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Luminescence properties of Ce^{3+}-doped lithium borophosphate glasses and their correlations with the optical basicity

Li-Hua Zheng [a,b], Xin-Yuan Sun [c], Ri-Hua Mao [d], Hao-Hong Chen [b], Zhi-Jun Zhang [e], Jing-Tai Zhao [e,*]

[a] University of Chinese Academy of Science, Beijing 100864, PR China
[b] Key Laboratory of Transparent and Optical Functional Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China
[c] Department of Physics, JinggangshanUniversity, Ji'an 343009, PR China
[d] Laboratory for Advanced Scintillation Materials & Performance, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China
[e] School of Material Science and Engineering, Shanghai University, Shanghai 200072, PR China

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ABSTRACT

Ce^{3+}-doped lithium borophosphate glasses were prepared by melt quenching method, their luminescence properties were investigated by excitation and emission spectra, as well as X-ray excited luminescence (XEL) spectra. The broad emission band with the maximum center around 338 nm attributing to 5*d*–4*f* transitions of Ce^{3+} ions is observed, and the optimal concentration of CeO_2 is found to be 0.75 wt.% in the CeO_2-doped $57.5Li_2O$–$5B_2O_3$–$37.5P_2O_5$ scintillating glasses. Both the excitation and emission bands show a red shift in the $45Li_2O$–yB_2O_3–$(55\text{-}y)$ P_2O_5–0.75 wt.% CeO_2 glasses due to the increasing value of the optical basicity with the increase of *y*. Moreover, the strongest XEL intensity of $45Li_2O$–yB_2O_3–$(55\text{-}y)P_2O_5$–0.75 wt.% CeO_2 glasses reaches a maximum at $y = 16.5$, which might be associated with the decreasing concentration of the non-bridging oxygen and the change ratio between BO_4 groups and total amount of borate groups by increasing B_2O_3. From the standpoints of the high Li^+ concentration and fast fluorescence decay time (28.5 ns), Ce^{3+}-doped lithium borophosphate glasses are potential candidates for neutron detection.

1. Introduction

Neutron diagnostics is an indispensable tool for both inertial confinement fusion (ICF) and magnetic confinement fusion (MCF) research to effectively probe and control high-energy fusion plasma [1–3]. The available technology for neutron detection is generally based on nuclear reaction, which relies on scintillating materials containing neutron-capture elements including ^6Li, ^{10}B, ^{155}Gd or ^{157}Gd [4,5]. The rare-earth (RE)-doped scintillating glasses, with the considerable advantages of low-cost, large-volume, and easy shaping of elements, are always the promising materials for neutron detection [1–3]. Up till now, some Ce^{3+}-activated silicate, phosphate and borate-based glasses containing concentrated ^6Li or ^{10}B elements have been explored for scattered neutron diagnostics purpose [6–8]. However, the intrinsic structure defects in scintillating glasses, such as anion vacancies and non-bridging oxygen, have lowered the energy transfer efficiency from the host glass to the incorporated emission centers, leading to the relatively low light output [9]. On the other hand, the scintillating glasses containing high content of ^6Li element are usually featured with the diversification tendency, which results in the complexity of glass synthesis, particularly in the large-volume glasses [10]. So the trade-off between the content of the lithium and the glass stability should be taken considerably into account in the designed scintillating glasses for neutron detection.

To our best knowledge, the luminescence properties of Ce^{3+}-doped borophosphate glasses have not been studied. The content of the non-bridging oxygen is reported to decrease with the addition of B_2O_3 up to $y = 27.5$ in $45Li_2O$–yB_2O_3–$(55\text{-}y)$ P_2O_5 glasses [11]. Also, the presence of boron helps the self-reduction of Ce^{4+} to its Ce^{3+} [12]. Most importantly, the Li_2O–B_2O_3–P_2O_5 system has relatively wide glass-forming region, which will be beneficial to the higher content of the lithium element [13].

Herein, we report our recent investigation on the luminescence properties of Ce^{3+}-doped lithium borophosphate glasses in this work. Optical transmittance, photoluminescence or X-ray excited luminescence of the doping concentration-dependent and composition-dependent glasses were characterized and effects of glass compositions were discussed with respect to the variation of the so-called optical basicity relation to the electron donation ability of the oxygen.

