Bulgarian Chemical Communications, Volume 45, Special Issue B (pp. 222-225) 2013

γ -ray induced effects in Sm-doped strontium borate glasses

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Received October 17, 2013; Revised November 25, 2013

Strontium borate glasses SrB_4O_7 doped with Sm ions are prepared by conventional melting-quenching method. The effect of γ–ray irradiation on the glass samples is studied by measuring the absorption spectra and the photoluminescence. It is found that the γ -ray irradiation caused partial reduction of Sm^{3+} to Sm^{2+} at room temperature. Borate framework is supposed to be responsible for the Sm^{3+} to Sm^{2+} transition.

Keywords: Sm^{3+} doped SrB_4O_7 glass, γ-ray radiation, photoluminescence, room temperature dosimeters

INTRODUCTION

Strontium borate glasses SrB_4O_7 due to their simple preparation, low cost, high transparency, easy shaping and long term stability found applications in many optoelectronic devices, as solid state laser materials (owing to their persistent spectral hole burning), non-linear parametric converters and broadband optical fiber amplifiers [1-3]. Furthermore, the absorbance of borate glasses is very close to that of human tissue, thus makes them very attractive for radiation dosimetry applications, based on their luminescent properties [4]. In that aspect, the search for new dosimieric materials is still constant to meet up the medical and environmental needs.

Strontium borate SrB_4O_7 glass is well known as a suitable host material to accommodate divalent lanthanide ions (Eu^{2+}, Sm^{2+}, Yb^{2+}) on the Sr^{2+} site. Therefore, when doped with rare earth (RE) ions strontium borate matrix become very attractive for radiation dosimetry due to the RE^{3+} to RE^{2+} transition [1]. When doped with Samarium, which is generally stable at its trivalent state, Sm^{3+} must be reduced to Sm^{2+} and keep it stabilized. The well known and effective method to transfer Sm^{3+} to Sm^{2+} is by heating the sample under reduction atmosphere in H_2 stream [5]. Although this method is very effective, it requires a rather complicated gas flow system that is difficult to perform practically. Another reduction method is to irradiate the glass sample with femto-second laser pulses [6] or with high energy radiation (γ-irradiation [7], β-irradiation [8] or x-ray irradiation [9]). For a first time Pei at al [1] reported that three valent RE^{3+} ions were successfully reduced to RE^{2+} ions in SrB_4O_7 host without reduction atmosphere. Since then an intense attention has been paid on the incorporation of RE^{3+} ions in strontium borate matrices towards different practical applications.

In the present work synthesis of Sm^{3+} doped SrB_4O_7 glasses with two different concentrations is reported. The absorption and photoluminescence spectra before and after γ-irradiation are recorded and analyzed. In addition, the refractive index values are measured at the visible spectral range.

EXPERIMENTAL DETAILS

Two glasses compositions were prepared by mixture of SrO, B_2O_3 and Sm_2O_3, by varying the ratio of the starting materials. A conventional melting- quenching method was used to prepare the samples. For the first composition we added 7 % Sm_2O_3 in a mixture of SrO and B_2O_3. For the second one the Sm_2O_3 content was increased to 10%, varying the SrO to B_2O_3 ratio in the mixture.

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Table 1. Chemical composition (in weight %) and sample code.

	Chemical composition (in weight %)	Sample code
1.	28% SrO + 65% B2O3 + 7% Sm2O3	0.28SrO-0.65BO-0.07Sm
2.	40% SrO + 50% B2O3 + 10% Sm2O3	0.4SrO-0.5BO-0.1Sm

The nominal glasses compositions by weight % are given in Table 1.

Further, the obtained glasses were annealed at 400ºC for 48h for thermal and structural stability enhancement. Samples of 1mm thickness were cut and polished to optical quality. To study the effect of γ-irradiation, the samples were irradiated with ^{60}Co isotope with the dose rate of 0.1mGy.s^{-1}. The optical absorption spectra of the initial state (denoted hereinafter as non-irradiated) and the state after γ-ray irradiation (denoted as γ-ray irradiated) were measured at room temperature in the spectral range 200-1800nm using Shimadzu spectrophotometer. Photoluminescence spectra were measured with a monochromator equipped with PMT (Hamamatsu) detector at room temperature. The laser excitation at 405 nm was used. In addition, the refractive indices of synthesized glass compositions were measured by polarizer-sample-analyzer ellipsometry at the visible spectral range [10].

RESULTS AND DISCUSSIONS

Figure 1(a,b) shows the absorbance spectra of both glass compositions at wavelengths from 300nm to 1700nm. As it seen, γ-ray irradiation induced significant absorbance in 0.28SrO-0.65BO-0.07Sm sample, with several intensive characteristic peaks at the ultraviolet and infrared spectral range.

