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STUDIES ON GAMMA – IRRADIATED SODIUM TETRABORATE GLASSES CONTAINING YTTERBIUM

A. A. Kutub, M. S. Elmanhawaawy and M.O. Babateen

Department of Physics, Faculty of Applied Sciences, Umm AL – Qura University, P.O. Box 253, Makkah AL – Mukkaramah , Saudi Arabia .

ABSTRACT

A series of glass samples of $(Na_2 B_4 O_7)_{100-x} – (Yb_2 O_3)_x$ were prepared by the usual melt quenching technique where x varied from 0 to 5 mol % .Optical absorption spectra were measured before and after gamma- irradiation of the glasses. Gamma-irradiation causes a shift of the fundamental absorption edge to longer wavelengths and induces a new absorption band around 550 nm for all glass compositions. The position of this band remains unaltered by increase in either the Yb_2O_3 content or the gamma-dose. A second band at 360 nm only appears for glasses doped with Yb_2O_3; its position remains unaffected by a storage time of 2500 h. The radio-thermoluminescence (RTL) curve for the base glass ($Na_2 B_4O_7$) shows two peaks around 90 ^oC and 200 ^oC. The inclusion of Yb_2O_3 in the base glass causes a gradual suppression of the low temperature peak with increasing Yb_2O_3 concentration. At 4 mol% Yb_2O_3, it disappears and the RTL curve subsumes a single well-defined peak at high temperatures. The RTL peaks tend to shift to higher temperatures with increase in Yb inclusions.

INTRODUCTION

It is well known that rare earth ion impurities in oxide glasses can influence the mechanisms responsible for the formation of the radiation-induced colour centres. The rare earth ions, being added to glass as impurities, compete with the intrinsic defects in the glass to trap electrons and holes produced by irradiation. The effect of rare earth ions on the electron or hole trap depends strongly on the chemical nature of the rare earth metal, its valence state and its concentration as well as the glass composition. In the rare earth ions, the electronic transitions occur among the inner shielded 4f electrons. Hence, both the absorption and emission bands are relatively sharp and are not significantly influenced by their surroundings [1-5]. There have been numerous studies of radiation induced optical absorption in glasses and many of them have been reviewed [6-9]. Morsi et al. [10] reported the effect of neutron and gamma-irradiation on some properties of borate glasses containing uranium. Abbas et al. [11] studied the interaction of gamma-rays with lithium disilicate glasses doped with neodymium and uranium. Vij [12] devoted a whole chapter to the radio-thermoluminescence characteristics of glasses doped with various types of elements. It is now well-established that the development of radiation-induced centres in glass has promoted its use as a solid state dosimeter.

The present work aims to investigate the optical spectra of the gamma-irradiated binary glass system of ($Na_2B_4O_7 – Yb_2O_3$). Effects of varying the gamma-dose as well as the

Yb_2O_3 concentration are also reported. Radio-thermoluminescence (RLT) of these glasses is investigated and the influence of Yb doping on RLT is studied.

EXPERIMENTAL TECHNIQUES

Glass Preparation

The glass prepared for this study was of the alkali sodium tetraborate (e. g. $Na_2B_4O_7$). The compositions were expressed in mol % $(Na_2B_4O_7)_{100-x}(Yb_2O_3)_x$ where x = 0.0 , 1.0 , 2.0 , 3.0 , 4.0 , and 5.0 mol % ; the chemicals used were of nominally 99.99 % purity . Before weighing, the borates were placed in a drying oven at 400 °C for 2 h and transferred to a vacuum desiccator and allowed to cool. The calculated amounts of powders were mixed in an alumina crucible and placed into a closed high – temperature furnace where it was held for 2 h under atmospheric conditions at temperatures ranging from 800 °C to 950 °C, increasing with increasing Yb_2O_3 content. The melt was stirred occasionally using an alumina rod. By slow heating it was hoped to reduce mechanical and volatilization losses. The melt was finally poured into a clean stainless steel plate and cast into a disc shaped with a diameter of 1.5 cm and a thickness of 1.8 mm. The disc was immediately transferred to another furnace which was already at 300 °C. The furnace was maintained at this temperature for 1h and then switched off to cool to room temperature. The glass samples were polished using diamond paste down to a minimum grit size of 0.1 μm. Samples having thickness in the range 1.3 to 1.6 mm were obtained. The X-ray diffraction examination of the glasses showed no discrete lines or structure and confirmed that the samples were essentially non-crystalline.

