

# Spectroscopic studies of gamma-irradiated transition metals-doped soda lime phosphate glass

Fatma H El-Batal, Sherief M Abo-Naf\*

Glass Research Department, National Research Center (NRC), Dokki, 12622 Cairo, Egypt

and

Fathy M Ezzldin

National Center for Radiation Research & Technology, Nasr City, Cairo, Egypt

*Received 3 November 2004; revised 1 April 2005; accepted 1 June 2005*

Optical absorption spectra of 3d transition metals have been measured in soda-lime phosphate glass before and after successive gamma irradiation. In general, the transition metals exhibit the lower oxidation state or octahedral coordination in phosphate glass. The experimental optical spectra are related to the respective specific transition of each transition metal ion. Transition metal-doped phosphate glasses reveal varying response to the effect of successive gamma irradiation. The intensity and growth behaviour of the radiation-induced bands are seen to depend on the type of the 3d transition metal. The response of the doped-phosphate glass to gamma rays irradiation is related to the formation of characteristic induced colour centers and the subsequent annihilation or approach of saturation.

**Keywords:** Optical absorption, Phosphate glasses, Transition metals, Gamma-ray irradiation

**IPC Code:** G01J3/42

## 1 Introduction

The 3d transition metals have been recognized as colouring agents in oxide glasses<sup>1</sup>. Each metal can exist in several oxidation or coordination states within the glass and the equilibrium between these states will depend on the melting conditions and the glass type and composition<sup>2</sup>. Each state can give rise to different absorption spectra, which have been extensively measured and explained by the application of ligand field theory<sup>3-5</sup>.

Phosphate glasses have been the object of recent interest because of their valuable physical properties. They have a very high transmission in the ultraviolet region compared to silicate glasses. They are suitable materials for high power lasers because of low thermo-optical coefficient and large emission<sup>6</sup>. Most bioactive materials are also based on phosphate glasses or ceramics<sup>7</sup>. Also, phosphate glasses are useful in immobilization of radioactive wastes<sup>8</sup>, and can be applied in energy storage devices and solid state batteries<sup>9</sup>. Such numerous applications can be achieved by proper selection of phosphate glass compositions.

The first objective of this work was undertaken in order to investigate the absorption spectra of the first transition metal series in a soda lime phosphate glass.

The work was extended to measure the effect of gamma irradiation on the ultraviolet-visible spectra of such doped-glasses.

## 2 Experimental Details

### 2.1 Preparation of glasses

Glass batches were prepared from the base chemical composition P<sub>2</sub>O<sub>5</sub> 45%, Na<sub>2</sub>O 30%, CaO 25% (mol %) to which was added the appropriate per cent of each transition metal oxide to obtain clear brilliant coloured glasses as given in Table 1. The batches were melted in alumina crucibles in electric furnace at 1100±20°C for 90 min, and the melts were cast and annealed in a muffle furnace regulated at 320°C. The muffle was left to cool at a rate of 30°C/hour to room temperature.

### 2.2 Optical absorption measurements

Visible and ultraviolet optical absorption spectra were measured for highly polished glass samples of specified thickness (2±0.02mm) before and within 15 min after gamma irradiation using a recording Uvikon 860 (Kontron, Zurich, Switzerland) spectrophotometer covering the range from 200 to 900 nm.

Table 1—Chemical composition of the glass batches (mol %)

Glass No.	Na <sub>2</sub> O	CaO	P <sub>2</sub> O <sub>5</sub>	Added transition metal oxide gm/100gm glass
1	30	25	45	-
2	30	25	45	5 TiO <sub>2</sub>
3	30	25	45	0.5 V <sub>2</sub> O <sub>5</sub>
4	30	25	45	0.05 Cr <sub>2</sub> O <sub>3</sub>
5	30	25	45	0.20 MnO <sub>2</sub>
6	30	25	45	1.0 Fe <sub>2</sub> O <sub>3</sub>
7	30	25	45	0.05 CoO
8	30	25	45	0.07 NiO
9	30	25	45	0.50 CuO

### 2.3 Gamma irradiation

An Indian <sup>60</sup>Co gamma cell (2000.Ci) was used as a gamma ray source with a dose rate of 1.5 Gy/sec (150 rad/sec).

## 3 Results

### 3.1 Optical absorption spectra

The UV-visible absorption spectra before and after successive gamma irradiation of the undoped and various transition metal-doped phosphate glasses are shown in Figs 1 and 2.

#### 3.1.1 Parent blank glass

The parent phosphate glass is colourless and reveals no characteristic band before irradiation in the visible region but showed an ultraviolet band at about 250 nm (Fig. 1) and this band is usually assigned to iron impurities in phosphate glasses<sup>10-12</sup>. On subjecting the glass to gamma irradiation, a shifting of the beginning of absorption to higher wavelengths is observed together with the resolution of a very broad band extending from about 380 to 600 nm with a maximum at about 430 nm. With progressive irradiation, the intensity of the broad band increases accompanied with a progressive shifting of the beginning of absorption to higher wavelength.

#### 3.1.2 Titanium-doped glass

The measured absorption spectrum of the pink TiO<sub>2</sub>-doped phosphate glass before irradiation is given in Fig. 2 which reveals the occurrence of two visible bands at 540 and 710 nm accompanied by a shifting of the UV absorption towards higher wavelengths. Several researchers<sup>13-15</sup> have indicated that the first-band is related to Ti<sup>3+</sup> in octahedral symmetry but with some tetragonal distortion. The other small band at 710 nm is accepted as a shoulder to the peak and is likely to be caused by the Jahn-

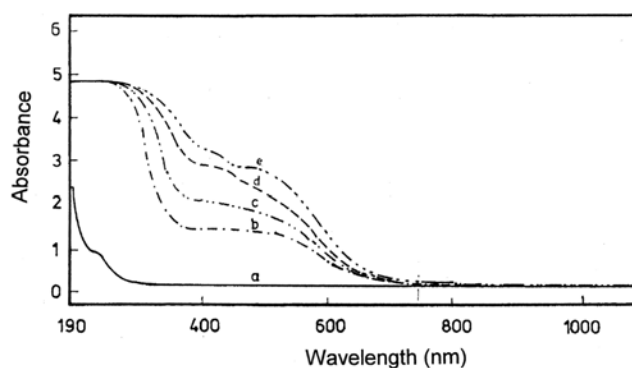


Fig. 1—Absorption spectra of undoped parent soda lime phosphate glass before and after successive gamma irradiation

Teller effect, giving tetragonal distortion and leading to a splitting of the ground state<sup>14,15</sup>. On successive gamma irradiation, titanium ions in phosphate host seem to suppress any possible alteration.