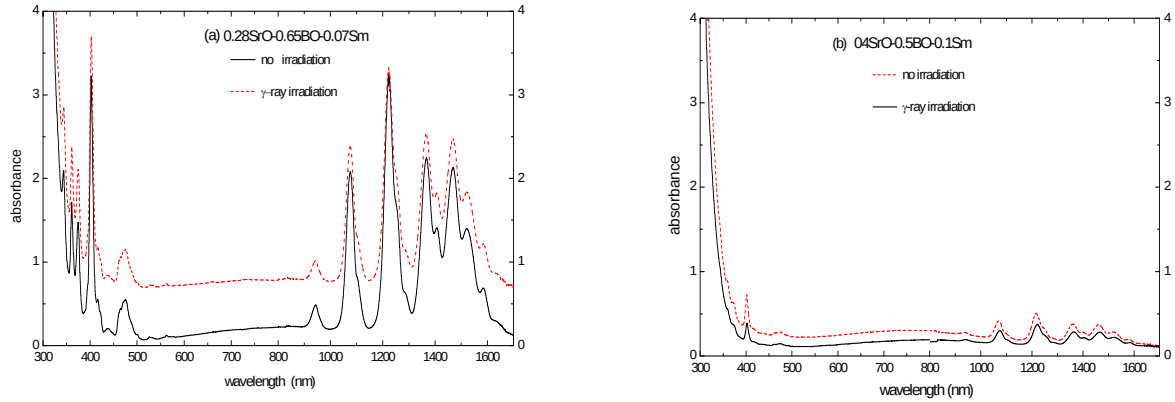

Fig. 1. Absorbance spectra of (a) 0.28SrO-0.65BO-0.07Sm and (b) 0.4SrO-0.5BO-0.1Sm glass.

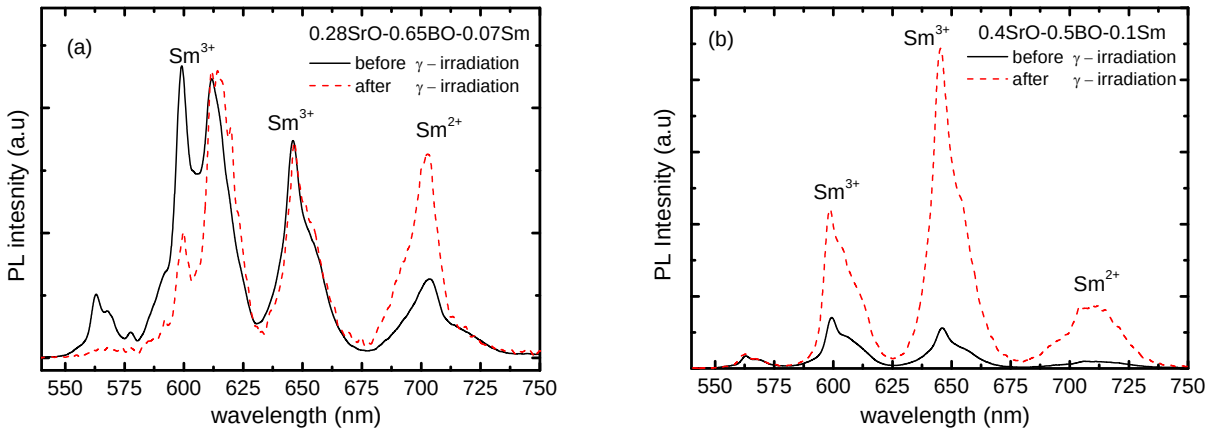

Fig. 2. PL (a.u) spectra of Sm-doped glass compositions before and after γ-ray irradiation at room temperature.

Furthermore, two very intensive absorption peaks around 400 nm and 1200nm are detected, which could be considered for further application of the above glass composition as narrow band cut off

filters. At the same time, there is almost no obvious absorbance change in 0.4SrO-0.5BO-0.1Sm composition.

Photoluminescent (PL) spectra at room temperature of both compositions before and after γ-ray irradiation are presented at Fig.2 (a,b). The emission lines in the range from 680nm to 720nm correspond to the ^5D_o-^7F_J (J=0,1,2,3,) transitions of the Sm^{2+} ions [11,12]. Evidently, the γ -ray irradiation caused Sm^{3+} reduction to Sm^{2+} in the host glass matrix. The effect is stronger in the case of 0.28SrO-0.65BO-0.07Sm composition, leading to more intensive peak of Sm^{2+} around 700 nm and diminishing the intensity of Sm^{3+} luminescence between 550-600 nm.