Spectrophotometric and irradiation studies

The absorption spectra, both before and after irradiation were recorded at room temperature in the wavelength rang from 190 to 3100 nm using a Shimadzu UV/VIS/NIR spectrophotometer model UV 3150 PC. The samples were irradiated for 70h and 110h at a dose rate of 28.1 Gy h^{-1} using a ^{60}Co irradiation unit. The output was measured using a substandared Farmer dosimeter (Nuclear Enterprises Type 2570 A) fitted with a 0.03 cm3 ionization chamber, this calibration was checked with a $FeSO_4$ chemical dosimeter. Optical absorption measurement for the gamma-irradiated glasses were carried out within about 5 min. after irradiation and also after different periods of storage time ranging from a few hours to as long as 105 days (2500h) at room temperature. The base of absorption in all spectral curves is the decadic logarithm.

Radio-thermoluminescence(RLT) measurements

Radio-thermoluminescence of the dosed glasses were measured using a Victoreen thermoluminescence dosimeter reader (Model 2800 M). This model is a microprocessor based system with a reader head designed to accommodate a variety of TLD configurations. The basic function of the RTL reader is to heat the irradiated sample using a reproducible controlled temperature cycle (20 – 400 °C) at a linear heating rate of 10 °C/s and to detect the light emitted by a low noise and high gain photomultiplier converting it to a current signal which is amplified, integrated and displayed as a charge signal on a CRT display. Degitized RTL curves and integral RTL data can be printed or transferred to a computer for analysis and evaluation.

RESULTS AND DISCUSSION

Optical absorption spectra of unirradiated glasses.

Complete optical absorption spectra were recorded at room temperature for annealed bulk glass samples (thickness ranging from 1.3 – 1.6 mm) of the ($Na_2B_4O_7$ – Yb_2O_3) glass system as indicated in Table I. Fig.1 shows the absorption in arbitrary units as a function of wavelength ranging from 190 to3100 nm. It is clear from this figure that the base glass sample ($Na_2B_4O_7$) was colourless and its absorption spectra gave no characteristic features in the wavelength region studied. The following points may be noted:

Table 1: Composition data for sodium tetraborate glasses containing ytterbium oxide

Glass Sample	Composition (mol %) $Na_2B_4O_7$	Yb_2O_3
1	100.0	0.0
2	99.0	1.0
3	98.0	2.0
4	97.0	3.0
5	96.0	4.0
6	95.0	5.0

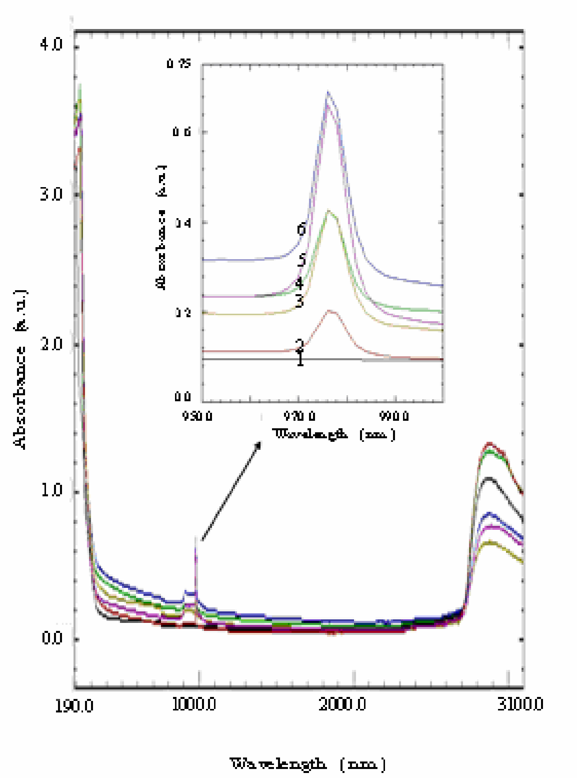

Figure 1: Absorption as a function of wavelength for bulk ($Na_2B_4O_7$–Yb_2O_3) glasses (Table I).