#### 3.1.3 Vanadium-doped glass

The measured spectrum in V-doped phosphate glass before gamma irradiation is shown in Fig. 2. The absorption spectra reveal two broad absorption bands in the visible region; the first is centered at about 450 nm and the second band is split to two peaks at about 660 and 690 nm. These bands can be assigned to V<sup>3+</sup> in octahedral symmetry<sup>16</sup>. The ultraviolet spectrum reveals two UV absorption bands, a charge transfer high intense band at about 230 nm and another small peak is observed at about 240 nm. Upon first gamma irradiation (dose 0.5×10<sup>6</sup> rad), the overall spectrum shows an increase in the intensities of the absorption bands. The ultraviolet spectrum shifts towards higher wavelengths and the visible spectrum reveals a broad absorption band extending from about 400 nm to about 500 nm. With progressive irradiation the broad visible band shows splitting to two peaks, the first at about 500 nm and the second at about 610 nm.

#### 3.1.4 Chromium-doped glass

Cr<sup>6+</sup> has a 3d<sup>0</sup> configuration and therefore exhibits only sharp charge transfer band giving rise to strong absorption around 370 nm because of its large intensity<sup>5,17</sup>.

The spectra of Cr-doped phosphate glass before and after gamma irradiation are shown in Fig. 2. The glass before irradiation is green in colour and gives four major absorption bands; one broad in the ultraviolet region with maximum around 350 nm and three visible bands at about 430, 660 and 880 nm. The first

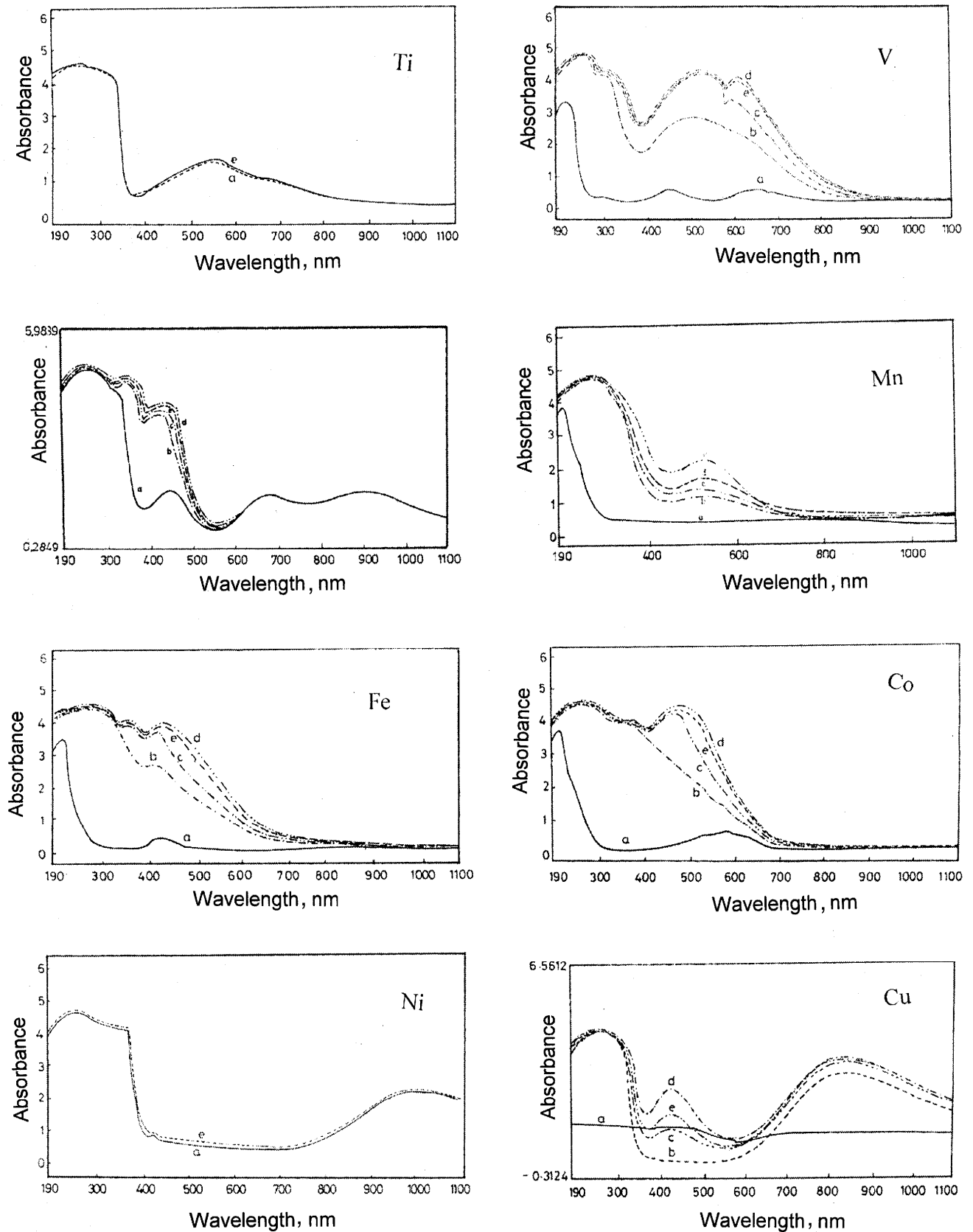


Fig. 2—Absorption spectra of TM-doped soda lime phosphate glass before and after successive gamma irradiation

two visible absorption bands are accepted<sup>1-5,17</sup> to correspond to  $\text{Cr}^{3+}$  in octahedral symmetry. The absorptions have been shifted towards the infrared region as would be expected from a weaker ligand field. The absorption band at 880 nm is not previously shown in glasses melted under atmospheric condition. However, it had been reported that a band around 840 nm was observed in Cr-containing glasses melted under reducing condition<sup>14,8</sup>. Upon gamma irradiation, the band at 430 nm shows a pronounced increase in its intensity with the first dose ( $0.5 \times 10^6$  rad) accompanied by a shift to lower wavelength and then becomes stable with further progressive gamma irradiation.

