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Photoluminescent properties and Raman spectra of ZnO-based scintillating glasses

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ABSTRACT

Glasses in SiO_2–ZnO–BaO system with the different ZnO/BaO ratio were studied. In some cases, BaF_2 was introduced to substitute for BaO on the equal base. Photoluminescent spectra showed that ZnO in glass matrices behaved somewhat differently from ZnO crystals. Especially, the introduction of fluorine ions led to dramatic shift of UV emission band of glasses closer to that of ZnO crystals. Raman spectral analysis provided consistent results. In particular, Raman bands in the high frequency region are sensitive to effects of different ZnO/BaO or BaF_2/BaO ratio on structure of glasses.

1. Introduction

Much recent research work has been done on ZnO as a promising material in short wavelength opto-electrical devices. So far ZnO thin films produced by means of MBE, CVD, MOCVD and sol–gel and nanostructured ZnO, such as nanoparticles, belts, rods have already been intensively studied, and some interesting phenomena resulting from one- or two-dimension structures were reported [1–3]. There are also some successful attempt to develop high quality n-type doping of ZnO, while the p-type doping is rather difficult because of its self-compensating effect and low solubility of the acceptor dopants [4–6]. Comparatively, there are only a few reports about researches on ZnO in glassy matrix. Recently we have investigated zinc oxide containing glasses, with efforts to form ZnO nanoaggregates in the glass matrices [7,8]. Results show that the luminescence of ZnO in glasses is somewhat different from bulk ZnO crystals due to influences of other ingredients surrounding ZnO in the glass. Especially, the introduction of p-type dopant F^- ions leads to some dramatic change in the emission spectra of the samples. Raman spectra have been an important way to get structural information of vitreous materials, because they can provide useful evidences about polymerized structure. In order to trace some delicate structure information of the molecular bonds associated with these spectral variations, Raman spectra of some glasses were measured, presented and discussed together with their luminescence spectra in this paper.

2. Experimental procedure

The investigated glasses are divided into two groups one belonging to the system of SiO_2–ZnO–BaO with the different ZnO/BaO ratio, while another introducing BaF_2 to substitute for BaO on the equal bases. Detailed glass compositions are given in Table 1. All the samples were prepared by traditional melting method with the high purity SiO_2, ZnO, $BaCO_3$, and/or BaF_2 as starting materials. First, glass batches were mixed together and transformed into high alumina crucibles. The loaded crucibles were then kept into an electric furnace at a temperature of 1500 °C for 3 h. After that the glass melts were poured into stainless steel mold which was preheated at a temperature of 500 °C. Then glass samples were heated at a temperature 10 or 20 °C below T_g for 2 h to release the internal stresses formed during quenching. All the glass samples were well polished for measurements of luminescence spectra using a spectrofluorometer (Fluorolog3-P, Jobin Yvon, France). Raman spectra were measured using 532 nm excitation wavelength, dispersing/filtering optics based on a notch filter followed by a 550 cm focal length monochromator, and an LN_2-cooled CCD detector. All the optical spectra were measured at room temperature and in air.

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Table 1
Glass composition

Sample no.	Compounds (mol%)				ZnO/BaO ratio
	SiO_2	ZnO	BaO	BaF_2	
1	35	40	25	–	1.6
2	35	45	20	–	2.25
3	35	50	15	–	3.33
4	35	35	25	5	1.40
5	35	35	20	10	1.75
6	35	35	15	15	2.33

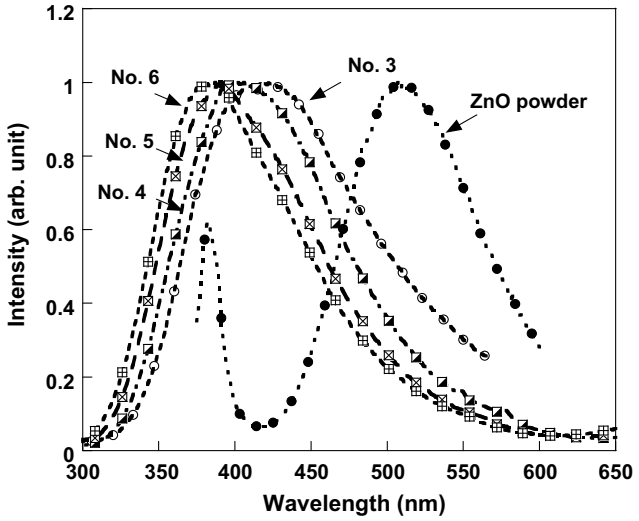

Fig. 1. Emission spectra of glasses with different amount of BaF_2 for substitution of BaO on the equal bases (ZnO powder emission spectrum is also shown for comparison).

