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Photoluminescence of undoped and B-doped ZnO in silicate glasses

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Abstract

Photoluminescence of undoped and B-doped ZnO in silicate glasses was investigated by varying the concentration of ZnO (35–50 mol%) and B dopant (0–10 mol%) in the glass matrices. The broad and intense near band edge emissions were observed while the visible light emission was very weak. UV luminescence in all samples was red-shifted relative to the exciton transition in bulk ZnO and enhanced by decreased ZnO concentration due to higher degree of structural integrity and the lower aggregation degree of ZnO. Donor B dopant played the double roles of filling conduction bands to broaden band gap when its concentration was lower than 5 mol%, and emerging with conduction bands to narrow the gap when B dopant exceeded this value.

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1. Introduction

As an important ceramic material as well as a wide band gap semiconductor, zinc oxide (ZnO) has shown many technological applications, for examples, in gas sensors, catalysis, solar cells, transducers, and varistors [1]. Recently, much attention moves to its potential applicability to optoelectronic devices such as light-emitting and laser diodes which are based on its amplified spontaneous fluorescence and laser emission covering a wide visible region due to its large band gap [2–4]. At the same time, the strong near band gap excitonic emission with the sub-nanosecond lifetime in ZnO is also of interest for superfast scintillators [5]. Since ZnO has the large exciton binding energy (60 MeV), it permits making excitonic effects more pronounced even above the room temperature so as to be more favorable for exciton-related device applications [3].

A great deal of research has been reported on the synthesis and fabrication of ZnO films, powders and ceramics using various novel techniques [2–4,6]. On the other hand, little attention has been paid on ZnO existing in the glass matrix. As the matter of fact, using glass as an alternative to crystal for many applications is an attractive solution since the glasses can be fabricated much easier with the lower cost which is of special significance for the huge scintillating detectors for the applications in high energy physics [7–9].

In the present work, the ternary ZnO–SiO_2–BaO and the quaternary ZnO–SiO_2–BaO–B_2O_3 glasses are studied as the scintillating materials for the first time. Although comprehensive studies have been performed on the scintillating glasses in the last decade, scintillators based on the emission of ZnO quantum dots in a glass matrix is a new approach [7]. Compared with the popularly researched Ce^{3+}-doped fast scintillating glasses, ZnO excited glasses offer unique advantages of even faster decay time and the possibility of introducing much higher concentration of exciters. The latter is due to the role of ZnO as an

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intermediate in glass network [7], thus, the microstructure of glasses might be refined and/or adjusted more easily to realize the improved functional properties.

2. Experimental

Glass samples were prepared using the direct melt-quenching synthesis method with the glass compositions as shown in Table 1. SiO_2 is the main component acting as the network former, and BaO is the network modifier beneficial to increase density of the glass, the latter is requested for high energy physics application due to desire of higher radiation hardness [6]. B was added as the donor that often exerts dramatic influence on electrical and optical properties of wide band gap semiconductors [3]. While, as the network former, B_2O_3 plays the same role of SiO_2 to stabilize the glass structure so as to be introduced by substituting the same amount of SiO_2. Zinc oxide was used as both the main component of the matrix and the emission exciters with the concentration ranging from 35 to 50 mol%.

Reagent grade SiO_2, $BaCO_3$, ZnO and H_3BO_3 were used as the starting materials. They were carefully weighed and mixed, and melted in corundum crucibles in an electric furnace at a temperature of 1400 °C for about 3 h. The glass melts were put into the preheated steel moulds for quenching in air and annealed in an electric oven at 500 °C for 1–1.5 h. Then the annealing oven was turned off until the samples were finally cooled to room temperature. Glass samples were prepared and polished for measurements of photoluminescence spectra over the UV and visible region (250–650 nm) which were recorded by Perkin Elmer Spectrofluorometer using excitation light at the wavelength $\lambda_{exc} = 262$ nm.

3. Results and discussion

Normalized photoluminescence spectra of the ternary SiO_2–BaO–ZnO and the quaternary SiO_2–BaO–ZnO–B_2O_3 glass samples are shown in Figs. 1 and 2, respectively. In both figures, the broad and intense near band edge emissions at UV range are observed from these six samples. They are attributed to free-excitons recombination while the broad bands are of the characteristic emission of non-crystalline semiconducting materials [10]. UV luminescence in all samples was red-shifted relative to the exciton transition in bulk ZnO. However, the visible light emissions normally dominating the photoluminescence spectra of crystalline ZnO and ZnO nanoparticles [11] are very weak in those cases. It is known that the visible emission of ZnO is produced by transition of excited optical center from

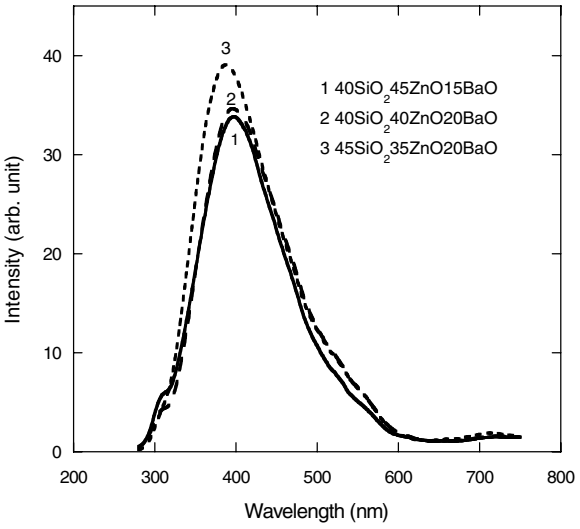

Fig. 1. Photoluminescence spectra of glass samples containing no donor ($\lambda_{exc} = 262$ nm).

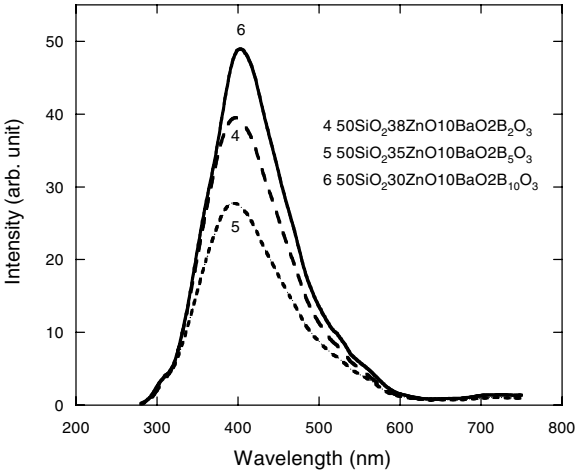

Fig. 2. Photoluminescence spectra of glass samples containing donor B ($\lambda_{exc} = 262$ nm).

Table 1
Glass compositions

No.	Oxides (mol%)				Emission wavelength (nm/eV)
	ZnO	SiO_2	BaO	B_2O_3	
1	45	40	15		398/3.11
2	40	40	20		395/3.13
3	35	45	20		393/3.20
4	50	38	10	2	397/3.12
5	50	35	10	5	392/3.16
6	50	30	10	10	403/3.08