JOURNAL OF MATERIALS SCIENCE 26 (1991) 3964–3968

Gamma irradiation-induced effects in sodium diborate glasses doped with some transition metals

A. A. KUTUB, M. S. ELMANHARAWY
Department of Physics, Faculty of Applied Sciences, Umm AL-Qura University, Makkah AL-Mukarramah, Saudi Arabia

Sodium diborate glasses ($Na_2B_4O_7$) doped with 0.5 mol % Fe, Cu and V were irradiated by γ-rays at room temperature at a dose rate of 175 Gy h^{-1} for 8 and 30 h. The spectral absorption of these glasses before and after irradiation was measured in the range 185–2500 nm and was compared with that of the base glass ($Na_2B_4O_7$). The spectral measurements were used to explore the effect of Fe, Cu and V in low quantities on the formation of colour centres in the base glass and, in particular, the sensitivity of these glasses to low and high doses of γ-rays.

1. Introduction

The irradiation of glasses with high-energy radiations, such as X-rays or γ-rays, creates free electrons and holes, some of which are trapped at intrinsic defects in the network [1, 2]. Any impurities in the glass will compete with the intrinsic defects as trapping sites for these carriers; the transition elements often play such a role. Some of the new electronic configurations cause preferential light absorption and so they are called colour centres [3, 4].

Transition elements may be present in glasses in various quantities and forms and may be introduced deliberately or as impurities. It is well known that transition elements easily change their valency under the action of radiation [5–7] and it is of great practical importance to understand this behaviour.

The effects of irradiation on glass systems have been reported by many researchers [3, 4, 8–11]. Bishay [12] studied the absorption band induced by γ-rays in some lead borate glasses. Sanad *et al.* [13] studied the effects of heat treatment and irradiation on barium borate glass containing iron oxide. Ahmed *et al.* [14] reported the effects of irradiation on ($CaO–B_2O_3–Al_2O_3$) glass containing Cu. Kutub and Elmanharawy [15] also reported some γ-irradiation effects in sodium borate glass containing Fe.

The aim of the present work was to study, by means of optical absorption, the roles of small additions (~ 0.5 mol %) of some selected transition metal oxides on the radiation response of sodium diborate glasses. The thermoluminescence induced by γ-irradiation is also reported.

2. Experimental procedure

Glasses having the composition $(Na_2B_4O_7)_{100-x}$ (transition metal oxides, $TM)_x$, where $x = 0$ and 0.5 mol % TM, were prepared from reagent grades of ($Na_2B_4O_7$) and the transition metal oxides Fe_2O_3, CuO and V_2O_5. Before weighing, the borates were placed in a drying oven at 400 °C for 1 h and then transferred to a vacuum desiccator and allowed to cool.

Melting of the glasses which were placed in a recrystallized alumina crucible was done in an electrically heated furnace at 1000 °C for 1 h. During this time, the melt was occasionally stirred with an alumina rod. By slow heating it was hoped to reduce mechanical and volatilization losses. The melt was finally poured on to a clean stainless steel plate and cast into a disc shape of 1.5 cm diameter and about 2 mm thick; the disc was immediately transferred to another furnace which was already at 400 °C. The furnace was maintained at this temperature for 1 h and then switched off, and allowed to cool to room temperature. The glass samples were polished using diamond paste, down to a minimum grit size of 0.1 μm.

The optical absorption measurements were carried out before and after irradiation at room temperature in the wavelength range 185–2500 nm using a Varian model CARY 2390 spectrophotometer. The samples were irradiated for 8 and 30 h at a dose rate of 175 Gy h^{-1} using a ^{60}Co irradiation unit. The output was measured using a substandard Farmer dosemeter (Nuclear Interprises Type 2570 A) fitted with a 0.03 cm^3 ionization chamber, this calibration was checked with a $FeSO_4$ chemical dosemeter.

Optical absorption measurements for the γ-irradiated glasses were carried out within about 5 min after irradiation, and also after different periods of time ranging from a few hours to as long as 167 days (4000 h) at room temperature.

The thermoluminescence of the γ-irradiated glass samples was measured immediately after irradiation. The Harshaw 3000 A TLD system was used, where the

0022–2461/91 $03.00 + .12

sample was heated using reproducible controlled temperature cycles (from room temperature to 400 °C); a linear heating rate of 3 °C s^{-1} was employed. The detected thermoluminescence of the sample was recorded as a function of temperature on an external X–Y recorder.

