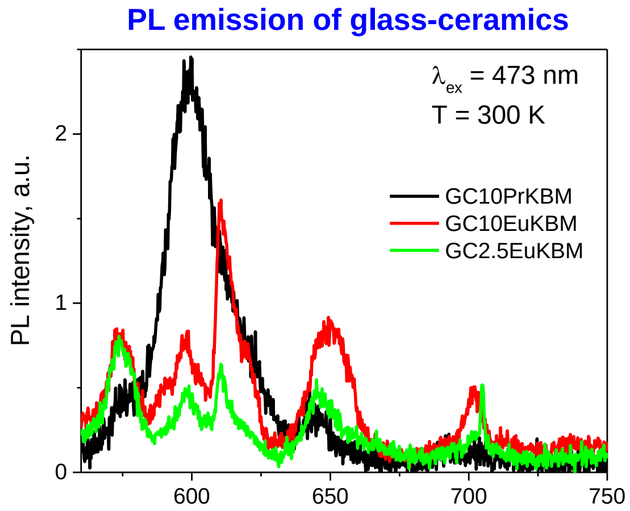
1) Mass loss up to 350 °C related with water evaporation.
2) Glass transition temperature estimated as 390 °C.
3) Peaks on DTA curve at 463 and 531 °C correspond to crystallization of bismuth phosphates.
4) Melting of system appears at 600 °C.

PL emission of pristine and Eu-doped glasses



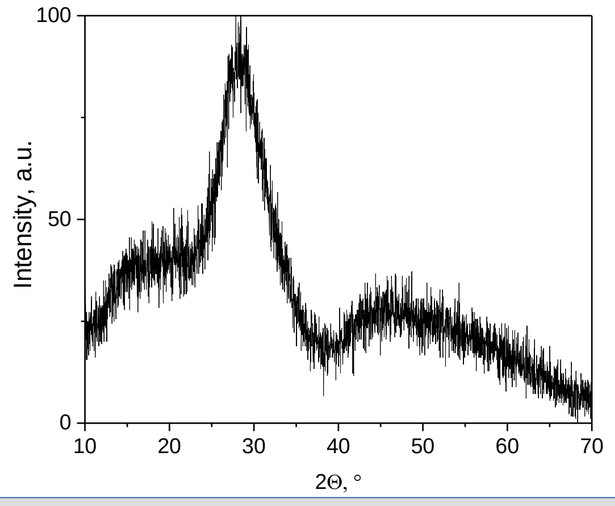
1) Luminescence spectra of undoped glass reveal wide band with two component maxima at 560 and 620 nm.
2) Doping of GL0 with Eu^{3+} substantially increases intensity of luminescence for case of PL excitation into absorption band of 7F0→$^5D_2$ (473 nm) transition in Eu^{3+}

PL emission of glass-ceramics



1) Luminescence spectra of GC with Pr-containing oxide reveals wide bands related with transitions in Pr^{3+} ions.
2) Bands in PL spectra of GC with Eu-containing oxide related with $^5D_0 \rightarrow {}^7F_J$ (J = 0 - 4) transitions in Eu^{3+} ion.
3) Redistribution of intensity of PL bands take place with change of content of Eu^{3+}-doped oxide

XRD measurements for GL0 sample



The XRD pattern indicates a presence only amorphous phase in GL0 sample

Comments and Conclusions

1) Set of bismuth-containing phosphate-molybdate glasses and glass-ceramics have been prepared by melt quenching technique.
2) XRD and SEM studies reveal the absence of crystallized regions in as-prepared glasses.
3) The presence of wave-like and crest structures on SEM images indicate an anisotropy of the studied glasses.
4) Obtained samples possess relatively low glass transition temperature and small water-affinity but, in the same time, they are subject to crystallization.
5) Doping of studied glass with only 1 wt % of Eu^{3+} ions increases the luminescence intensity of studied glass in about 2 orders.
6) The energy transfer from glass host absorption centers to Eu^{3+} ions may took place but this issue requires further studies.
7) The band peaking at 600 nm in PL spectra of the GC10PrKBM sample is related with superposition of emission lines of $^1D_2 \rightarrow {}^3H_4$ and $^3P_0 \rightarrow {}^3H_6$ transitions in Pr^{3+} ions.
8) The samples of GCxEuKBM series indicate effect of oxide content on PL spectra of studied glass ceramics.
9) Line broadening may be due to Eu^{3+} and Pr^{3+} ions migration from surface region of oxide to glass region during glass-ceramics preparation.

8th International Conference "Nanotechnology and Nanomaterials" (NANO-2020), 26 - 29 August 2020 , Lviv, Ukraine