2. Experimental section

Two series of lithium borophosphate glasses with the nominal composition of $57.5Li_2O$–$5B_2O_3$–$37.5P_2O_5$-*x* wt.% CeO_2 ($x = 0.0$, 0.5, 0.75 and 1.0) and $45Li_2O$–yB_2O_3–$(55\text{-}y)$ P_2O_5–0.75 wt.% CeO_2 ($y = 0.0$, 5.5, 11, 16.5, 22 and 27.5) were prepared from Li_2CO_3 (AR, ≥98.0%), H_3BO_3 (AR, ≥99.5%), $NH_4H_2PO_4$ (AR, ≥99.5%) and CeO_2. Batches of

* Corresponding author. Tel.: +86 2152412073.
E-mail address: jtzhao@mail.sic.ac.cn (J.-T. Zhao).

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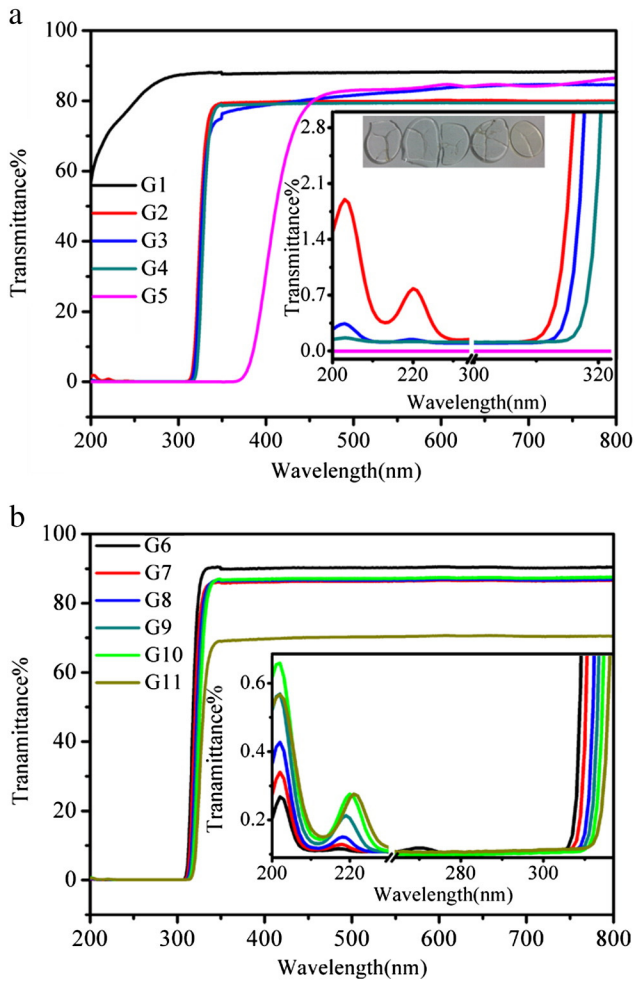

Fig. 1. Transmittance spectra of the series of glasses with different x (a) and y (b) values (the inset shows the enlargement of the transmittance spectra in the wavelength range of 200–319 nm).

about 10 g raw materials were well ground in an agate mortar and melted in a platinum crucible at 785–865 °C for 30 min in ambient atmosphere. The homogeneous melt was quickly poured onto a preheated stainless steel mold. The quenched glasses were finally annealed at 300 °C for 3 h followed by cooling down naturally to room temperature. All glass samples were prepared homogeneously and were polished to the thickness of 2 mm. The theoretical Li^+ density of the glass is up to 10.8 wt.%, which is higher than the highest one that is reported in the $20Al(PO_3)_3$–80LiF glass doped with 3 mol% PrF_3 for conventional ^6Li glass scintillators [2].