3. Results and discussion

3.1. Glass without transition metal

The unirradiated base glass sample of $Na_2B_4O_7$ used in the present investigation was colourless. No characteristic bands in the ultraviolet or the visible range were noticed.

On subjecting the sample to γ-radiation, the colour changed to faint violet after 8 h exposure at 175 Gy h^{-1} and to violet when the irradiation time was increased to 30 h.

Fig. 1 shows absorption spectra recorded at room temperature for both unirradiated and irradiated $Na_2B_4O_7$ glass samples. The spectra reveal a shift of the absorption edge to a longer wavelength. This shift becomes more pronounced with increasing radiation dose (Fig. 1b). In addition, a new peak is observed around 550 nm, its position remaining unchanged with increasing radiation dose. The induced visible absorption of binary alkali borate glasses was early attributed to electrons trapped by oxygen vacancies of neighbouring alkali ions [16]. Bishay [4, 17] attributed the induced band to positive hole centres formed by loss of electrons from the oxygens during irradiation. This is in good agreement with optical [4, 17] as well as electron spin resonance [4, 18, 19] studies on similar glass systems. Accordingly, the effects produced in glass by irradiation can be represented by the general equation

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

The stability of the glass samples irradiated for 8 and 30 h was studied by remeasuring their spectral absorption at room temperature after different periods of time ranging from a few hours to as long as 167 days (4000 h). It is clear from Fig. 1a and b that the wavelength of the absorption edge shifts back to shorter wavelengths with increasing time, and this is summarized in Table I.

In addition, the intensity of the newly induced peak around 550 nm decreased gradually with time. These results confirm our previous work in which the sample was exposed to 206.4 Gy h^{-1} for 12 and 24 h [14]. Similar results have been reported by other workers [9, 13].

3.2. Glass containing transition metals

3.2.1. Glass containing Fe

The colour of the base glass changed from colourless to pale brown when doped with 0.5 mol % Fe_2O_3. A weak characteristic band of Fe_2O_3 at 440 nm was observed. It is known that the absorption spectra of ferric ion, Fe^{3+}, show three weak absorption bands at 380, 420, and 435 nm [20]. The absorption due to ferrous ion, Fe^{2+}, is the well-known single broad deep absorption band centred at 1050 nm.

γ-irradiation of ($Na_2B_4O_7$–Fe_2O_3) glass sample causes the original faint brownish colour to become darker. Fig. 2a and b show absorption spectra recorded at room temperature for the irradiated $Na_2B_4O_7$ doped with 0.5 mol % Fe_2O_3. It is obvious that irradiation of ($Na_2B_4O_7$–Fe_2O_3) causes the wavelength of the absorption edge to shift to longer values. This shift becomes more pronounced when the irradiation time is increased.

The Fe characteristic band observed at 440 nm becomes covered by the induced ultraviolet band. The induced absorption peak around 550 nm, which appeared in the irradiated $Na_2B_4O_7$ glass, was much