### 3.1.5 Manganese-doped glass

The Mn-doped glass spectrum in phosphate glass before irradiation (Fig. 2) shows an ultraviolet band at about 210 nm due to the presence of iron impurities and two small curvatures or kinks at about 360 nm and about 600 nm. With gamma irradiation, the spectrum reveals the pronounced appearance of a broad visible band centered at about 530 nm which is related to  $\text{Mn}^{3+}$  and becomes more pronounced with progressive irradiation<sup>19,20</sup>. The ultraviolet absorption shows an increase in intensity accompanied by shifting to higher wavelengths.

### 3.1.6 Iron-doped glass

The spectrum of the iron-doped phosphate glass is shown in Fig. 2. The glass before irradiation shows an ultraviolet band at about 210 nm and another small visible band at about 420 nm. These bands can be assigned to  $\text{Fe}^{3+}$  in predominantly octahedral coordinated state<sup>2,10</sup>. Upon gamma irradiation, the intensity of the visible absorption band increases. The ultraviolet band remains nearly constant but in the visible region progressively increases with radiation. With higher doses of radiation another band is observed at about 460 nm.

### 3.1.7 Cobalt-doped glass

The experimental spectrum of the bluish cobalt-doped phosphate glass (Fig. 2) consists of an ultraviolet band at about 210 nm and three weak visible peaks at about 520, 580 and 640 nm. Recent studies suggest the prevalence of octahedral coordination of cobalt in sodium phosphate glass<sup>22</sup>. Upon gamma irradiation, the absorption extending from the beginning of measurement up to about 600 nm reveals an increase in its intensity. With progressive gamma irradiation two induced visible bands are identified at about 460 and 520 nm.

### 3.1.8 Nickel-doped glass

The spectrum of the glass before irradiation (Fig. 2) shows an ultraviolet absorption extending up to 370 nm, a small visible peak at about 420 nm and a very broad near-infrared band with maximum at about 1000 nm. Most studies suggest that  $\text{Ni}^{2+}$  is present predominantly in octahedral sites in sodium phosphate glass<sup>2,5,12,23</sup>. The experimental spectra reveal no obvious changes with progressive accumulated gamma irradiation. It seems that Ni in phosphate host resists spectral changes.

### 3.1.9 Copper-doped glass

Before irradiation, the spectrum (Fig. 2) reveals an ultraviolet absorption extending up to about 330 nm and a shallow visible basin absorption. Upon gamma irradiation, a single broad band with a maximum at about 840 nm which can be assigned to the  ${}^2E_g(D) \rightarrow {}^2T_{2g}(D)$  transition<sup>5</sup>. Recent studies confirm that this band is characteristic of copper in distorted octahedral symmetry<sup>24</sup>. A new broad visible absorption band is also observed at about 420 nm and becomes very prominent with progressive gamma irradiation. This additional band at 420 nm was previously identified by Ohishi *et al.*<sup>25</sup> and thought to be caused by transitions in tetragonal symmetry.

Table 2 gives an account of absorption bands of undoped and TM-doped soda lime phosphate glasses, their assignments and references.

## 3.2 Induced spectra

Figure 3 shows the induced spectra obtained by subtracting the optical densities obtained from the studied glasses after successive gamma radiation from optical densities of the same glasses before irradiation and can be summarized as:

- The glasses containing  $\text{TiO}_2$  and  $\text{NiO}$  show marked resistance to the action of gamma rays and their UV-visible absorption spectra remain unchanged with radiation.
- The induced ultraviolet absorption band of the undoped glass at about 240 nm shifts to longer wavelengths accompanied by a progressive increase in its intensity with irradiation. The induced visible absorption band at about 450 nm is observed to split to two absorption peaks at 400 and 530 nm by high doses of gamma rays.
- The induced spectra of V-doped glass reveal some spectral changes with irradiation. The induced ultraviolet sharp band at about 280 nm

Table 2—Positions of observed and predicted absorption bands and transitions of TM-doped phosphate glass

Ion	Band position		Transition	Reference	
	Observed (nm)	Predicted			
		cm <sup>-1</sup>			cm <sup>-1</sup>
Ti <sup>3+</sup>	540	(18518)	17500	<sup>2</sup> T <sub>2g</sub> (D)→ <sup>2</sup> E <sub>g</sub> (D)	14,15
	710	(14085)	14300	<sup>2</sup> T <sub>2g</sub> → <sup>2</sup> E <sub>2g</sub>	15
V <sup>3+</sup>	450	(22222)	23500	<sup>3</sup> T <sub>1g</sub> → <sup>2</sup> A <sub>2g</sub> (P)	14,16
	660	(15152)	15500	<sup>3</sup> T <sub>1g</sub> (F)→ <sup>2</sup> T <sub>2g</sub> (F)	14,16
	690	(14493)	14490	<sup>3</sup> T <sub>1g</sub> (F)→ <sup>3</sup> T <sub>2g</sub> (F)	14,16
Cr <sup>3+</sup>	430	(23256)	22900	<sup>4</sup> A <sub>2g</sub> (F)→ <sup>4</sup> T <sub>1g</sub> (F)	14
	660	(15152)	15250	<sup>4</sup> A <sub>2g</sub> (F)→ <sup>2</sup> T <sub>1g</sub> (G)	14
	880	(11364)	11900	<sup>5</sup> E <sub>g</sub> (D)→ <sup>5</sup> T <sub>2g</sub> (D)	14
Mn <sup>2+</sup>	360	(27778)	25575	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> A <sub>1g</sub>	20,43
	600	(16667)	28000		20,43
Mn <sup>3+</sup>	520		20000	<sup>5</sup> E <sub>g</sub> → <sup>5</sup> T <sub>2g</sub>	20,43
Fe <sup>3+</sup>	380		26360	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> E <sub>g</sub> (G)	25
	420	(23810)	23400	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2</sub> (G)	25
Co <sup>2+</sup>	520	(19231)	19231	<sup>4</sup> T <sub>1g</sub> (F)→ <sup>4</sup> T <sub>1g</sub> (P)	5,11
	580	(17241)	18400	<sup>4</sup> T <sub>1g</sub> (F)→ <sup>4</sup> T <sub>1g</sub> (P)	5,11,22
	640	(15625)	16250	<sup>4</sup> T <sub>1g</sub> (F)→ <sup>4</sup> A <sub>2g</sub> (F)	5,11,22
Ni <sup>2+</sup>	420	(23810)	24000	<sup>3</sup> A <sub>2g</sub> (F)→ <sup>3</sup> T <sub>1g</sub> (P)	11,14,22
	1000	(10000)	11299	<sup>3</sup> A <sub>2g</sub> (F)→ <sup>3</sup> T <sub>2g</sub> (F)	11,14,22
Cu <sup>2+</sup>	420	(23810)		<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>g</sub>	25
	840	(11905)	12700	<sup>2</sup> E <sub>g</sub> (D)→ <sup>2</sup> T <sub>2g</sub> (D) <sup>2</sup> B <sub>1g</sub> → <sup>2</sup> A <sub>1g</sub> <sup>2</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub>	14,25