Transmittance spectra of Ce^{3+}-doped lithium borophosphate glasses were measured with the Cary 5000, UV–VIS-NIR Spectrophotometer in the range of 200–800 nm. Photoluminescence (PL) spectra were performed on a Hitachi F-4600 FL fluorescence spectrophotometer at the voltage of 400 V through slit width of 2.5 nm. The photoluminescence (PL) decay was obtained using FLS 980 fluorescence spectrometer. The XEL spectra were measured on a FluoMain X-ray excited luminescence spectrometer, which is equipped with the F30III-2 excitation source and Hamamatsu R928-28 photo receiver. All measurements were carried out at room temperature.

3. Results and discussions

The transmittance spectra of the two series of glasses with different x and y values are shown in Fig. 1(a) and (b), respectively. Clearly, the absorption cut-off edge of the undoped glass (G1) is lower than 200 nm. The absorption edges in the cerium doped glasses attribute to the charge transfer from the non-bridging oxygen to metal ions [15]. Both the absorption peaks around 212 nm and the absorption edges in the cerium doped glasses are assigned to the $4f$–$5d$ transitions of Ce^{3+}. A red shift of the absorption edge of cerium doped glasses is observed with increasing CeO_2 or y. For the x series glasses, the red shift of absorption edge (or the decrease of the optical band gap, as shown in Table 1) or peaks is due to availability of more oxygen in the glass network with the addition of cerium content. The absorption edge of G5 ($x = 1.25$ wt.%) glass suffers a big red shift due to the absorbance of Ce^{4+}, which can be inferred from the yellowish color of G5 glass. The absorption peak fades out completely when $x = 1.25$ wt.% with the increase of x, while for the y series glasses, the concept of optical basicity or the electron donating power of oxygen ligands [16], can be used to explain the red shift of the absorption edge and absorption peak. The electron donor power of oxygen atom in the glass is influenced by surrounding cations, especially by the glass network formers. If the bonding of oxygen with other cations shows more covalence, the less able that the oxygen donate charge to a solute metal ion in the glass, that is, the smaller the optical basicity of the system. In the present case, the P^{5+} ion shows more covalent degree with bonding to oxygen compared with B^{3+} one, indicating the increased optical basicity of glass matrix with the increase of B_2O_3 content [17]. But for the ternary $45Li_2O$–yB_2O_3–$(55\text{-}y)$ P_2O_5 glasses, the increase of y causes the increase of the ratio of bridging oxygen anions which have much smaller microscopic optical basicity because the polarization effect on the bridging oxygen is greater than the terminal oxygen [17]. Finally, those two factors might result in the slight increase of the true optical basicity with

Table 1
Compositions and theoretical optical basicity Λ_{th} of the lithium borophosphate glasses.

	Li_2O (mol%)	B_2O_3 (mol%)	P_2O_5 (mol%)	CeO_2 (wt.%)	Λ_{th}[a]	x, y	Optical band gap (eV)
G1	57.5	5	37.5	0.0		$x = 0.0$	–
G2	57.5	5	37.5	0.5		$x = 0.5$	3.84
G3	57.5	5	37.5	0.75		$x = 0.75$	3.83
G4	57.5	5	37.5	1		$x = 1.0$	3.81
G5	57.5	5	37.5	1.25		$x = 1.25$	3.20
G6	45	0	55	0.75	0.424	$y = 0$	3.93
G7	45	5.5	49.5	0.75	0.432	$y = 5.5$	3.91
G8	45	11	44	0.75	0.441	$y = 11$	3.88
G9	45	16.5	38.5	0.75	0.451	$y = 16.5$	3.86
G10	45	22	33	0.75	0.461	$y = 22$	3.84
G11	45	27.5	27.5	0.75	0.472	$y = 27.5$	3.81

where X_1, X_2, X_3, …, X_n are equivalent fractions based on the amount of oxygen that each oxide contributes to the overall glass, and Λ_1, Λ_2, Λ_3, …, Λ_n are the basicities assigned to the individual oxides [14]. The basicities of Li_2O, B_2O_3 and P_2O_5 are 1, 0.42 and 0.33 respectively.

[a] The theoretical basicity Λ_{th} of glass composition is calculated as follows:

$$\Lambda_{th} = X_1\Lambda_1 + X_2\Lambda_2 + X_3\Lambda_3 + \ldots + X_n\Lambda_n$$