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Gamma Irradiation Induced Photochemical Reactions in V-Doped Borate Glasses

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Glasses of the composition $X\mathrm{Na_2O} \cdot 4\mathrm{Al_2O_3}\ (96\text{-}X)\ \mathrm{B_2O_3}$ (mole%) where $X = 10, 20, 30$ to which 0.03 g V_2O_5 per 100 g glass was added, were prepared by normal melting. Their absorption characteristics together with the corresponding V-free base glasses were determined before and after gamma irradiation. The characteristic spectra of the unirradiated glasses show absorption bands at 315, 470, 560–580, 610–650, 700–870, and 860–1000 nm, indicating the presence of vanadium ions in more than one oxidation state, viz, V^{5+}, V^{4+}, and V^{3+}. Gamma irradiation of V-containing glasses causes the formation of color centers in the glass matrices, with absorption bands at 330, 500, and 610 nm, and photoreduced $[V^{3+}]$ and $[V^{2+}]$ ions with absorption bands at 350–355 and 530–570 and 520 nm, respectively. Photoreduced $[V^{4+}]$ may also be formed, giving rise to absorptions at 690–700 and 750–800 nm. The induced vanadium ions are found to absorb at shorter wavelengths than the intrinsic ones. An explanation based on the difference in the field energy of the two states is given.

Introduction

Numerous studies have been carried out on the optical, ESR and EPR properties of borate, phosphate, and silicate glasses containing vanadium (*1–12*). Glasses containing vanadium can exhibit a range of colors from green to yellow to almost colorless as the alkali oxide content is increased. This arises from the fact that vanadium can exist in several valence states; V^{5+}, V^{4+}, V^{3+}, or V^{2+}, depending on glass composition and melting conditions (*13*).

It has been stated (*7*) that the V^{2+} state is practically unknown. However, Kumar and Purabi (*14*) found from their irradiation study on silicate glasses containing V_2O_5 and CeO_2 that V^{2+} could be formed in such glasses by photoreduction of V^{3+} ions.

The present study is an effort to throw some light on the photoreactions that may take place if gamma irradiation is allowed to fall on borate glass which contains V_2O_5 only and which is prepared by melting in air.

To differentiate the bands which may be induced by irradiation of V-containing glasses from those due to color centers formed in the glass matrix, an irradiation was also carried out on V-free glasses of the corresponding base compositions.

Experimental

Analytical reagent grade materials were used in preparation of the glasses (Table I). The batch materials were mixed and then melted in Pt-2% Rh crucibles at 1200°C for

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TABLE I

COMPOSITIONS OF THE GLASSES STUDIED

Glass No.	Composition	(mole%)	Additives g/100 g glass
1	$10Na_2O$, $4Al_2O_3$, 86	B_2O_3	$0.03V_2O_5$
1*b*	$10Na_2O$, $4Al_2O_3$, 86	B_2O_3	—
2	$20Na_2O$, $4Al_2O_3$, 76	B_2O_3	$0.03V_2O_5$
2*b*	$20Na_2O$, $4Al_2O_3$, 76	B_2O_3	—
3	$30Na_2O$, $4Al_2O_3$, 66	B_2O_3	$0.03V_2O_5$
3*b*	$30Na_2O$, $4Al_2O_3$, 66	B_2O_3	—

2 hr in an electric furnace in air. Small charges were prepared, and to ensure homogeneity the melts were stirred several times before each charge and after charging was completed. The melted glasses were cast into rectangular slabs and transferred to an annealing furnace at 400°C which was then switched off and allowed to cool to room temperature. The glass pieces were ground and polished for optical measurements. The latter were performed on the unirradiated and the irradiated glasses using a Beckman DR Spectrophotometer in the range 300–1500 nm. Irradiation was carried out using a ^{60}Co gamma cell at a dose rate of 12×10^4 rad/hr.