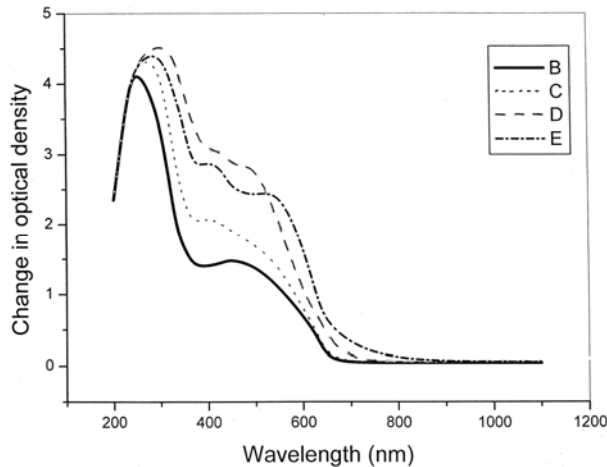


Fig. 3—Induced spectra of base phosphate glass

reveals slight increase in intensity with progressive irradiation. The induced visible absorption band at about 460 nm reveals marked increase in intensity together with a shifting to about 495 nm with the second dose and assumes slight change with progressive irradiation. The small kink observed at about 565 nm is highly intensified showing quite identification and shifting to about 595 nm with progressive irradiation.

- (d) The induced spectra of Cr-doped glass reveal minor changes with irradiation. The ultraviolet band is only visible as a kink at 280 nm with very higher doses. A prominent broad band is observed with two component peaks, a sharp one at about 360 nm and a broad one at about 420 nm. The two mentioned peaks are stable and almost unaffected by progressive irradiation.
- (e) The induced spectra of Mn-doped glass reveal stable ultraviolet band at about 280 nm which is unaffected by irradiation. The induced visible band at about 520 nm remains in position but its intensity first increases with gamma radiation to the dose of 1.5 M rad and then decreases with prolonged irradiation but still higher than the intensity of the original.
- (f) The induced spectra of Fe-doped glass reveal stable ultraviolet band at about 280 nm which is unaffected by irradiation. The induced visible spectra show some changes with irradiation. The single induced band at about 400 nm shows splitting to two component peaks, the first at about 380 nm and the second at 430 nm together with shifting to longer wavelengths by progressive gamma irradiation. Also, a new broad band is observed with maximum at about 930 nm with the highest dose.

- (g) The induced spectra of Co-doped glass reveal relatively stable two ultraviolet bands the first at about 290 nm and the second one at about 400 nm. With progressive gamma irradiation, a new induced visible band is observed at about 450 nm which is shifted to about 470 nm with slightly increasing intensity with higher dose.
- (h) The induced spectra of copper-doped glass show peculiar spectra with irradiation Fig. 3. All the spectra reveal increasing intensity with progressive irradiation until the third dose (3 M rad) and it slightly decreases with the final fourth dose (6 M rad). The induced ultraviolet band is broad with maximum at about 280 nm. The first dose of gamma radiation develops a decreasing broad shallow basin extending from about 380 nm to about 600 nm. With further progressive

irradiation, a new induced band is identified at about 420 nm and grows with radiation to the third dose (3 M rad) and slightly decreases with the fourth dose (6 M rad). A second broad band is observed with maximum at about 800 nm.

Table 3 depicts induced absorption bands of undoped and TM-doped soda lime phosphate glasses, their origin and references as shown in (Fig. 4).

### 3.3 Growth behaviour of induced bands

Experimental results obtained from undoped and all transition metal-doped phosphate glasses (except Ti- and Ni-doped) show almost an initial fast growth in the induced absorption followed by a slower growth of the induced bands, reaching some sort of equilibrium or saturation condition as the dose rate is increased.

Table 3—Induced bands position and their assignments of undoped and doped-phosphate glass

	Band position	Assignment	Referene
(1) base undoped phosphate glass	Ultraviolet bands	Electron Center	27,33,47
	Visible bands 400-420 nm 530-540 nm	Phosphorus oxygen Hole centers POHC'S	27,33,47
(2) Ti-doped glass	Reveals no response		35,41,47
(3) V-doped glass	Ultraviolet band	Electron Center	16,27,47
	Visible bands 460-495 nm 560-600 nm	Photochemical reaction of vanadium species	16,42,47
(4) Cr-doped glass	Ultraviolet bands	Electron Center	17,27,47
	Visible band 430 nm	POHC+ photochemical reaction of chromium species	17,47,48
(5) Mn-doped glass	Ultraviolet band	Electron Center	27,29,43,47
	Visible band 520-540 nm	POHC+ photochemical reactions of manganese species	27,29,43,47
(6) Iron-doped glass	Ultraviolet band	Electron Center	27,32,47,49
	Visible bands 400nm 460 nm 930 nm	POHC + photochemical reactions of iron species	27,47,49
(7)Cobalt-doped glass	Ultraviolet band	Electron Center	27,32,36,47
	Visible band 460 nm 520 nm	POHC+ photochemical reaction of cobalt species	12,27,32,36, 47
(8)Nickel-doped glass	No response to gamma irradiation		
(9)Copper doped glass	Ultraviolet band	Electron center	27,32,47
	Visible band	Photochemical reaction of Cu <sup>+</sup> species	27, 32, 42, 45