1. The fundamental optical absorption edge of glasses doped with Yb_2O_3 is fairly sharp, as has been observed for other borate glasses, for example $Na_2B_4O_7$ – NiO glasses [13] , $Na_2B_4O_7$ - Pb_3O_4 – CuO glasses [14] and ZnO-B_2O_3 glass system [15] rather than the usual $Na_2B_4O_7$ glass. It seems to shift to longer wavelengths as the Yb_2O_3 content is increased.
2. The absorption band around 976 nm is observed for all glass samples doped with Yb_2O_3 as is also observed for lead fluoroborate glasses doped with ytterbium [16], Yb^{3+}- Er^{3+} codoped phosphate glasses [17] and rare-earth doped silica glasses [18], and there is an increase in absorption as the Yb_2O_3 content is increased. Righini et al. [18] attributed the absorption band at 976 nm to the $^2F_{5/2}$ $^2F_{7/2}$ transition of the Yb^{3+} ions. It is evident from some previous work on the spectral absorption of ytterbium in different glasses [16-18] that the 4f electrons are well-shielded by the outer $5s^2$ electrons.
3. There is a broad absorption tail that extends from 400 to 2700 nm for the base glass ($Na_2B_4O_7$) and from 990 to 2700 nm for all glass samples doped with ytterbium, without showing any peak in these regions.
4. The absorption band around 2900 nm which is observed in all glass samples is believed to be associated with water trapped in glasses during experiment due to their hygroscopic nature.

Effect of gamma-dosage on the ($Na_2B_4O_7Yb_2O_3$) glass systems

The effect of gamma-dosage on the glass samples (Table I) was investigated and the results are shown in figures 2,3 and 4.On subjecting the samples to gamma-irradiation, the colourless samples acquired a faint brown colour which changed to brown with increasing irradiation dose. When the samples are subjected to a dosage of 28.1 Gyh^{-1} for 3h, no new characteristic features are observed, but for longer irradiation times of 24h (Fig.2), 70h (Fig.3) and 110h (Fig.4) a shift of the absorption edge to longer wavelengths is observed for all glass samples, indicating a transfer of boron atoms from the tetrahedral BO_4 group to the triangular BO_3. Increasing irradiation dose is known to break the B-O in borate glasses forming non-bridging oxygen. Moreover, gamma irradiation also induces a new peak around 550 nm for all samples examined; increasing in intensity with increasing radiation dose. Its position remains unchanged with increasing either the Yb_2O_3 content or the radiation dose. Similar results have been observed for other irradiated borate glasses [10, 19, 20].Another distinct absorption band at 360 nm is also observed for the irradiated Yb_2O_3 doped glasses (Fig.2) which appears as a broad band in glasses irradiated for 70h (Fig.3) and becomes more pronounced when irradiated for 110h (Fig.4). Much work [10, 21] has been done to illustrate the nature of induced colour centres in borate glasses. It has been suggested that if one or two non-bridging oxygens lose an electron,the interstitial cation will change its position in the matrix and consequently the non-bridging oxygen will trap a hole giving rise to colour centres. Similarly, one may consider that upon irradiation of the colourless base glass, hole trapped colour centres with characteristic absorption at 360 nm are created, a view which is supported by optical and electron resonance studies [3, 17, 22]. Accordingly, the effects produced in glass by irradiation can be represented by the general equation:

$$\text{defect in glass} + h\nu \rightarrow \text{positive hole} + \text{electron} \qquad (1)$$