Results and Discussions

The nonirradiated glasses Nos. 1, 2, and 3 are faintly yellowish green in color. Their absorption spectra are given in Fig. 1. This shows that V-containing alkali borate glasses are characterized by several absorption bands in the ranges 315, 470, 580 → 560, 650 → 610, 870 → 700 and 1000 → 860 nm. The arrow means that the band shifts

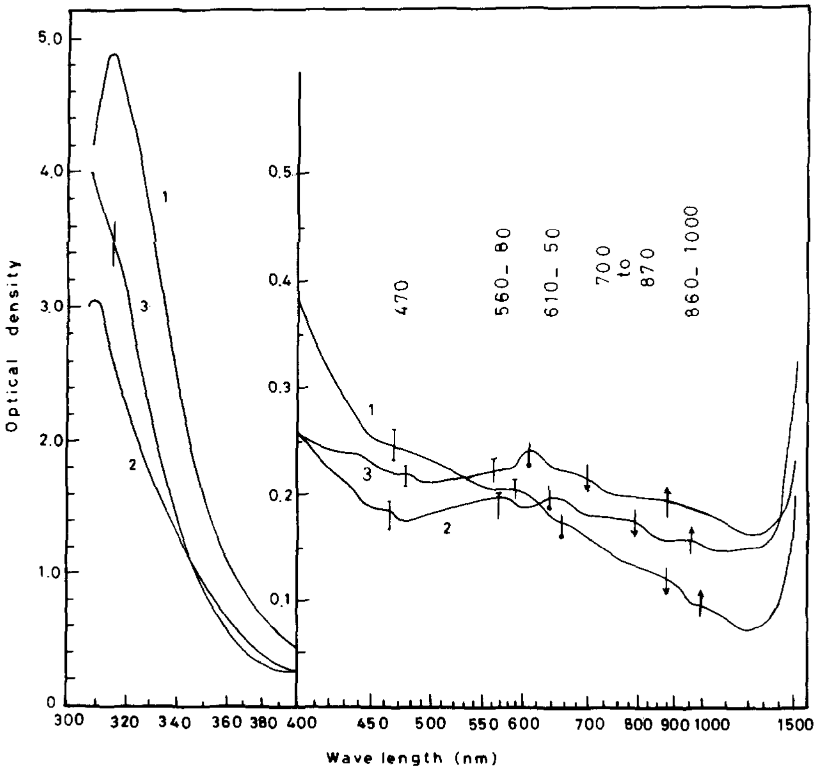

FIG. 1. Absorption spectra of $X Na_2O \cdot 4Al_2O_3 (96\text{-}X) B_2O_3$ (mole%) glasses containing 0.03 g V_2O_5/100 g glass. X = 10 (No. 1), 20 (No. 2), 30 (No. 3).

toward the indicated wavelength as the alkali content increases. This may be related to the increase of the coordination number of boron atoms as the alkali oxide concentration is increased (*12*).

Although the band at the near uv region (315 nm) was previously considered as a charge transfer band of V^{5+} ions (*15–17*), the observed decrease of its intensity as the alkali content increased from 10 to 20 mole% may allow us to assume that this band is related to V^{4+} ions. Similar results are found (*7*) in some borophosphate glasses containing vanadium in the tetravalent state. The charge transfer band of V^{5+} is expected to be present at shorter wavelengths which may explain the intense band observed at shorter wavelengths as the alkali content is increased to 30 mole% (Fig. 1).

Most of the V^{4+} and V^{3+} bands appear in the visible region and near ir region (*8, 9*). According to previous investigations on vanadium-containing glasses and solutions (Table II), the observed bands around 470, 560–580, and 610–650 nm can be attributed to V^{3+} ions while those at 700–870 and 860–1000 nm to V^{4+} ions. If V^{2+} is present in octahedral symmetry in glass, low-intensity bands should occur at 406, 625, and 952 nm (*11*) which overlap with the stronger V^{3+} and V^{4+} bands.

Assuming that vanadium ions are present in an octahedral field, the assignment of the observed bands could be achieved by considering the energy diagrams of d^1, d^2, and d^3 states in an octahedral field (*11*). The assignments of vanadium bands in similar borate glasses have been described in detail elsewhere (*13, 17*).

Figure 2 presents an example of the effect of gamma irradiation on V-free glasses No. 2*b*. Similar results are obtained for 1*b* and 2*b*. The position of the gamma irradiation induced bands in the spectra of such glasses is nearly the same as those previously reported for similar glasses (*18, 19*). Three bands occur near 330, 500, and 610 nm. Their intensities depend on the concentration of Na_2O and on gamma dose as well; this is consistent with the results obtained by Beekenkamp (*20*). The induced spectra of the V-free glasses showed an increase in intensity of the band at 500 nm, as the Na_2O content is increased. This can be correlated with the increasing concentration of the nonbridging oxygen ions in the glasses.