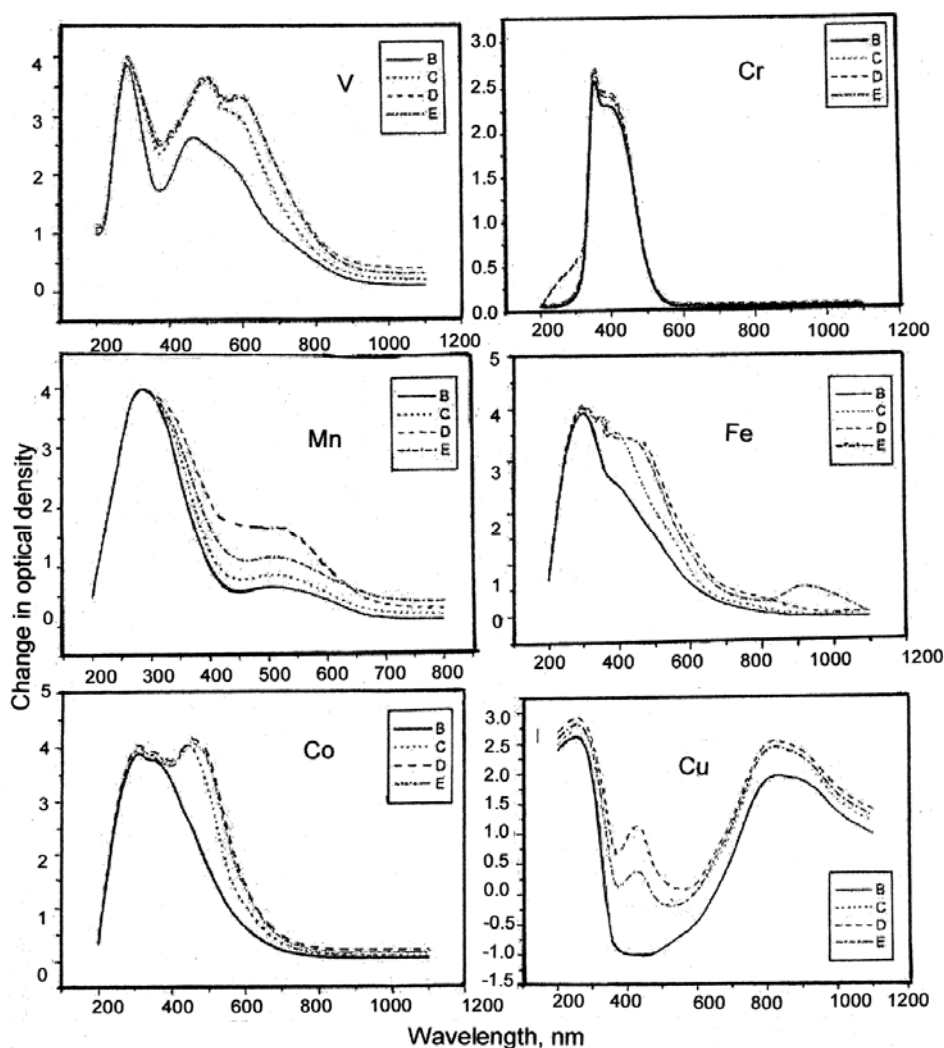


Fig. 4—Induced spectra of TM-doped soda lime phosphate glass

## 4 Discussion

### 4.1 Effect of gamma-rays irradiation on glasses

The radiation damage processes in glasses are generically the same which occur in crystals<sup>26,28</sup>. There are three basic processes:

- (i) Radiolytic processes
- (ii) Knock-on damage
- (iii) Electron rearrangement.

### 4.2 Induced spectra in base phosphate glasses

The induced optical absorption bands created by irradiation depend on a number of parameters, including the glass former (e.g.,  $P_2O_5$ ), the type and concentration of the alkali or alkaline earth oxides, the concentration of OH, the redox conditions during the glass melting, and the temperature at which the glass is irradiated and measured<sup>27</sup>. Although this presents a formidable parameter space, comprehensive studies of

the silicate system (and to a lesser extent, the borate and phosphate systems) have resulted in a relatively unified understanding of the radiation damage in simple glasses<sup>26,28</sup>. The data obtained reveal that the three induced bands centered in the 2.0 to 2.3 eV range, near 2.9 to 3.0 eV, and at 5.1 to 5.5 eV, are common to all three glass systems. Only the 4.0 eV band appears missing from the borate and phosphate glasses.

Schreurs and Tucker<sup>29</sup> identified the two low energy induced bands in alkali phosphate glasses to be due to hole traps and the third induced absorption band at 5.1 eV to be due to an electron trap. When the 2.3 eV (520 nm) and 2.9 eV (420 nm) hole center bands were suppressed by competitive trapping in a manganese doped glass, a broad asymmetric band located at 2.25 eV (550 nm) was observed. They identified this band as  $Mn^{2+}$  that had trapped a hole on

the basis of the similar center energy and shape to that of  $Mn^{3+}$ . However, the center of the  $Mn^{3+}$  band occurs in other glasses at higher energies<sup>30</sup>, in the range 2.5 - 2.6 eV (500 to 480 nm). Williams and Friebele<sup>31</sup> assumed that the induced band observed in Mn-doped phosphate glass is a composite of  $Mn^{3+}$  and the alkali electron center.

Bishay<sup>32</sup> postulated that the 2.3 and 2.9 eV (520, 420 nm) bands are attributed to the high and low temperature phosphorus-oxygen hole centers (POHC) in the doped glass. These two induced defects have been determined by Griscom *et al.*<sup>33</sup> to be holes trapped on two or one non-bridging oxygen atoms of a  $PO_4$  structural unit, in analogy to the  $HC_2$  and  $HC_1$  defect centers in silicate glasses. The induced band in the alkali phosphate glasses near 5.1 eV (240 nm) correlates with the 4.8 eV (280 nm) band in *p*-doped silica, the absorption being associated with the  $P_2$  defect comprising an electron trapped in an anti-bonding orbital of  $PO_2$  in induced spectra in glasses containing transition metal ions. When a glass containing multi-valent transition metal ions is irradiated, these ions are available as potential traps for the radiolytic electrons and holes. Whether the ions trap the charges in preference to the intrinsic traps depends on the relative capture cross-section and traps depths. The presence of the dopants does not alter the intrinsic trapping of the glasses. Rather, by providing alternate sites, they sometimes retard the formation rate and increase the recovery rate of the intrinsic centers<sup>32-37</sup>.

#### 4.3 Contribution of the optical absorption of transition metal-doped phosphate glass

By correlating the observed absorption spectra of doped glasses with atomic transitions predicted from ligand field theory as been reviewed by Bates<sup>3</sup>, Paul<sup>5</sup> and Wong and Angell<sup>38</sup>, it can be suggested that transition metals are predominantly found in octahedral coordination in phosphate glasses. This would be expected since the stabilization energy associated with this symmetry is higher than for tetrahedral symmetry. The one exception to this case is  $Cu^{2+}$  which is believed to be in tetragonally distorted symmetry due to the Jahn-Teller effect. The absorption spectra can be interpreted on the following basis:

(1) The undoped phosphate glass reveals no visible absorption but shows an ultraviolet band at about 250 nm which different researchers attributed it to. the presence of iron impurities<sup>10,12</sup>.