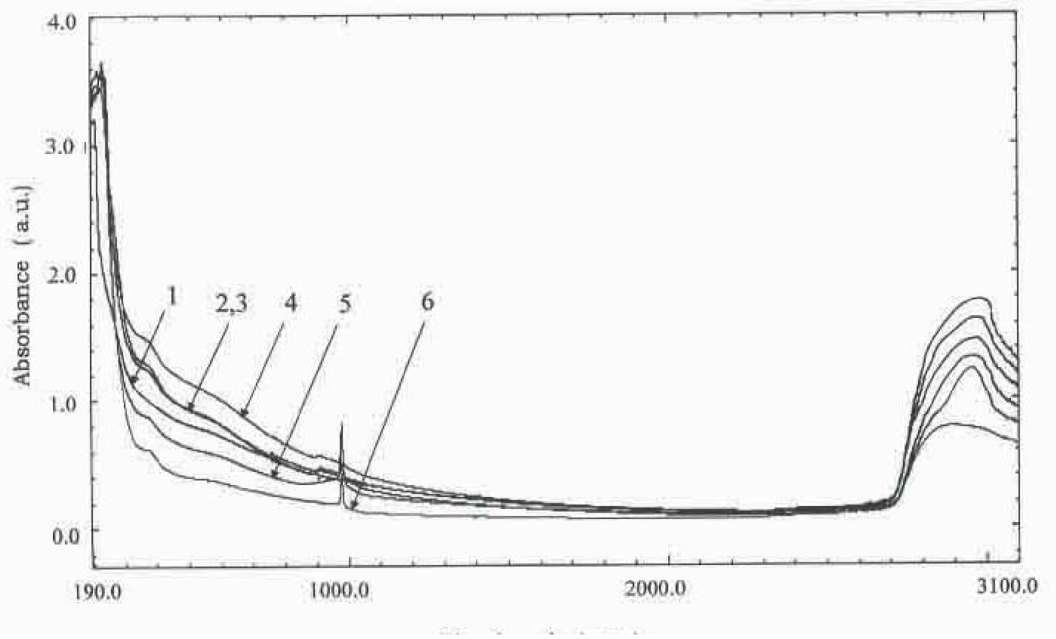

Figure 2: Absorption spectra of ($Na_2B_4O_7$ –Yb_2O_3) bulk glasses (Table I) irradiated at a rate of 28.1 Gyh^{-1} for 24h (thickness ranging from 1.3 -1.6 mm).

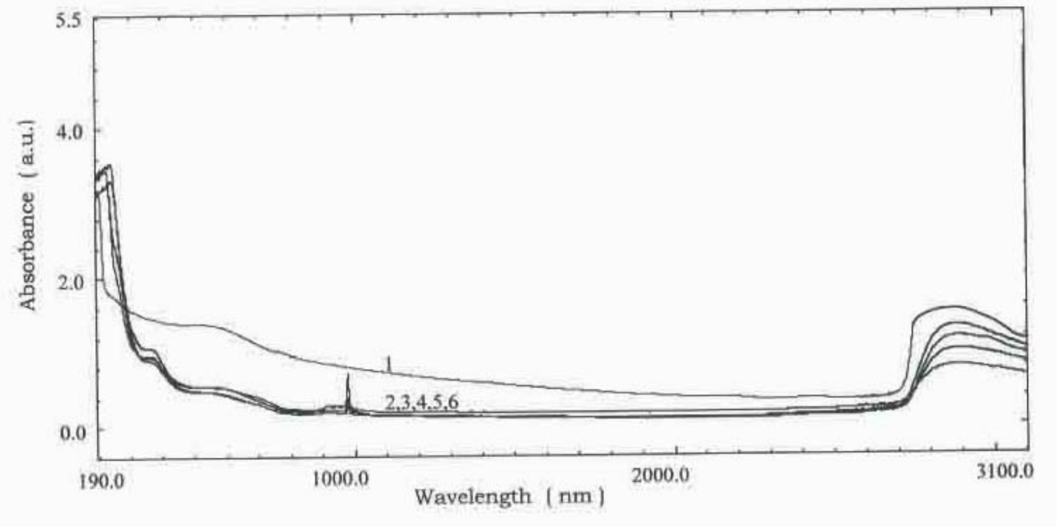

Figure 3: Absorption spectra of ($Na_2B_4O_7$–Yb_2O_3) bulk glasses (Table I) irradiated at a rate of 28.1 Gyh^{-1} for 70h (thickness ranging from 1.3 -1.6 mm).