3. Results and discussion

Fig. 1 presents the normalized room temperature emission spectra of glass samples in two groups with 265 nm excitation, which is close to the maximum of the excitation spectra of ZnO-related luminescence in previously studied borosilicate glasses [8]. The emission spectrum of ZnO powders is also included for comparison. It is noticed that the luminescence of ZnO in glasses is somewhat different from ZnO crystalline powders. All glass samples show wide emission bands at the near-UV regions while a wide defect-originated emission at 530–600 nm from ZnO is not observed. All the BaF_2-free glasses of the first group show an emission band centered at about 430 nm, as reported in Fig. 1 for sample no. 3. For glasses containing both BaO and BaF_2, the dominant emission band moves to shorter wavelengths from around 395 nm to 387 nm with increasing amount of BaF_2 substitution for BaO, approaching the UV emission band (380 nm) of ZnO powders.

It is generally accepted that the common photoluminescence (PL) spectral pattern in bulk ZnO consists of the UV emissions due to near-band-edge (NBE) excitons recombination and visible emissions from a transition of shallowly or deeply trapped electrons, as shown in Fig. 1 by PL spectrum of ZnO powders used as raw materials to prepare the present glasses. With respect to the visible emission process, the presence of oxygen vacancies (V_o) has been considered as one of the most correlative factors [9]. These defects are represented by a level approximately 1.3–1.6 eV (deep) or 0.3–0.5 eV (shallow) below the conduction band edge [10]. For glasses in the first group, oxygen vacancies are known as one of the main structural defects owing to the involvement of fairly higher amount of modifying oxides BaO so that the observed emission band dominant at 430 nm (2.88 eV) could be assumed to be due to a transition of a photogenerated electron from the shallow donor level (V_o) to the valence band edge (3.07–2.87 eV). Although the majority of previously reported work on visible emissions from ZnO crystals and films has focused on the green and red emissions, the observation of the blue emission in the present work is not surprising when considering the fact that visible emission of ZnO are influenced largely by preparation processes which produce different surface morphology and structural defects [11,12]. In the case of the second group samples, however, introduced F^- ions play a special role in occupying the lattice sites of V_o [13], thus, the density of shallow defects as mentioned above is effectively reduced. Since both UV and visible emission processes compete with each other, elimination of the visible emission spontaneously increases the NBE excitons emission. Therefore, the enhanced UV emission round 395 nm appears which has been generally agreed to be associated with excitonic recombination.

Raman spectra of all six glasses are given in Figs. 2 and 3 between 200 and 1300 cm^{-1}, for different ZnO/BaO or BaO/BaF_2 ratio while Raman bands in the higher frequency region are compared

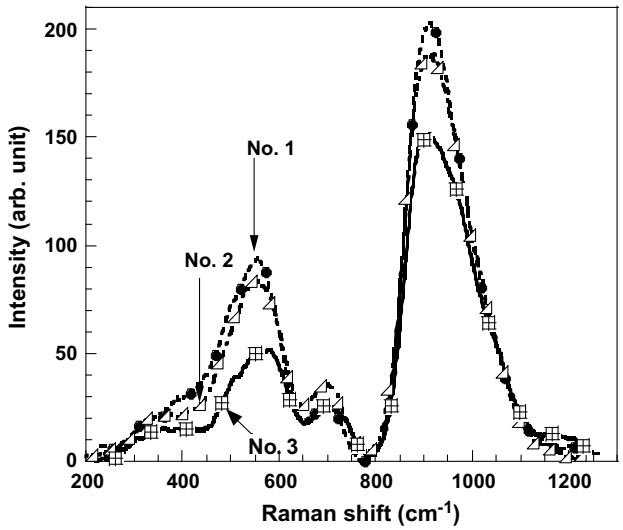

Fig. 2. Raman spectra of glass sample Nos. 1–3 with different ZnO/BaO ratio.

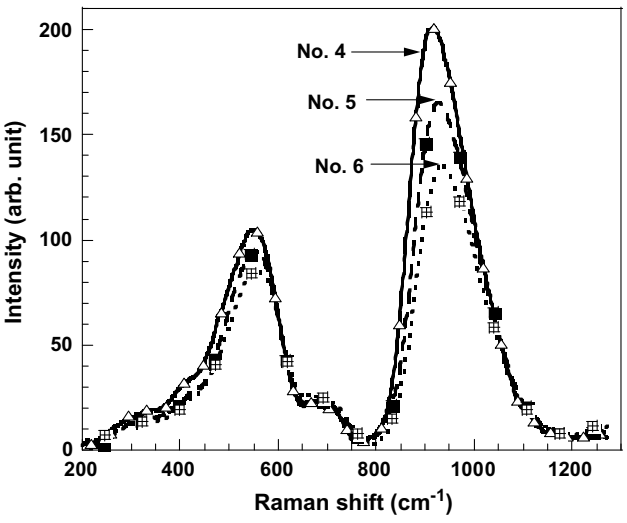

Fig. 3. Raman spectra of glass sample Nos. 4–6 with different ZnO/BaO ratio.