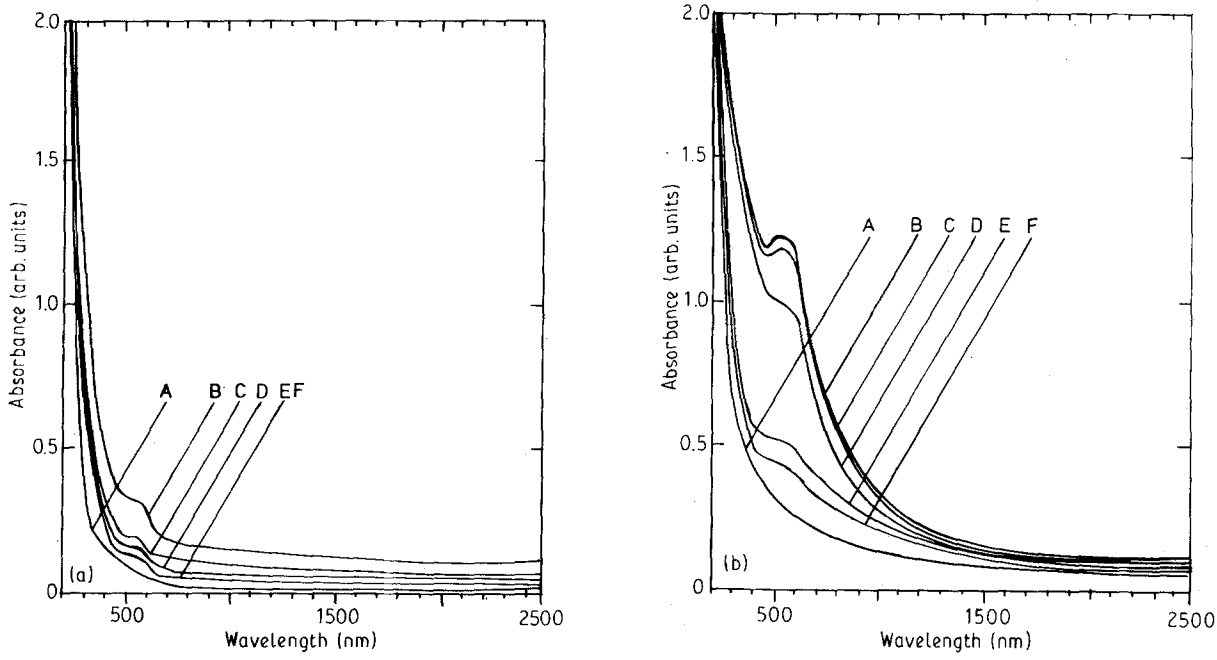

Figure 1 The optical absorption spectra of $Na_2B_4O_7$ glass (sample 1) before and after irradiation for (a) 8 h, (b) 30 h: (A) before irradiation, (B) directly after irradiation, (C) 3 h after irradiation, (D) 60 h after irradiation, (E) 2000 h after irradiation, (F) 4000 h after irradiation.

TABLE I The relation between time of irradiation and absorption edge wavelength after irradiation

Notation	Glass sample	Composition (mol %)	Time of irradiation (h)	Absorption edge wavelength (nm)						Sample thickness (mm)
				Before irradiation	Time elapsed after irradiation (h)					
					0	3	60	2000	4000	
1	$Na_2B_4O_7$	100	8	230	255	250	245	240	235	1.7
			30	201	240	238	230	220	210	1.35
2	$Na_2B_4O_7$–Fe_2O_3	95.5–0.5	8	355	360	360	358	356	355	1.20
			30	355	380	380	370	365	360	1.20
3	$Na_2B_4O_7$–CuO	95.5–0.5	8	315	355	350	345	330	320	1.15
			30	330	483	480	460	365	360	1.30
4	$Na_2B_4O_7$–V_2O_5	95.5–0.5	8	350	360	358	355	353	352	1.15
			30	340	360	358	356	350	345	1.10