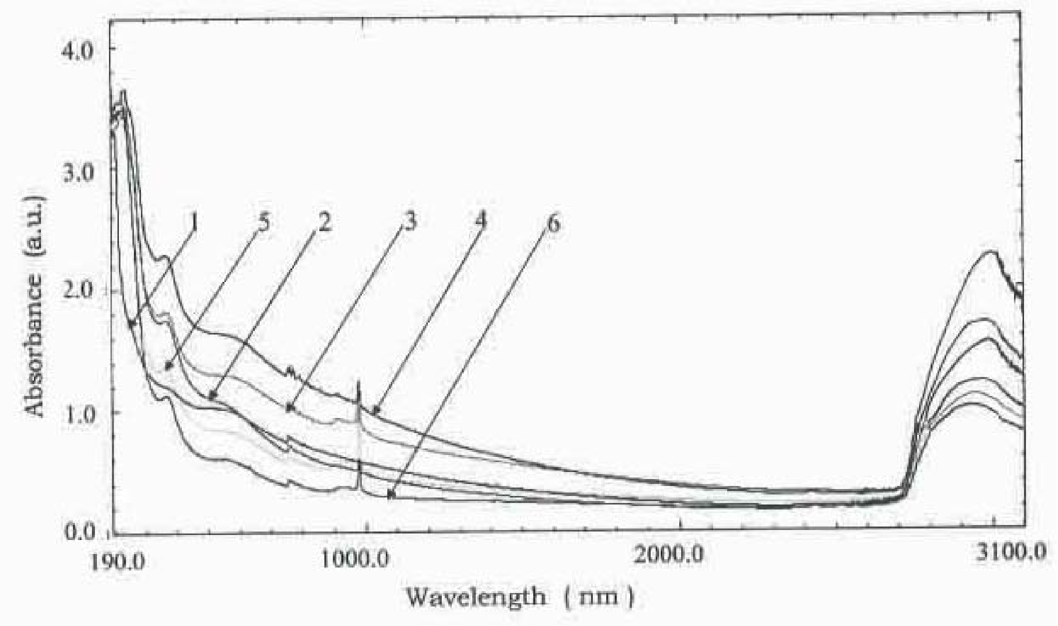

Figure 4: Absorption spectra of $(Na_2B_4O_7–Yb_2O_3)$ bulk glasses (Table I) irradiated at a rate of 28.1 Gyh^{-1} for 110h (thickness ranging from 1.3 -1.6 mm).

Effect of time on the stability of colour centres

The stability of the base glass sample $Na_2B_4O_7$ (Glass No. 1) and samples doped with 2 and 5 mol % (Glasses No. 3 and 6) irradiated for 110h was studied by remeasuring their spectral absorption at room temperature after different periods of storage time ranging from a few hours to as long as 104 days (2500 h). It is clear from figures (5, 6 and 7) that the intensity of the newly-induced peaks around 550 nm and 360 nm decreased gradually with storage time. These results confirm our previous work in which the sample was exposed to 206.4 Gyh^{-1} for 12 and 24h [9] and to 175 Gyh^{-1} for 8 and 30h [19]. Similar results have been reported by other workers [7, 10]. It is also evident from figures (6 and 7) that the absorption peak induced by the Yb inclusion in these glasses remains unaffected by the storage time.