TABLE II

POSITION OF ABSORPTION BANDS OF V^{4+} AND V^{3+} IONS IN SOME VANADIUM COMPLEXES AND GLASSES

Vanadium in	Position (nm) V^{3+}	V^{4+}	Reference
Phosphate	450	850	2
glasses	700	—	
Sodium	360	—	
borate	570–610	—	3
	650–960		
$Na_2O \cdot 2SiO_2$	440	410	
	650	610	8
		1090	
Soda-lime	620–680	410	
silica	740	600	9
		1090–1000	
Alkali-rich	—	1000	
borates and	—	1600	12
germanate			
$V(C_2O)_6^{3+}$ in	430	—	15
perchloric	580	—	
acid			

The absorption spectra of the irradiated V-containing glasses Nos. 1, 2, and 3 are shown in Figs. 3, 4, and 5, respectively. It should be noticed that several absorption bands occur close to about 320–330, 350–355, 500, 520, 530–570, and 600 nm. Furthermore, two induced bands are observed at 690–700 and 750–800 nm which disappear as the gamma dose is increased. Some of the absorption bands originally present vanish or shift toward longer wavelengths as the gamma dose increases.

The observed induced bands in V-containing glasses may be attributed to forma-

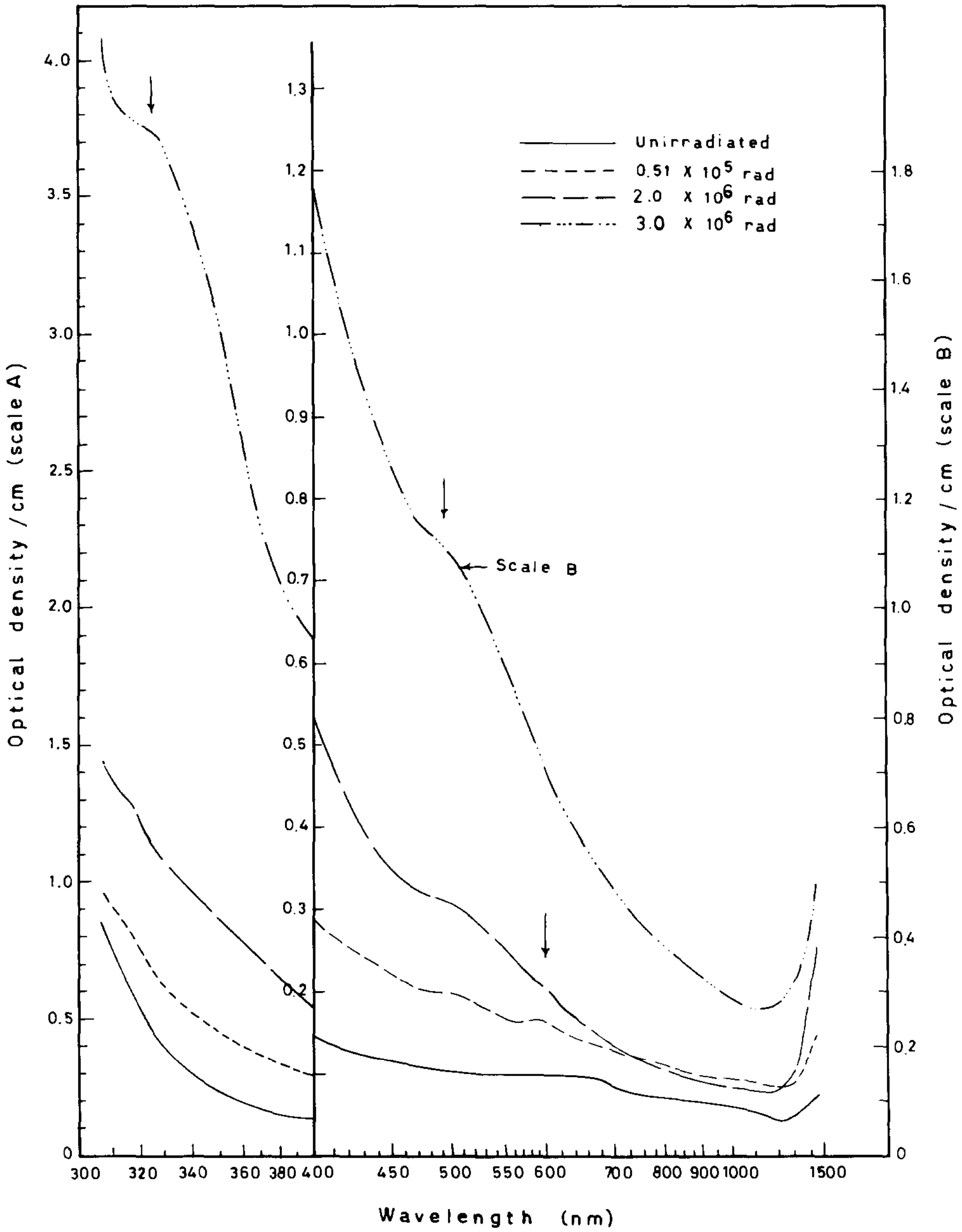

FIG. 2. Absorption spectra of glass No. 2*b* ($20Na_2O \cdot 4Al_2O_3 \cdot 76B_2O_3$ (mole%)), exposed to different gamma doses.

tion of color centers in the glass matrix and to the presence of photoreduced vanadium ions.

Comparison of Fig. 2 with Figs. 3–5 indicates that the induced bands at 320, 500, and 600 nm in the spectra of the three latter glasses are due to color centers formed in glass matrices.

The irradiation-induced bands at 690–700 and 750–800 nm should be compared with

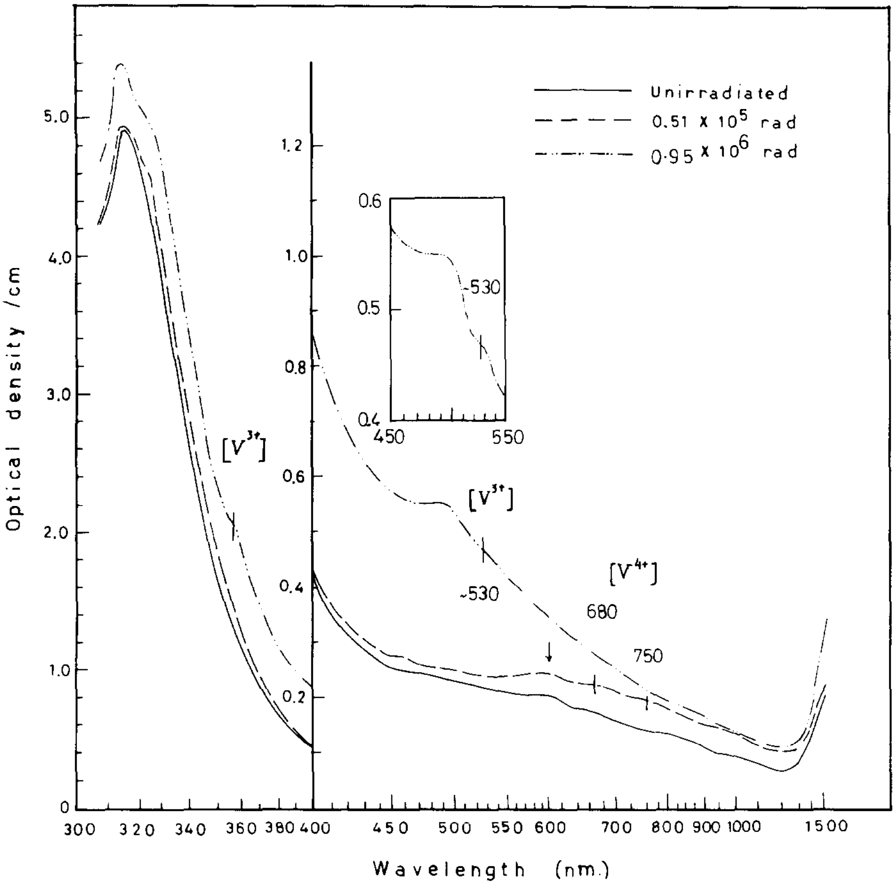

FIG. 3. Absorption spectra of glass No. 1, $10Na_2O \cdot 4Al_2O_3 \cdot 86B_2O_3$ (mole%), 0.03 g V_2O_5/100 g glass, exposed to different gamma doses.