(2) Both the pink colour of Ti-doped glass and the appearance of the visible absorption band at 540 nm (Fig. 2) confirm the presence of titanium predominantly as  $Ti^{3+}$  in octahedral coordination. Also, the appearance of the peak at 710 nm is likely to be caused by the Jahn-Teller effect giving tetragonal distortion and leading to a splitting of the ground state<sup>6,12</sup>. Titanium-doped phosphate is observed to resist the action of liberated or freed electrons during gamma irradiation. A similar behaviour was observed by Kreidl and Hensler<sup>39</sup> and Bishay<sup>40</sup> in titanium-doped phosphate glasses. Bishay and Gomaa<sup>41</sup> observed a decrease in the intensity of the induced absorption as  $TiO_2$  was increased in silicate glasses. They attributed this behaviour to the formation of  $Ti^{3+}$  ions as a result of gamma irradiation. The released electrons may annihilate the positive hole centers and thus decrease the visible induced absorption or attains saturation. In the studied phosphate glass, titanium is assumed to be mostly in the octahedral  $Ti^{3+}$  state. The stability of this glass towards gamma irradiation seems to be a combined effect of both  $Ti^{3+}$  and phosphate host acting to trap liberated electrons without any visual absorption change or net induced spectra. Several researchers have arrived to the same conclusion<sup>39,40</sup>.

(3) The greenish colour of V-doped phosphate glass and the quite appearance of the two visible bands at about 430 nm and 660 nm (Fig. 3) combined together indicate the presence of appreciable amount of  $V^{3+}$  ions in the glass but not excluding other vanadium species such as  $V^{5+}$  and  $V^{4+}$  ions. The induced curves reveal almost stability of the ultraviolet spectra while the visible spectra show some increase in intensity with marked splitting and specifically in the region where trivalent vanadium ions are effectively absorbing. This result leads us to assume that some of the minor pentavalent or tetravalent vanadium ions present have the liability to capture electrons freed by gamma-ray irradiation and change according to the following photochemical reactions to  $V^{3+}$ :



Kutub and El-Manharawy<sup>42</sup> and El-Batal and Ghoneim<sup>16</sup> reached at the similar result previously.



- (4) The emerald greenish colour of Cr-doped glass and the appearance of the two visible bands at 440 and 660 nm, (Fig. 2) combined together indicate the presence of octahedrally coordinated  $\text{Cr}^{3+}$  ions in appreciable amount but not neglecting the possible presence of  $\text{Cr}^{6+}$  ions. The induced spectra show two induced bands, the first at about 385 nm and the second at about 430 nm. It seems that the first band is correlated with  $\text{Cr}^{6+}$  ions and the second band with  $\text{Cr}^{3+}$  ions. Therefore, it can be assumed that on gamma irradiation a new ultraviolet band is developed at about 380 nm indicating the formation of  $\text{Cr}^{6+}$  ions by capturing positive holes, which attain equilibrium with the rest of  $\text{Cr}^{3+}$  ions on the basis of the respective condition of the host glass. El-Batal and Ezz El-Din arrived at the comparable conclusion for Cr-doped borate glasses<sup>17</sup>. The presence of an ultraviolet band at about 235 nm is assumed to be due to iron impurities.
- (5) The Mn-doped glass is faint colour showing no characteristic visible bands but only small curvature or kinks at about 360 nm and 600 nm (Fig. 2) and this may indicate the presence of  $\text{Mn}^{2+}$  ions which are known to have very low extinction coefficients<sup>5</sup>. On gamma irradiation, the characteristic broad band at about 540 nm is quite observed and becomes more prominent with radiation. The same result was previously observed in Mn-doped cobalt glasses and was explained by assuming that some fraction of the  $\text{Mn}^{2+}$  ions present can trap a hole and be converted to  $\text{Mn}^{3+}$  according to the photochemical reaction<sup>43</sup>.



Also, irradiation of the undoped phosphate glass leads to the formation of two induced intrinsic bands at 400 and 530 nm (Fig. 2), one of which (530 nm) lies very close to the absorption band due to  $\text{Mn}^{3+}$  ions. Thus, the induced visible band observed in Mn-doped glass may actually be a composite of these two, namely the intrinsic base glass and that due to photochemically formed  $\text{Mn}^{3+}$  ions.

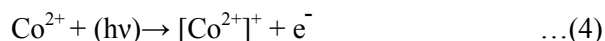
- (6) The experimental result of Fe-doped glass reveals the appearance of a marked ultraviolet band at 220 nm and a small visible peak at 425 nm. The induced spectra (Fig. 3) reveal a stable and high intense ultraviolet band at about 285 and two

other peaks at 330 and 450 nm by progressive irradiation. Most published work<sup>1-5</sup> assume that iron is present in both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  and the relative amounts of each depending on the concentration of iron oxide, condition of melting, type and composition of the glass.

Earlier study on iron in phosphate glasses had indicated<sup>11</sup> that  $\text{Fe}^{2+}$  showed two absorption bands in the infrared region, while  $\text{Fe}^{3+}$  showed three resolved bands. Both states were in octahedral coordination and the charge transfer ultraviolet band was attributed to  $\text{Fe}^{3+}$ . Also, Edwards *et al.*<sup>11</sup> assumed that phosphate glasses compared with silicate glasses, are more reducing with respect to iron and this effect can be discussed by considering the effect of coordination and bonding of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  on their activity coefficients in various glasses. Recent study indicates<sup>44</sup> that ferrous and ferric ions are in octahedral coordination and that, ferric ions may occupy two different sites.

- (7) Both the light bluish colour of Co-doped glass and the appearance of the broad triply-split band with three peaks at about 520, 580 and 630 nm indicate the possible presence of cobalt in both tetrahedral and octahedral coordination states of cobalt (Fig. 2). On successive gamma irradiation, the absorption spectra are seen to be characterized by the appearance of a visible band at about 480 nm and two ultraviolet absorption bands at about 250 and at 360 nm. The first visible band seems to be correlated with  $\text{Co}^{2+}$  in octahedral coordination. France *et al.*<sup>44</sup> had pointed out that cobalt is a useful dopant for determining the structure of a glass since the octahedral site preference energy is close to zero and the metal can easily switch from octahedral to tetrahedral symmetry according to the composition. It is possible gamma irradiation can do the same effect. The ultraviolet bands are, previously assumed to be, related with iron impurities<sup>10-12</sup>.