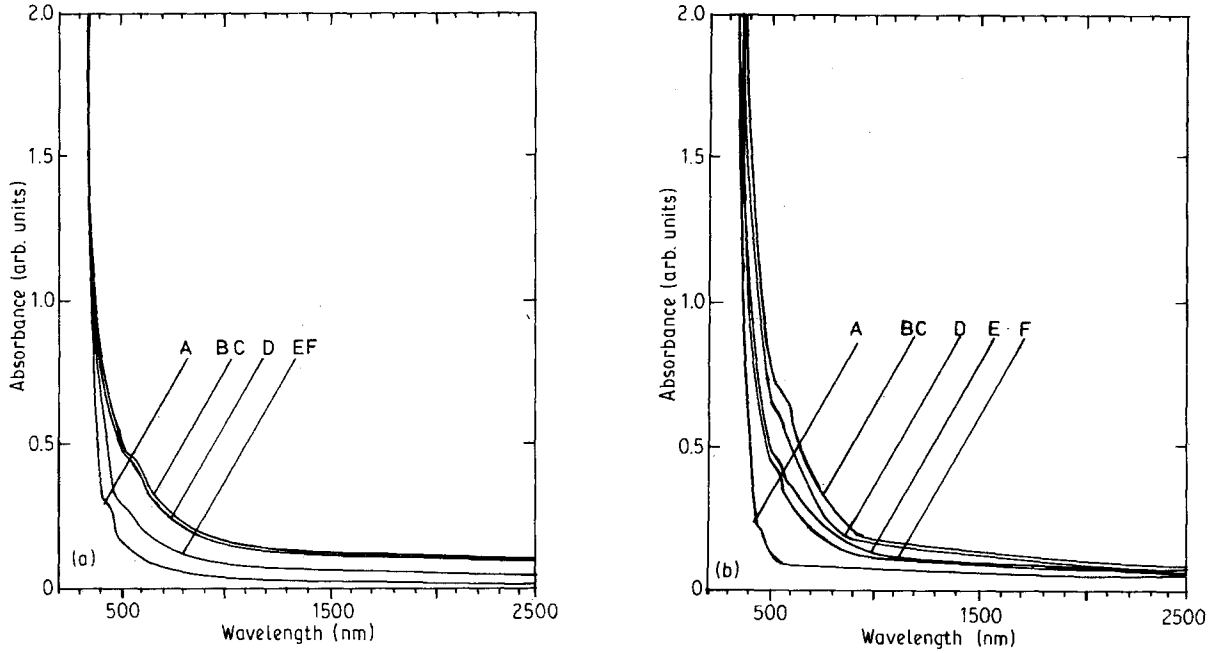

Figure 2 The optical absorption spectra of Fe-doped glass (sample 2) before and after irradiation for (a) 8 h, 30 h: (A) before irradiation, (B) directly after irradiation, (C) 3 h after irradiation, (D) 60 h after irradiation, (E) 2000 h after irradiation, (F) 4000 h after irradiation.

weaker in the Fe-doped glass. It seems that the inclusion of iron in low concentrations in $Na_2B_4O_7$ glass has the effect of suppressing, particularly at high doses, the radiation-induced peak at 550 nm.

3.2.2. Glass containing Cu

The inclusion of 0.5 mol % CuO in the colourless $Na_2B_4O_7$ base glass changes the colour to blue. The effect of doping the base glass with CuO is shown in Fig. 3, where absorption spectra recorded at room temperature are presented. It is also noticed that doping with CuO produces a characteristic band around 800 nm. This band is the typical band found in all glasses containing Cu and is attributed to cupric ions [20–23].

Bamford [24] reported that the blue coloration is associated with presence of the divalent copper ions (Cu^{2+}).

γ-irradiation of ($Na_2B_4O_7$–CuO) glass samples causes the blue colour to become faint brownish. It is clear from Fig. 3 that γ-irradiation causes the absorption edge to shift to longer wavelength and the shift becomes more pronounced at higher radiation dosage (Fig. 3b).

The Cu characteristic band observed at 800 nm increases in intensity with increasing radiation dose. This agrees with the results of Ahmed *et al.* [14] who reported a similar increase in intensity of the characteristic band. This band is attributed to Cu^{2+} ions originally present in the glass sample. On irradiation, the following photochemical reactions could take place

$$\text{defect} + h\nu \rightarrow \text{trapped electron} + \text{free hole} \quad (2)$$

$$Cu^{+} + \text{free hole} \rightarrow Cu^{2+} \quad (3)$$

3.2.3. Glass containing V

The doping of the colourless $Na_2B_4O_7$ base glass with 0.5 mol % V_2O_5 changes the colour to faint yellow. The effect of this doping on the absorption spectra