Generally, the excitation and emission of rare-earth doped glasses are due to the transitions from the $4f^n$ electronic states of RE^{3+} ions (RE^{3+} electronic configuration of $4f^n5s^25p^6$), which are highly sensitive to the symmetry, structure and phonon energy of the host matrix. During the irradiation, free electrons and holes are created and some electrons can be trapped by Sm^{3+} ions, leading to the formation of Sm^{2+} ions, while holes can be trapped by other defects. In SrB_4O_7 glass matrix, all of the boron atoms are tetrahedrally coordinated with oxygen atoms and form a three-dimensional borate network [13]. Therefore, the basic structure of SrB_4O_7 can be expressed as SrO.nB2O3 (with different n values, different anion units are linked together, forming different networks –thus the number of triangularly coordinated boron atoms (BO_3) per tetrahedral coordinated boron atoms (BO_4) is equal to n-1 [3,13]). As a result the divalent ions in SrB_4O_7 are completely surrounded by the tetraherdral BiO_4 and therefore are hardly expected to be attacked by oxygen. From another side, since the ionic radii of Sm^{2+} (1.32Å) is very similar to those of Sr^{2+} (1.31Å), with the same valence state, some Sr^{2+} can be replaced by Sm^{2+} without expecting serious distortion in the structure. Therefore, the two main anion units: BO_3 and BO_4 are expected to play significant role for the Sm^{3+} reduction. These two units are supposed as the basis of the infrared spectra as well [14]. The above statement is well confirmed by the photoluminescence results presented at Fig.2 (a). The increasing the B_2O_3 ratio in a glass composition, the Sm^{3+} to Sm^{2+}reduction is more efficient.

In addition, the refractive index measurements using polarizer-sample-analyzer ellipsometry were performed at 632.8nm, 594.1nm, 543.5nm and 473nm. The refractive indices for different compositions shown in Fig. 3 were calculated by using the formula [10]:

$$n_0 = n_i \tan\theta_i[1-\frac{4\rho}{(1+\rho)^2}\sin^2\theta_i]^{1/2} \quad (1)$$

where n_i is the refractive index of the ambient air, and θ_i is the incident angle for measurements and ρ is an ellipsometric parameter, defined by the ratio of r_p to r_s (denoted as reflection coefficients in the parallel (p) and perpendicular (s) planes to the incident plane, respectively. As it seen, there is a difference in refractive index values for both compositions.

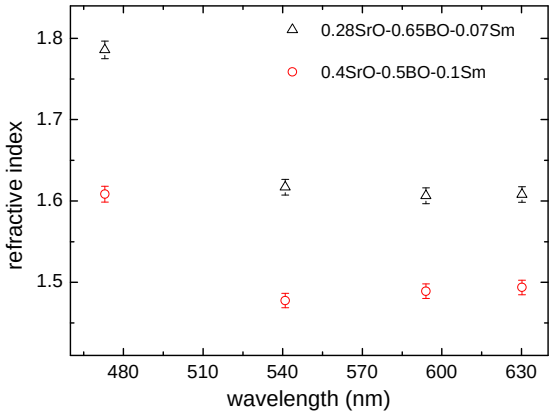

Fig. 3. Refractive index values measurements using polarizer-sample-analyzer ellipsometry. The standard deviation is ± 0.001.

Although at the first trial there is a partial reduction of Sm^{3+} to Sm^{2+} transitions, further adjustment of Sm concentration and B_2O_3 ratio are necessary for dozimetry requirement applications at room temperatures.

CONCLUSIONS

Sm doped SrB_4O_7 glasses have been synthesized by conventional melt quenching method. The performed luminescence measurements verified that Sm^{3+} ions can be partially reduced to Sm^{2+} by γ-ray irradiation at room temperature. The γ -irradiation doze can be estimated from the luminescence peaks intensity change. The effect is stronger in 0.28SrO-0.65BO-0.07Sm composition with less Sm concentration, but with larger B_2O_3 content. In addition, the above composition displays shows potential ability for narrow band filter application both at ultraviolet and infrared spectral range.

Acknowledgments: *This work has been done through bilateral collaboration project supported by National Science Council (NSC), Taiwan and Bulgarian Academy of Science under the contract #NSC99-2911-1-009-008. Glass compositions were obtained at the Crystal Growth Laboratory, Institute of Solid State Physics, Sofia.*

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ЕФЕКТИ ОТ ГАММА-ОБЛЪЧВАНЕ В Sm -ЛЕГИРАНИ СТРОНЦИЕВО БОРАТНИ СТЪКЛА

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Постъпила на 17 октомври 2013 г.; коригирана на 25 ноември, 2013 г.

(Резюме)

Стъкла от стронциев борат SrB_4O_7 легирани със Sm са получени по конвенционалният метод на топене-закаляване. Ефекта на облъчване с γ–лъчи е изследван чрез измерване на абсорбционните спектри и спектрите на фотолуминесценция. Установено е, че облъчването с γ–лъчи води до валентен преход на Sm^{3+} към Sm^{2+} йони при стайна температура. Предполага се, че боратните връзки са отговорни за този вид преходи.