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Photoluminescence of ZnO-aggregates in oxide glasses

M. Nikl [a,*], J. Pejchal [a], R. Jinhua [b], J. Zhang [b], G. Chen [b],
A. Beitlerova [a], A. Yoshikawa [c], T. Fukuda [c]

[a] *Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnicka 10, 16253 Prague, Czech Republic*
[b] *Department of Inorganic Materials, East China University of Science and Technology, 200237 Shanghai, China*
[c] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan*

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Abstract

Photoluminescence spectra and decay kinetics at room temperature were studied at the set of ZnO-containing mixed-oxide glasses of various compositions. The dominant broad emission band peaking round 390 nm is observed in most of the glasses regardless of their chemical composition. This emission is ascribed to the ZnO-aggregates originating both in their volume and at the interface with the glass host.

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1. Introduction

ZnO compound is under systematic attention and broad-scale research interest due to various foreseen applications in the field of UV light sources, transparent conductive films, but e.g. also surface acoustic wave devices, for recent review see [1]. Furthermore, its subnanosecond exciton-based emission in near UV was considered interesting to be used in superfast scintillators [2]. It can be prepared in the form of bulk single crystals [3,4], thin films [5] or various nanostructures [6]. Recently, also the luminescence of ZnO nanocrystals in a borosilicate glass matrix was reported and ZnO content in the melt was achieved up to 60% without any devitrification effects [7]. Embedding of ZnO nanocrystals in a glass matrix can help to stabilize their luminescence properties largerly influenced by the surface/interface of the nanoparticles, which in a free standing form can be easily attacked e.g. by humidity [8]. Flexible composition of the glass can help to modify the ZnO nanoaggregate characteristics by the doping or mixing e.g. with MgO or CdO, which is mentioned in the literature in the band-gap engineering of ZnO [9,10]. Apart from the surface (interface) states, the doping by donor or acceptor impurities can provide in ZnO-aggregates in a glass host the tool for the shift of the (trapped) exciton emission peak and also the radiative lifetime of the emission can be widely tuned in such a way [11].

It is the aim of this paper to continue the study of luminescence characteristics in the ZnO-containing oxide glasses. Namely, the influence of the glass matrix composition on the emission properties of the ZnO phase is systematically investigated.

2. Experimental

The starting materials for glass preparation include reagent grade SiO_2, GeO_2, BaO, Al_2O_3, SnO_2, H_3BO_3 and ZnO. The appropriate components were carefully mixed in the intended proportion and melted in the

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[*] Corresponding author. Tel.: +420 220318445; fax: +420 233343184.
E-mail address: nikl@fzu.cz (M. Nikl).

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Table 1
Composition of the melt of the glasses prepared

Sample no.	SiO_2 (%)	ZnO (%)	BaO (%)	B_2O_3 (%)	Al_2O_3 (%)	SnO_2 (%)	GeO_2 (%)
43	55	25	20				
47	35	45	20				
53	33	35	20	12			
54	31	35	20	14			
59	35	35	20		10		
65	45	35	12			8	
72		50	10	40			
75	20	58		20	2		
80		50	10				40

alumina crucibles in the electric furnace at the temperature about 1350 °C for 5–6 h. After melting, glass melts were put into the preheated steel moulds for quenching in air and annealed in an electric oven at 500 °C for 1 h to release the internal thermal stress. Then the annealing oven was turned off until the samples were finally cooled down to room temperature. Glass compositions prepared for this study are summarized in Table 1. Glass samples were cut and polished in the form of plates of 7 × 7 × 1 mm. At room temperature (RT) the measurements of photoluminescence spectra and decay kinetics were performed by a Spectrofluorometer 199S (Edinburgh Instruments). Excitation was performed by the steady-state (for spectra) and ns-pulsed (for decays) hydrogen-filled flashlamps. Absorption spectra at RT were measured at UV/VIS/NIR Shimadzu spectrophotometer UV-3101PC. Luminescence spectra were corrected for experimental distortions. Exponential approximation of the decays was obtained by performing the convolution of the considered function with the instrumental response and the least-square sum fitting procedure was used (Software package Spectrasolve from LASTEK Ltd.).