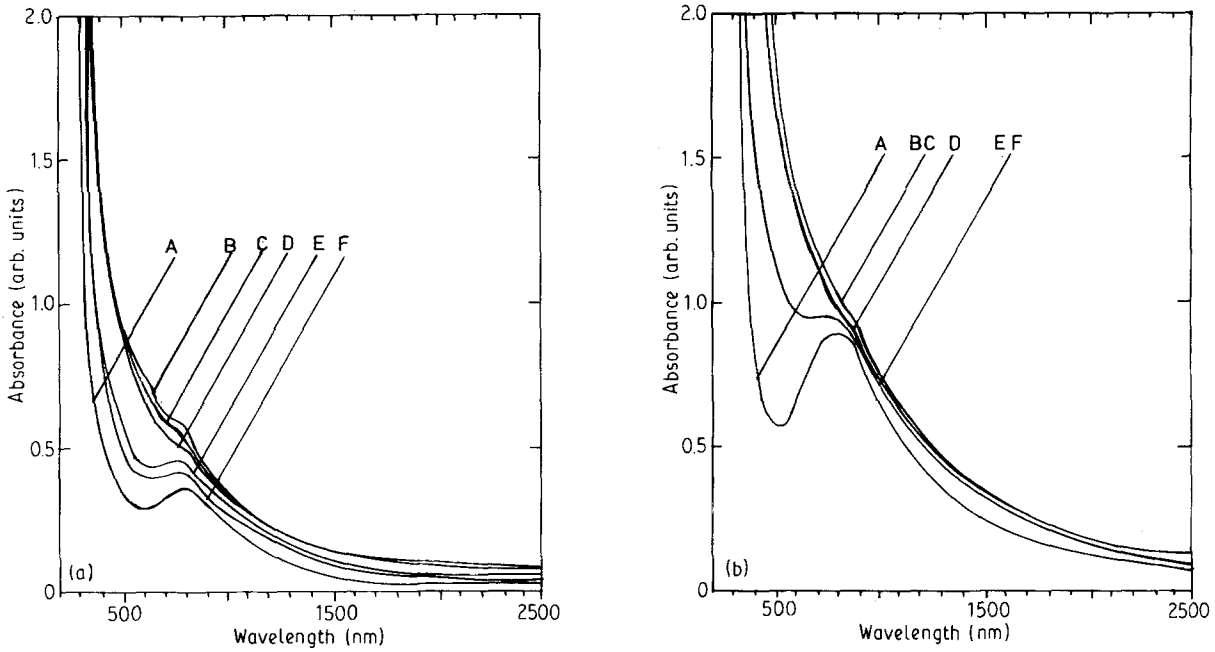

Figure 3 The optical absorption spectra of Cu-doped glass (sample 3) for (a) 8 h, (b) 30 h: (A) before irradiation, (B) directly after irradiation, (C) 3 h after irradiation, (D) 60 h after irradiation (E) 2000 h after irradiation, (F) 4000 h after irradiation.

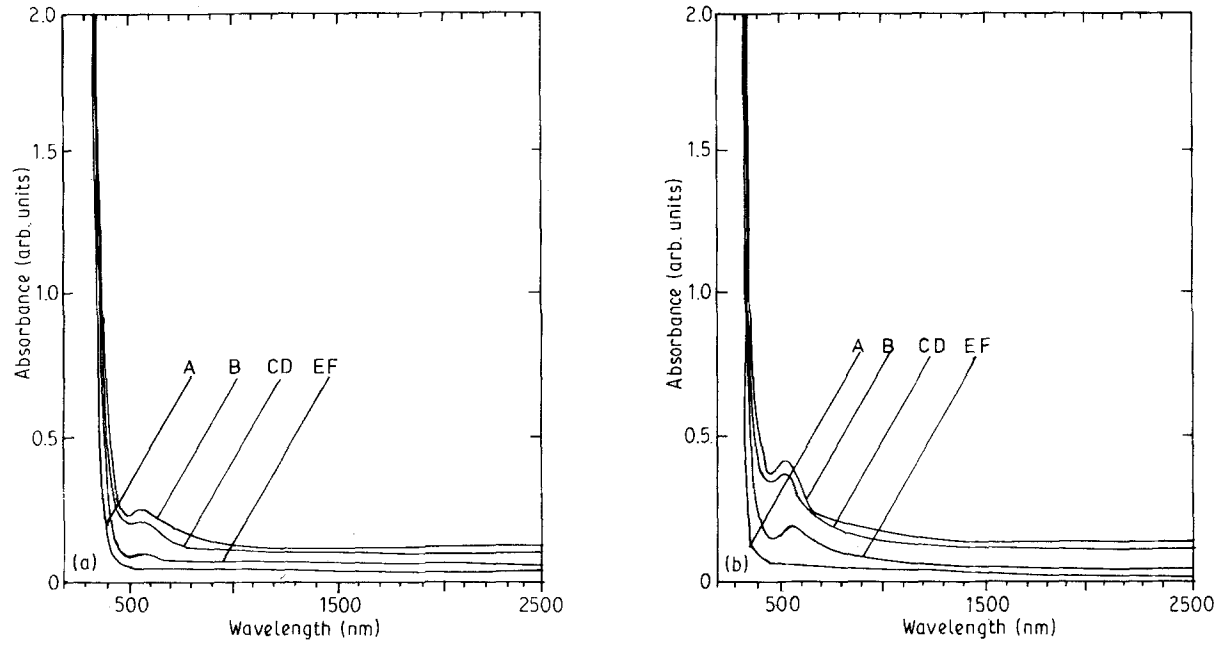

Figure 4 The optical absorption spectra of V-doped glass (sample 4) after irradiation for (a) 8 h, (b) 30 h: (A) before irradiation, (B) directly after irradiation, (C) 3 h after irradiation, (D) 60 h after irradiation, (E) 2000 h after irradiation, (F) 4000 h after irradiation.

recorded at room temperature is shown in Fig. 4a and b.