those of the V^{4+} ion observed at 700–870 and 860–1000 nm in the spectra of the unirradiated glasses. They should be considered to be shifted toward shorter wavelengths. This may suggest the formation of the photoreduced [V^{4+}] ions by electron capture of V^{5+}

$$V^{5+} + e \rightarrow [V^{4+}]. \quad (1)$$

The field energy Δ due to negatively charged ligands (O^{2-}) varies inversely as the fifth power of the distance between the vanadium ion center and the O^{2-} ion (*21*). Since the ionic radius of V^{5+} ion is smaller than that of V^{4+}, i.e., the interionic distance of V^{5+}–O^{2-} is smaller than that of V^{4+}–O^{2-}, the interionic distance of the photoreduced [V^{4+}] and O^{2-} should remain equal to that of V^{5+}–O^{2-}. In other words, the interionic distance of the induced [V^{4+}] will be smaller than that of the intrinsic V^{4+}. Hence the position of the absorption bands due to induced [V^{4+}] will be at shorter wavelengths as compared to those of the intrinsic V^{4+} ions. This may give a reasonable explanation for the shift of the induced [V^{4+}] bands toward shorter wavelengths. However, the disappearance of these two bands at high doses may also indicate the conversion of formed [V^{4+}] ions into another state.

It has been found that vanadium-containing glasses may show an absorption band at