Möncke *et al.*<sup>12</sup> recently postulated that irradiation of Co-doped glass produces photooxidized  $[\text{Co}^{2+}]^+$  by the suggested reaction:



The difference in the spectrum could be related to the formation of the electron centers accompanied by the evolution of hole centers to which the  $[\text{Co}^{2+}]^+$  would belong.

- (8) Both the pale yellowish colour of the Ni-doped phosphate glass together with the appearance of the visible band at about 420 nm and the broad near infrared band with maximum at about 950 nm support our assumption of the presence of nickel predominantly in octahedral coordination in phosphate glass with marked resistance to radiation.

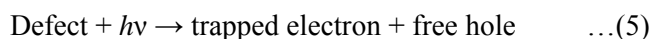
Experimental results reveal that progressive gamma irradiation produces coincidence of the obtained absorption spectra after radiation with that before without any change in the entire ultraviolet and visible spectral region.

However, Cotton *et al.*<sup>45</sup> in their recent reference book assume that this behaviour is related to some structural changes. In a recent publication by one of the authors<sup>37</sup>, the absorption spectra of nickel-doped silicate glasses are observed to show obvious changes with progressive gamma irradiation. It is therefore, assumed that the stability of the present glass towards gamma irradiation is partly dependent on the phosphate host and partly on the suppressing action of Ni<sup>2+</sup> ions. Further work is needed to justify this behaviour.

- (9) Before irradiation, the colour of the Cu-doped phosphate glass is faint showing no absorption bands in the studied spectrum (Fig. 2). With the first irradiation dose (0.5 M rad), an ultraviolet broad band is observed centered at about 280 nm followed by a shallow basin spectrum extending from 350 to 600 nm, is further followed by a very broad band centered at about 850 nm. On further successive gamma rays irradiations, the ultraviolet band remains stable and unchanged and a new medially broad band is observed at 425 nm and the near infrared broad band at 850 nm remains in position but increases in its intensity with irradiation until the 3 M rad dose. With the last dose (6M rad), the intensities of both the two visible bands slightly decrease. The appearance of the two mentioned visible bands indicates the formation of Cu<sup>2+</sup> ions with progressive gamma irradiation.

Before irradiation, the copper seems to be present in the studied phosphate glass mainly as Cu<sup>+</sup> ions as distinguished by the pale colour. Cu<sup>+</sup> has a 3d<sup>10</sup> configuration and therefore exhibits no d-d transitions and consequently has little absorption<sup>5</sup>. The nature of coordination of Cu<sup>+</sup> ions in phosphate glass was identified by Denath *et al.*<sup>46</sup> and found to be trigonally

distorted octahedral coordination and exhibited ultraviolet bands at 215 and 243 nm. The following suggested photochemical reactions are believed to occur by gamma irradiation:



#### 4.4 Contribution of the growth behaviour

Formation of the induced colour centers is certainly not a simple capturing process at existing intrinsic defects<sup>50</sup>, which would contradict the linear relation of absorption and radiation found by Weeks and Sonders<sup>51</sup>. It can, therefore, be assumed that gamma radiation create defects which subsequently trap electrons or holes. Lell *et al.*<sup>50</sup> reported that some researchers distinguished two phases in the formation of colour centers, an initial fast growth rate and a second slower rate frequently reaching saturation; they also indicated that some interaction between defect centers of various types would be possible. The change of, the rate of formation of colour centers, was initially attributed by Arnold and Compton<sup>52</sup> to population of existing defects in the glass by the radiolytic charges and the linear behaviour at higher doses to concurrent defect production and trapping. Another postulation was reported by Palma and Gagosz<sup>53</sup>, that at high dose rates, additional mechanism of radiation annealing i.e., actual removal of defect sites and healing of the glass network during irradiation may occur.

The results of growth behaviour can be understood when it is considered that the induced absorption in glasses of deferent chemical composition is the result of equilibrium between the formation and annihilation of colour centers. This equilibrium is influenced by the polarizing power, the coordination number of the network forming and modifying ion concentration, and the abundance of non-bridging oxygen.

Ionizing radiation will cause both intrinsic defects and impurities which may be present in glass to be converted to colour centers and Levy<sup>54,55</sup> assumed that the rate of conversion should be about the same for both. However, the number of colour enters formed by impurities must be limited to the number present in the glass and once all of a specific impurity has been converted, the absorption band created should reach a fixed saturation value. If ionizing radiation causes defects to be formed, this will be an inefficient process in most instances and the total number of defects will increase very slowly. The different

growth behaviours are simply based on the assumption that there are numerous colour centers with different growth rates contributing to the absorption at a specific wavelength. A further postulation may be recognized that there are several rate determining processes operating concurrently during gamma irradiation<sup>16,20</sup>.

## 5 Conclusion

Absorption spectra of 3d transition metals-doped phosphate glasses have been measured before and after successive gamma rays irradiation. The optical absorption before irradiation revealed characteristic spectra for each transition metal indicating the presence of predominantly in octahedral environment except for Cu-doped glass. Experimental data reveal obvious induced changes with gamma irradiation except with Ti- and Ni-doped glasses revealing resistance to the action of gamma rays irradiation. The response of the doped-glasses to gamma rays irradiation and the growth behaviour of the induced bands reveal fast growth at first followed by almost saturation after prolonged irradiation. This behaviour is related to several possibilities in formation and annihilation of the induced colour centers.