It is evident that the unirradiated ($Na_2B_4O_7$–V_2O_5) bulk sample (2.9 mm thick) does not exhibit any absorption bands above 400 nm. There is, however, a significant shift of the absorption edge relative to the undoped glass. On irradiation, the colour becomes very much fainter and a new absorption band is induced around 540 nm, which is more pronounced for a sample irradiated for 30 h. This band is characteristic of the V^{3+} ions [20, 25] and is attributed to a transformation of V^{5+} to V^{3+} ions according to photochemical Reactions 2 and 4

$$\text{defect} + h\nu \rightarrow \text{trapped hole} + \text{free electron} \quad (4)$$

$$V^{5+} + 2e \rightarrow V^{3+} \quad (5)$$

When the irradiated borate sample containing V was left for as long as 2000 h, the induced peak did not vanish completely; only a slight decrease in intensity occurred with time. This indicates a slow transformation of the V^{3+} ions to V^{5+} ions.

4. Thermoluminescence

Fig. 5 shows thermoluminescence curves for $Na_2B_4O_7$ glass samples dosed to 350 Gy and measured within

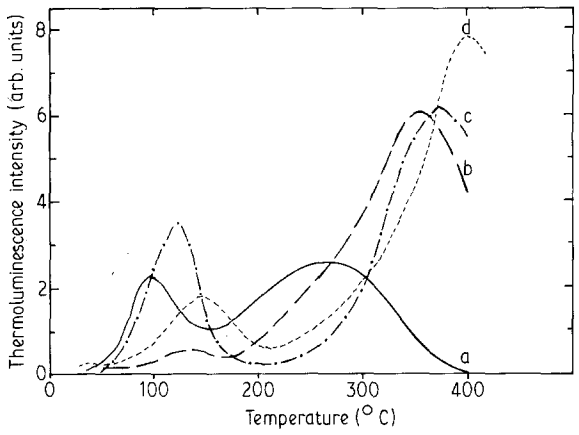

Figure 5 Thermoluminescences curves for γ-irradiated glasses: (a) $Na_2B_4O_7$, (b) $Na_2B_4O_7$–Fe_2O_3, (c) $Na_2B_4O_7$–CuO, (d) $Na_2B_4O_7$–V_2O_5.

the temperature range from room temperature to 673 K. The curve for the undoped glass sample shows two glow peaks around 377 and 543 K. This thermoluminescence is due to the recombination of irradiation-formed trapped electrons or holes with luminescence centres. The formation of these centres results from the interaction of radiation with the defects present in the glass sample according to Equations 2 and 4. It is, however, difficult to assign with certainty the reaction which is responsible for thermoluminescence to the recombination of a given type of centre.

Fig. 5 also shows that the doping of $Na_2B_4O_7$ glass with transition metals does not produce new glow peaks, over the temperature range studied, which could be attributed to centres created by the transition metal. The only observed effect of the transition metal inclusion is a shift of the original glow peaks to higher temperatures. This shift could be due to some sort of interaction between the luminescent centres, created by the interaction of radiation with defect, and the transition metal ion present in the glass sample. These observations are similar to those of Henaish *et al.* [26] who reported thermoluminescence characteristics of $Na_2B_4O_7$ glass containing Nd which showed two glow peaks caused by γ-irradiation.

5. Conclusions

Two radiation-induced effects occur in the spectral absorption of $Na_2B_4O_7$: a shift in the fundamental absorption edge to longer wavelength and the appearance of a stable new band at 550 nm with its position remaining practically unaffected with increasing radiation dose. Similar shifts of absorption edges to longer wavelengths also occur in spectra of $Na_2B_4O_7$ glasses doped with transition oxide metals.

However, the following specific effects were induced by radiation in $Na_2B_4O_7$ doped with transition oxide metals.