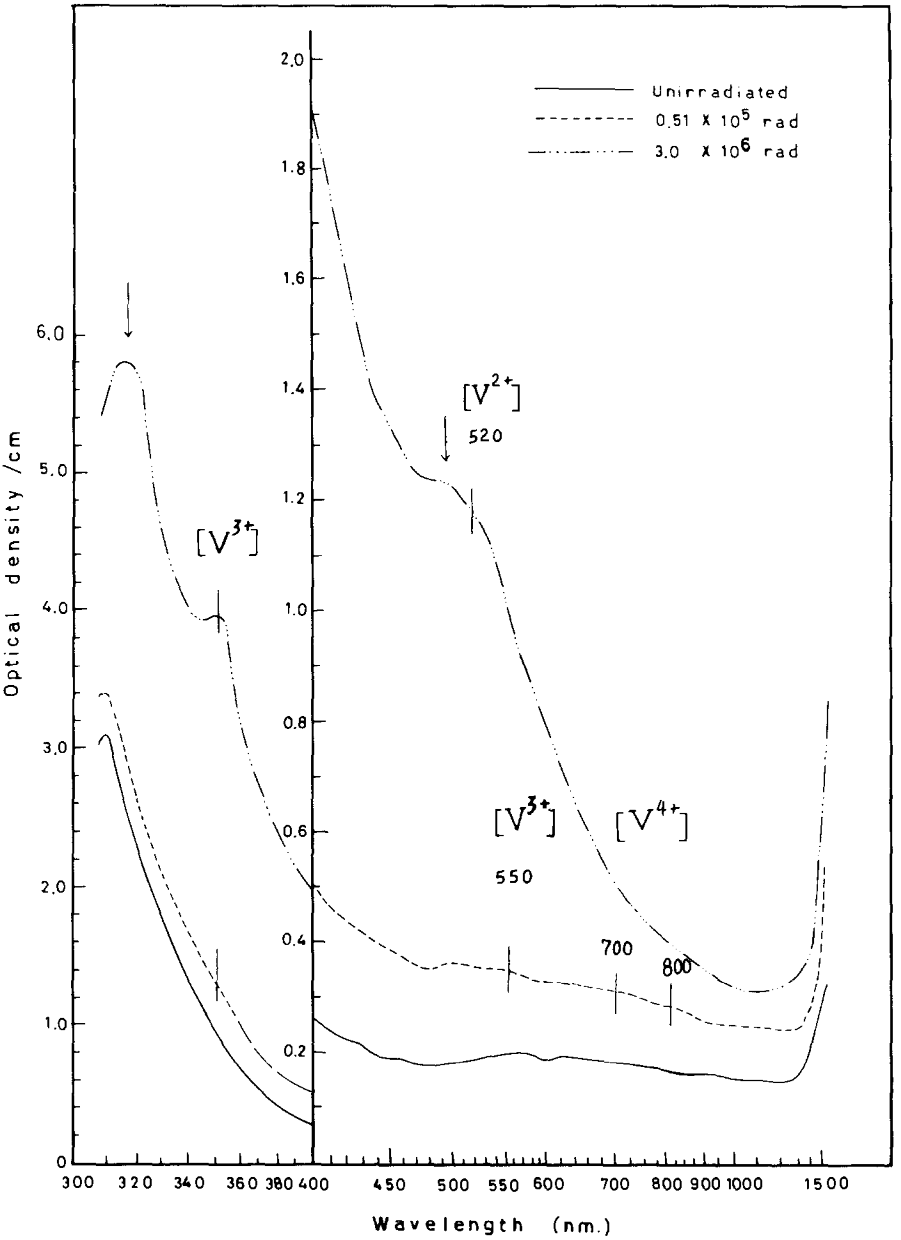

FIG. 4. Absorption spectra of glass No. 2, $20Na_2O \cdot 4Al_2O_3 \cdot 76B_2O_3$ (mole%), 0.03 g V_2O_3/100 g glass, exposed to different gamma doses.

350–355 due to V^{3+} ions (*3*). The developing of such a band in the present glasses indicates the formation of V^{3+} ion by gamma irradiation. A possible explanation is the photoreduction of V^{4+} ion into the trivalent ion:

$$V^{4+} + e^- \rightarrow [V^{3+}]. \qquad (2)$$

The V^{4+} ion could be either an intrinsic or an induced one.