3. Results and discussion

In Fig. 1 the absorption spectra of the glass samples from Table 1. are given. In most cases the absorption edge is situated below approximately 350 nm with a steep increase of the absorption below 280 nm. In the transparency region there is no sign of color centers or another well-shaped absorption bands. However, one can distinguish rather different steady value of the absorption in the transparency region, which is related to the optical homogeneity and presence of scattering centers in the material. While the glasses G43, 47, 53 and 59 show almost negligible absorption losses above 350 nm, G54, 72 and 75 show an intermediate quality and the last two samples, G65 and especially G80 show pronounced absorption losses within 1 mm optical pass in the samples.

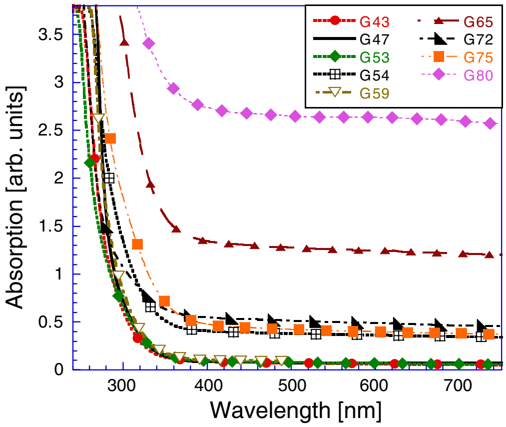

Fig. 1. Absorption spectra of the glass samples from Table 1 at RT.

Luminescence spectra in Fig. 2 show in the most of the samples wide band round 390 nm, which is in the case of G65 and G80 samples accompanied or even overcome by an emission at lower energies. Excitation wavelength was set at 265 nm, which is close to the excitation spectra maximum of ZnO-related luminescence in borosilicate glasses [7]. It is worth noting the following features in the samples with the dominant 390 nm emission: (i) similar band shape is obtained for the samples G43, 72 and 75 (Fig. 2a) despite of rather different chemical composition of the other-than-ZnO components; (ii) comparatively more different spectral shape is observed for rather similar-in-composition G53 and 54 samples (Fig. 2b). X-ray excited luminescence spectrum of an hydrothermally-grown ZnO single crystal [3] at RT is given in Fig. 2a as well. ZnO shows the excitonic emission round 390 nm and a wide defect-originated band round 530–600 nm, which is commonly observed spectral pattern in bulk ZnO and there is no unique interpretation for the defect origin [1,12]. It is interesting to note that the latter emission band is practically absent in most of the glass samples.

Photoluminescence decay was measured at 390 nm under the nanosecond pulse excitation at 265 nm. The example of the decay curve approximated by a three-exponential function $I(t)$ is given in Fig. 3. Three decay times of about 4 ns, 66 ns and 290 ns were obtained with relative intensities of about 1%, 9% and 90%, respectively. At two samples (G43 and G72) the decay was measured at several wavelengths between 340 and 500 nm and similar approximations were made as in Fig. 3. The decay time of the slowest (and most intense) component is plotted against the emission wavelength in Fig. 4 for G43 sample and shows smoothly increasing decay time value with the increasing wavelength.

In some of the boron or aluminium containing samples the fastest component of about 1 ns decay time became much stronger and constituted up to 5–10% of total emission intensity—Fig. 5.

It is feasible to ascribe the observed emission round 390 nm to the ZnO-like aggregates and broader character of the band could be explained by the quantum size effect and/or the emission of exciton trapped around the interface, doped-ion or defect states, which can contribute at both the high and low energy side of the spectra [9–11]. It is worth noting that e.g. exciton localization round deep