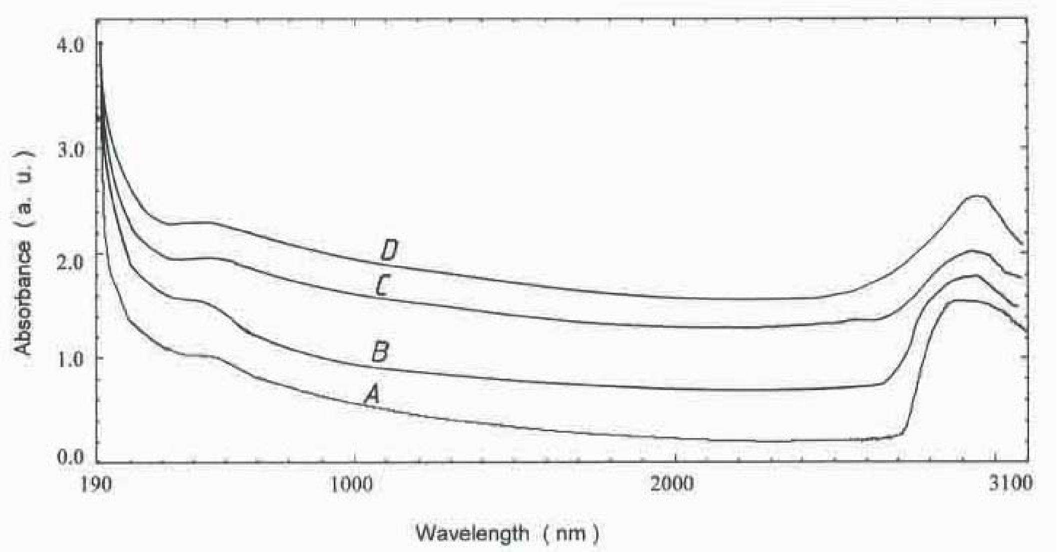

Figure 5: The optical absorption spectra of $Na_2B_4O_7$ glass (sample 1) after irradiation for 110h; A- directly after irradiation, B- 24h after irradiation, C- 500h after irradiation, D- 2500h after irradiation.

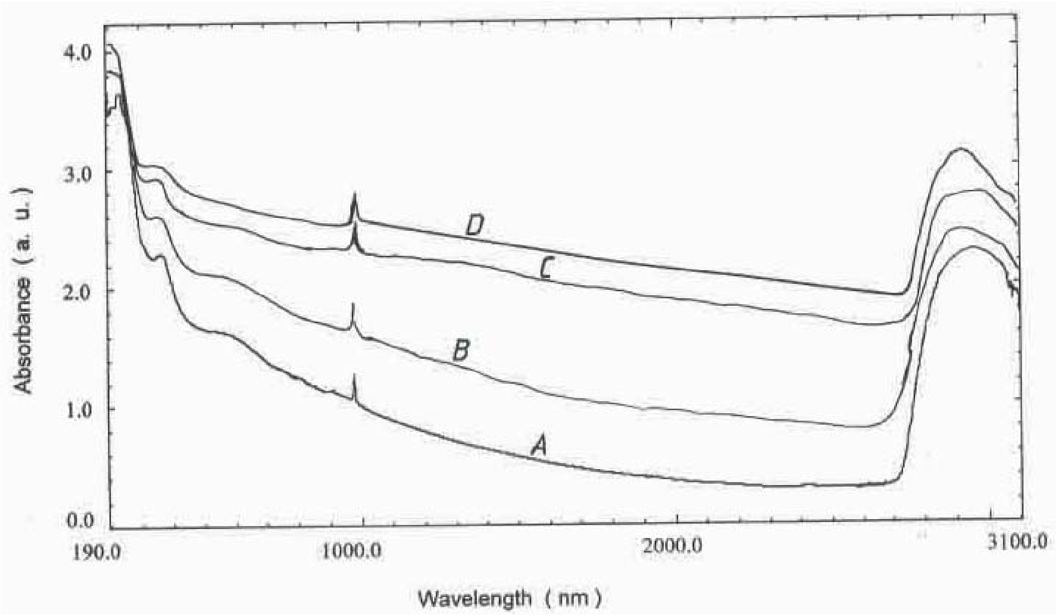

Figure 6: The optical absorption spectra of Yb-doped glass (sample 3) after Irradiation for 110h; A- directly after irradiation, B- 24h after irradiation, C- 500h after irradiation, D- 2500h after irradiation.