## References

- Weyl W A, *Coloured Glasses*, reprinted by Dawson's of Pall Mall, London (1959).
- Sigel G H (Jr), *Treatise on Materials Science and Technology*, vol 12, edited by Tomozawa M and Doremus R H, Academic Press, New York, 35 (1977).
- Bates T, *Modern Aspects of the Vitreous State*, vol 2, Edited by J D Mackenzie, Butterworths, London, (1962) pp 195-254.
- Bamford C R, a) *Phys Chem Glasses*, 3 (1962) 189; b) *Colour Generation and Control in Glass*, (Elsevier Science Publisher, Amestrdam) 1977.
- Paul A, *Chemistry of Glasses*, 2<sup>nd</sup> Ed (Elsevier, New York) 1990.
- Campbell J H & Suratwala T J, *J Non-Cryst Solids*, 263 & 264, (2000) 318.
- Hench L L, *J Amer Ceram Soc*, 74 (1991) 1487.
- Kim C & Day D E, *J Non-Cryst Solids*, 331 (2003) 20-31.
- Nocun M, *J Non-Cryst Solids*, 333 (2004) 90-94.
- Kurkjian C R & Sigety E A, *Phys Chem Glasses*, 9 (1968) 73.
- Edwards R J, Paul A & Douglas R W, *Phys Chem Glasses*, 13 (1972) 173-143.
- Moneke D & Ehrh D, *Glastech Ber Glass Sci Techno*, 74 (2001) 65-73.
- Paul A, *J Mater Sci*, 10 (1975) 692.
- France P W, Carter D F & Parker J M, *Phys Chem Glasses*, 27 (1986) 32-41.
- Abdel Shafi N & Morsi M M, *J Mater Sci*, 32, (1986) 5185-5189.
- El-Batal H A & Ghoneim N A, *Nucl Instr & Meth in Phys Res B*, 124 (1997) 81-90.
- El-Batal H A & Ezz El-Din F M, *J Amer Ceram Soc*, 76 (1993) 523-529.
- Paul A, *Phys Chem Glasses*, 15 (1974) 91.
- Paul A, *Phys Chem Glasses*, 11 (1970) 168.
- Ghoneim N A & El-Batal H A, *J Non-Cryst Solids*, 12 (1973) 189-198.
- El-Batal H A & Abbas A F, *Cent Glass&Ceram Res Inst Bull*, 19 (1972) 59-72.
- Ravikumar R V S S, Chandrasekhar A V, Ramamoorthy L, Reddy B T, Reddy Y P, Yamauchi J & Rao P S, *J Alloys & Compounds*, 364 (2004) 176-179.
- Moustafa F A, Ghoneim N A & Ezz El-Din F M, *Cent Glass&Ceram Res Inst Bull*, 32 (1985) 98-102.
- Ravikumar R V S S, Reddy V R, Chandrasekhar A V, Reddy B J, Reddy Y P & Rao P S, *J Alloys & Compounds*, 337 (2002) 272-276.
- Ohishi Y, Mitachi S, Kanamori T & Manabe T, *Phys Chem Glasses*, 24 (1983) 135.
- Griscom D L, in *SPIE vol 541, Radiation Effects in Optical Materials, The Society of Photo-Optical Instrumentation Engineering*, Bellingham, W A, U S A, (1985) pp 38-59.
- Friebele E J, in *Optical Properties of Glass*, edited by Uhlmann D R & Kreidl N J, *The American Ceramic Society*, Westerville, Ohio (1991) pp 205-262.
- Weber W J, Ewing R C, Angell C A, Arnold G W, Cormak A N, Delaye J M, Griscom D L, Hobbs L W, Navrotsky A, Price D L, Stoneham A M & Weinberg M C, *J Mater Res*, 12 (1997) 1946.
- Schreurs J W H & Tucker R F, p 616 in: *Proc Intern Conf Phys Non-Cryst Solids*, Delft, North-Holl & Amsterdam (1956).
- Mackey J H, Smith H L & Halperin A, *J Phys Chem Solids*, 27 (1966) 1759.
- Williams R T & Friebele E J, pp 299-449, in: *Handbook of Laser Science and Technology, Vol III, part I*, Edited by M J Weber, CRC press, Inc, Boca Raton, Fl (1986).
- Bishay A, *J Non-Cryst Solids*, 3 (1970) 54.
- Griscom D L, Friebele E J, Long K J & Fleming J W, *J Appl Phys*, 54 (1983) 3743.
- Van Wieringen J S & Kats A, *Philips Res Rep*, 12 (1957) 432.
- Arafa S, *Phys Chem Glasses*, 15 (1974) 42.
- El-Batal F H, Khalil M M I, Nada N & Desouky S A, *Materials Chemistry & Physics*, 82 (2003) 375-387.
- Khalil M M I, El-Batal F H, Nada N & Desouky S A, *Indian J Pure & Appl Phys*, 41 (2003) 651-666.
- Wong J & Angell C A, *Glass Structure by Spectroscopy*, Marcel Dekker, (1976).
- Kreidl N J & Hensler I R, *J Amer Ceram Soc*, 38 (1955) 423.
- Bishay A, *J Amer Ceram Soc* 44 (1961) 545.
- Bishay A & Gomaa I, *Phys Chem Glasses*, 9 (1968) 193-199.
- Kutub A A & El Manharawy M S, *J Mater Sci*, 26 (1991) 3964-3968.
- Ghoneim N A, Moustaffa F A & Ezz El Din F M, *Phys Chem Glasses*, 26 (1985) 55.
- Concas G, Congiu F, Manca E, Mantoni C & Pinna G, *J Non-Cryst Solids*, 192&193 (1995) 175-178.
- Cotton F A, Wilkinson G, Murillo C A & Bochmaun M, *Advanced Inorganic Chemistry*, (Wiley-Interscience Publisher, New York) (1999).

- 46 Denath R, Chaudbury J & Chandra Bera S, *Phys Stat Sol(b)* 157 (1990) 723.
- 47 Ehrt D, Natura U, Ebeling P & Muller M, *Proc 18(XVIII) Intern Cong Glass*, (10,1-6, San Francisco, USA, July (1998).
- 48 El Badry Kh M, Moustaffa F A & El-Batal F H, *Proc 18(XVIII) Intern Cong Glass*, San Francisco, USA, July (1998).
- 49 Ezz El Din F M, Abdel Rehim F, Shafi N A & H A ElBatal H A, *Phys Chem Glasses*, 20 (1988) 235.
- 50 Lell E, Kreidl N T, Hensler J R, pp 3-44, in: *Progress in Ceramic science, Vol 4*, edited by J E Burk (Pergamon Press, Rondon) 1966.
- 51 Weeks R A & Sonders E, P 869 in : *Paramagnetic Resonance*, E W Low, (Academic Press, New York) 1963.
- 52 Arnold G W & Compton W D, *Phys Rev*, 116 (1959) 802.
- 53 Palma G E & Gagosz R M, *J Phys Chem Sounds*, 33 (1972) 177.
- 54 Levy P W, *J Amer Ceram Soc*, 43 (1960) 389.
- 55 Levy P W, *A S T M Tech Publications* No 359 (1964).

**S DHARAN P-880 formatted**