1. Irradiation of $Na_2B_4O_7$ glass containing Fe causes the disappearance of the Fe characteristic band at 440 nm.

2. The Cu^{2+} absorption band at 800 nm increases in intensity when $Na_2B_4O_7$ glass containing Cu is irradiated presumably due to a change of Cu^{+} to Cu^{2+}.

3. Irradiation of $Na_2B_4O_7$ glass containing V induces a new absorption band around 540 nm which is associated with a transformation of V^{5+} to V^{3+} ions.

4. No thermoluminescence peak which could be attributed to centres created by the transition metal, has been detected over the temperature range from room temperature to 400 °C. The detected peaks are only those due to centres created by interaction of radiation with intrinsic defects.

References

1. E. J. FRIEBELE and D. L. GRISCOM, in "Treatise on Materials Science and Technology", Vol. 17, edited by M. Tomozawa and R. H. Doremus (Academic Press, New York, 1979) p. 257.
2. E. LELL, N. J. KREIDL and J. R. HENSLER, in "Progress in Ceramic Science", Vol. 4, edited by J. Barke (Pergamon Press, Oxford, 1966) p. 1.
3. A. BISHAY, *J. Non-Cryst. Solids* **3** (1970) 54.
4. *Idem, Phys. Chem. Glasses* **2** (5) (1961) 169.
5. M. M. MORSI and A. M. NASSAR, *J. Non-Cryst. Solids* **27** (1978) 181.
6. F. ASSABGHY, S. ARAFA, EL BOULOS, A. BISHAY and N. J. KREIDL, *ibid.* **23** (1977) 81.
7. L. D. BOGOMOLOVA, A. G. FEDOROV, V. A. JACHKIN and V. N. LAZUKIN, *ibid.* **37** (1980) 381.
8. N. J. KREIDL and J. R. HENSLER, *J. Amer. Ceram. Soc.* **38** (1955) 423.
9. M. M. MORSI, S. EL-KONSOL and M. A. ADAWI, *J. Non-Cryst. Solids* **58** (1983) 187.
10. A. L. HUSSEIN, F. A. MOUSTAFFA, I. GOMMA and L. R. SALEM, *J. Pure Appl. Phys.* **19** (1981) 1036.
11. A. F. ABBAS, A. A. AHMED, M. A. EL-FIKI and H. M. EISSA, *Phys. Chem. Glasses* **26** (4) (1985) 97.
12. A. BISHAY, *J. Amer. Ceram. Soc.* **43** (1960) 417.
13. A. M. SANAD, I. KASHIF, A. A. EL-SHARKAWY, A. A. EL-SAGHIER and H. FAROUK, *J. Mater. Sci.* **21** (1986) 3483.
14. A. A. AHMED, A. F. ABBAS and F. M. EZZ EL-DIN, *Phys. Chem. Glasses* **25** (1) (1984) 22.
15. A. A. KUTUB and M. S. ELMANHARAWY, *J. Non-Cryst. Solids* **104** (1988) 31.
16. R. YOKOTA, *Phys. Rev.* **95** (1954) 1145.
17. A. BISHAY, *J. Amer. Ceram. Soc.* **45** (1962) 389.
18. G. O. KARAPELYAN and J. M. YIDIN, *Sov. Phys. Solid State* **4** (1963) 1943.
19. S. LEE and P. J. BRAY, *J. Chem. Phys.* **39** (1963) 2863.
20. J. C. HADDON, E. A. ROGERS and WILLIAMS, *J. Amer. Ceram. Soc.* **52** (1) (1969) 52.
21. A. DURAN and J. M. FERNANDEZ NAVARRO, *Phys. Chem. Glasses* **26** (4) (1985) 126.
22. R. HARANI, C. A. HOGARTH and K. A. K. LOTT, *J. Mater. Sci.* **19** (1984) 1420.
23. A. A. KUTUB, A. E. MOHAMMAD-OSMAN and C. A. HOGARTH, *ibid.* **21** (1986) 3517.
24. C. R. BAMFORD, *Phys. Chem. Glasses* **1** (1960) 159.
25. *Idem*, "Color Generation and Control in Glass" (Elsevier, Amsterdam, 1977) p. 52.
26. B. A. HENAISH, M. A. KENAWY, A. F. ABBAS and L. R. SALEM, in "The First Egyptian-British Conference on Bio-Physics", Cairo University, Giza, Egypt, 26–28 October 1987.

Received 25 June
and accepted 19 November 1990