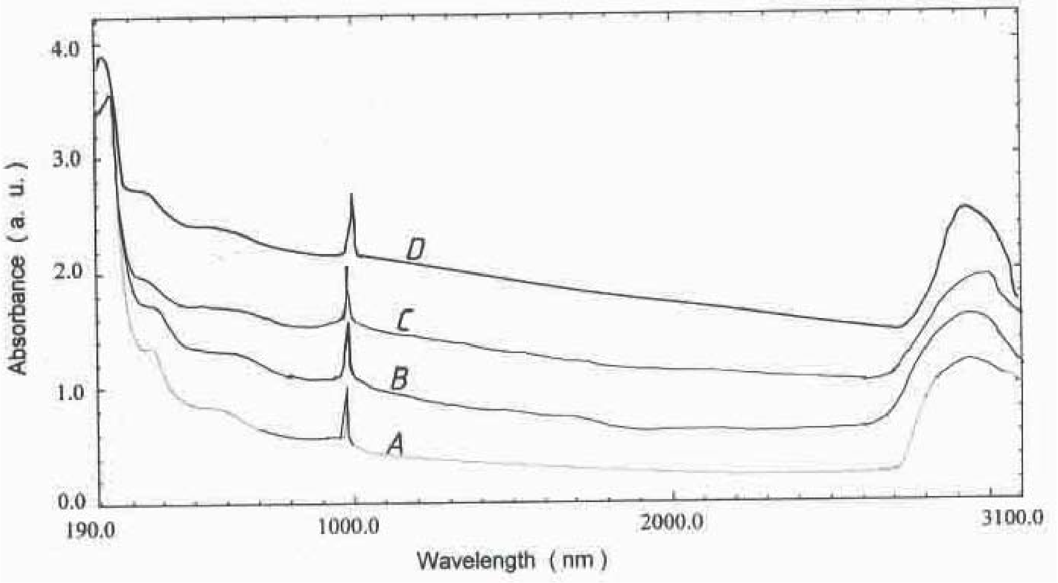

Figure 7: The optical absorption spectra of Yb-doped glass (sample 5) after Irradiation for 110h; A- directly after irradiation, B- 24h after irradiation, C- 500h after irradiation, D- 2500h after irradiation.

Radio-thermoluminescence

Radio-thermoluminescence (RTL) curves recorded for the investigated glass system are shown in Fig.8. Due to the hygroscopic nature of these glasses, all samples were annealed at 350 °C for 30 min prior to irradiation. RTL curves were measured directly after termination of irradiation using a heating rate of 10 $^{o}Cs^{-1}$ and a gamma- dose of $3.1x10^{3}$ Gy. It should be stressed that these glass samples differed in mass and thickness. For this reason, the RTL peak intensities of the various curves cannot be compared with one another. However, a comparison is possible between relative peak intensities of the same RTL curve. Fig. 8 shows that the RTL curve for $Na_2B_4O_7$ glass exhibits two peaks around 90 °C and 200 °C. The peak temperatures resemble those previously published for the same glass composition [9, 20]. Eventually, the RTL is due to the recombination of irradiation-formed trapped electrons or holes with luminescence centers created by the interaction of gamma- radiation with the defects present in the glass composition. It is, however, difficult to assign with certainty the reaction which is responsible for the recombination of a given type of centre. Fig.8 also shows the effect of Yb concentration on RTL characteristics of sodium tetraborate glass. No RTL peak which could be attributed to centres created by Yb metal has been detected over the temperature range from room temperature to 400 °C. However, the concentration of Yb seems to have a profound influence on the RTL characteristics of this glass composition. With increasing Yb content, the low temperature peak of the RTL curve decreases in intensity whereas that of the high temperature peak increases; complete disappearance of the low temperature peak being noted at high Yb content of 4 mol % and above. There is also a tendency for the RLT peaks to shift toward higher temperatures. The effect of Yb inclusion on the RTL of borate glasses could be due to some sort of interaction between the luminescent centres created by the interaction of radiation with defects and the rare earth metal ion present in the glass sample. Similar trends have been observed for other glass compositions [12]. Henaish et al. [22] also noted the same behaviour in sodium tetraborate glasses containing neodymium.