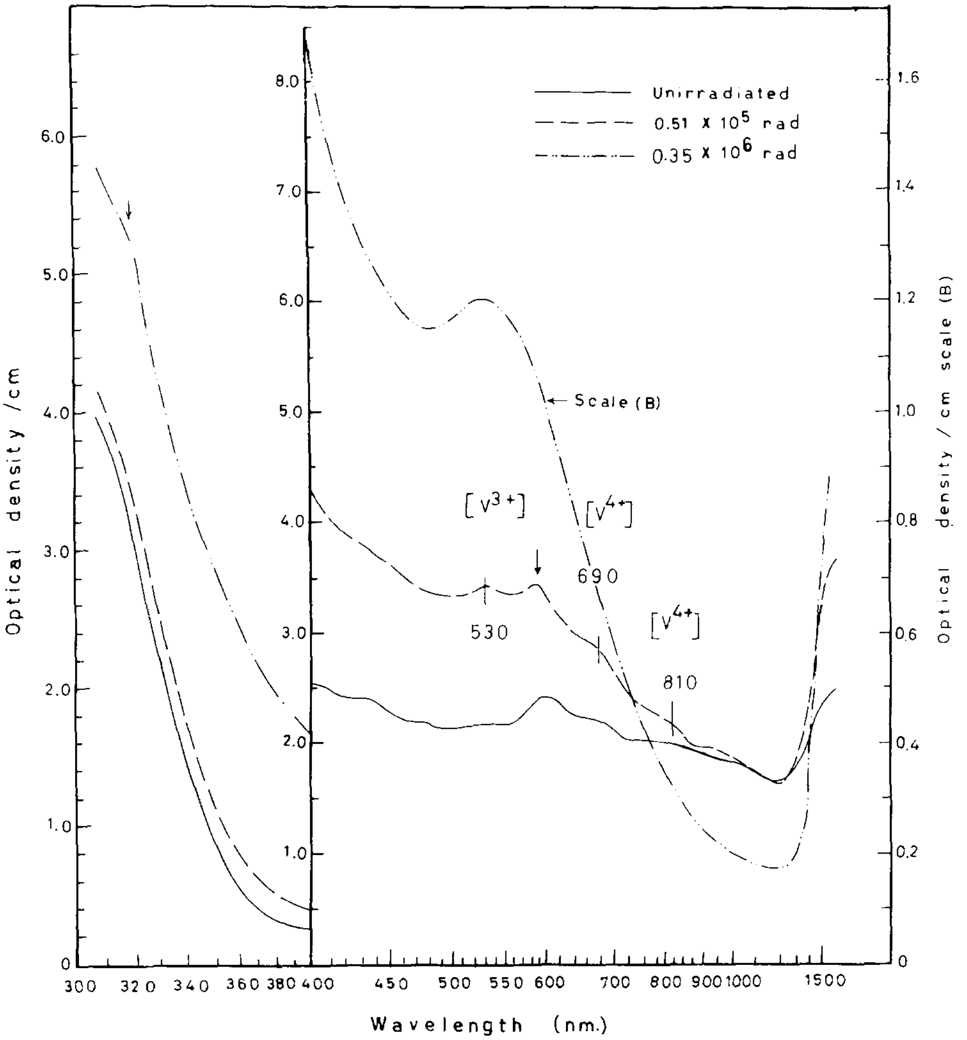

FIG. 5. Absorption spectra of glass No. 3, $30Na_2O \cdot 4Al_2O_3 \cdot 66B_2O_3$ (mole%), 0.03 g V_2O_5/100 g glass, exposed to different gamma doses.

Although, the V^{2+} ion state is almost unknown, the band at 520 nm has been attributed to photoreduced V^{2+} ion (*14*). The present induced band (520 nm) can, accordingly, be attributed to the formation of a V^{2+} ion by the photoreduction of V^{3+} ion:

$$V^{3+} + e^- \rightarrow [V^{2+}]. \qquad (3)$$

From Fig. 4 the band at 530–570 nm, ascribed to $[V^{3+}]$ is clearly observed in the spectrum of the low dosage, irradiated glass, while the band at 520 nm, ascribed to $[V^{2+}]$, is undetectable. The development of the latter band in the spectrum of the highly irradiated glass substantiates reaction (3), and the above-mentioned attribution. The foregoing discussion suggests that there is an equilibrium between reaction (1) and (2), with the formation of V^{2+} and V^{3+} as photoreduced ions in the present glasses.

A similar explanation may be invoked to explain the developing band at 350–355 and

530–570 nm of the induced [V^{3+}] which arises at shorter wavelengths compared with those of the intrinsic V^{3+} ion.

Conclusions

Vanadium is present as V^{5+}, V^{4+}, and V^{3+} ions in the sodium aluminoborate glasses melted under normal conditions. The pentavalent state exhibits a charge transfer band in the uv region, while the V^{4+} is characterized by one charge transfer band at about 315 nm and by two others in the near ir region at 700–870 and 860–1000 nm. The V^{3+} has absorption bands in the visible region at 470, 560–580, and 610–650 nm. The position of the intrinsic bands of vanadium ions depends upon the alkali content of the base glass.

Gamma irradiation of the V-free and V-containing glasses induces absorption bands at 330, 500, and 610 nm, due to trapped hole and trapped electron centers normally induced by the irradiation (*19*) process.

Gamma irradiation of V-containing glasses causes a reduction of the V^{5+}, V^{4+}, and V^{3+} ions into photoreduced [V^{4+}], [V^{3+}], and [V^{2+}] ions, respectively, according to the reactions

$$\begin{array}{c} V^{5+} + e^- \rightarrow [V^{4+}] \\ [V^{4+}] + e^- \rightarrow [V^{3+}] \\ V^{3+} + e^- \rightarrow [V^{2+}] \\ \hline V^{3+} + V^{5+} + 3e^- \rightarrow [V^{2+}] + [V^{3+}]. \end{array}$$

In addition the photoreduction of V^{4+}, originally present, may also occur:

$$V^{4+} + e^- \rightarrow [V^{3+}].$$

The induced [V^{4+}] ion produces absorption bands at 690–700 and 750–800 nm.

Those ions of the induced [V^{3+}] have absorption bands at 350–355 and 530–570 nm, while the induced [V^{2+}] ion has absorption bands at 520 nm. The absorption bands of the induced [V^{3+}] are present at shorter wavelengths than the corresponding bands of the intrinsic V^{3+} ions. If one accepts the view (*11*) that intrinsic low-intensity bands for V^{2+} might be predicted to occur at 625 and 952 nm, then the induced band at 520 nm can be considered to be present at shorter wavelengths also. These shifts are due to difference of ligand field energy of both the induced and the intrinsic ions.

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