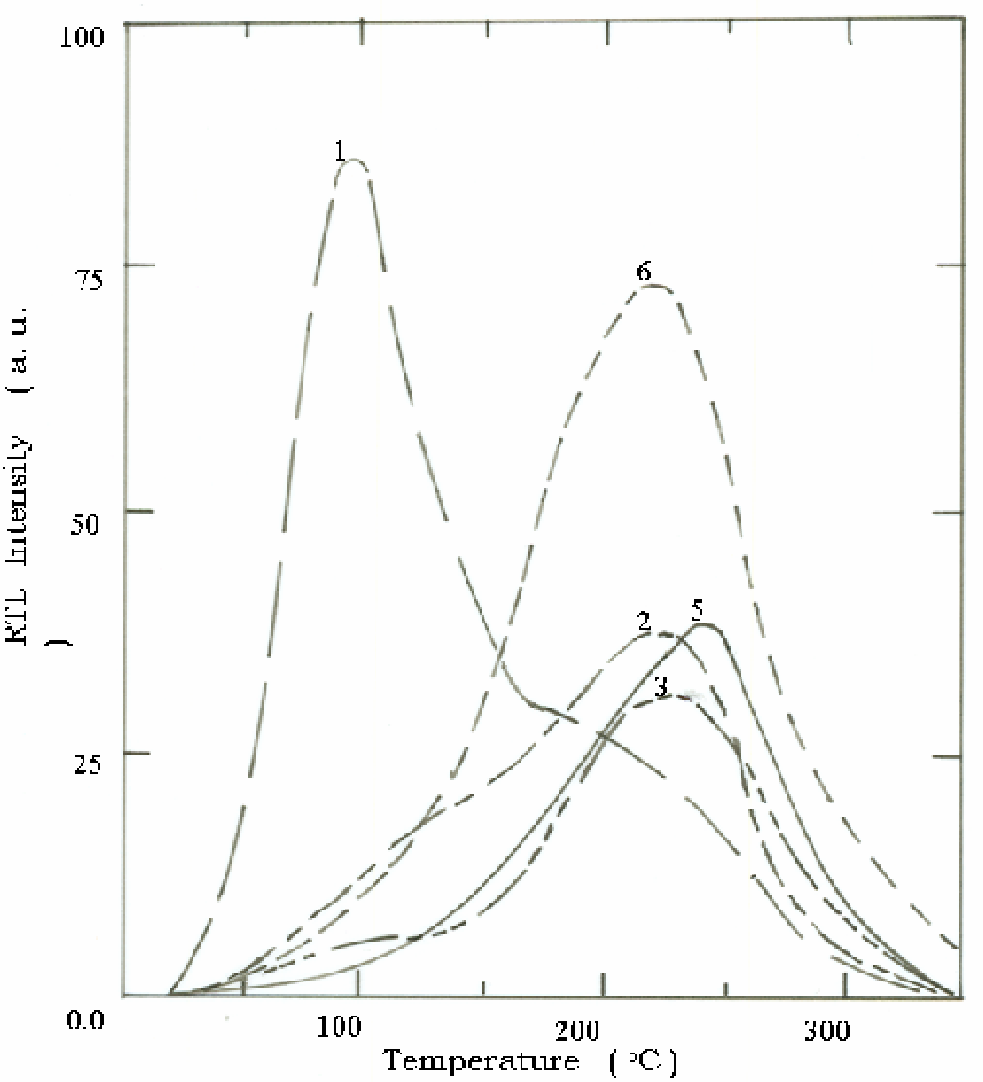

Figure 8: Radio- thermoluminescence curves for ($Na_2B_4O_7$–Yb_2O_3) glass samples (Table I) irradiated with gamma-rays.

CONCLUSION

The present work revealed the following interesting conclusions:

1. The inclusion of Yb_2O_3 in sodium tetraborate glass shifts the fundamental absorption edge to longer wavelengths and produces a new absorption peak at 976 nm.
2. Gamma-irradiation also induces a new absorption peak at about 550 nm for all glass compositions and a second peak at about 360 nm for glasses doped with Yb_2O_3 only.
3. The storage of the irradiated glasses for periods of time up to about 2500 h seems to cause only a reduction in intensities of the newly-induced peaks appearing around 550 nm and 360 nm.
4. No RTL peaks that could be attributed to the presence of Yb ions have been observed. However, Yb only causes a shift of the RTL peaks in the undoped glass to high temperatures and suppresses the low temperature peak appearing at 90 ^{o}C. High Yb concentrations cause the RTL curve to exhibit only a single well-defined peak appearing at high temperatures.

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