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Gamma ray interaction with copper-doped sodium phosphate glasses

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Abstract Copper-doped sodium phosphate glasses of various compositions and with varying copper contents were prepared. UV-visible and infrared spectroscopic studies were measured before and after successive gamma irradiation. Experimental results indicate that copper ions occupy different local sites depending on the host glass composition and concentration of copper ions. The changes in UV, visible and infrared spectral data, are discussed in relation to the structural evolution caused by the change in composition and states of copper ions. Copper ions have been found to show a shielding behavior toward the effects of progressive gamma irradiation causing a retardation of the growth of the induced defects caused by irradiation.

Introduction

Glasses containing transition metal ions are of great relevance because of their uses as memory and photoconducting devices [1], cathode materials in batteries [2], magnetic materials [3], etc. Studies of the incorporation of transition metal ions into the glass structure are important for determining and controlling the coloring mechanisms in different glass systems for various applications.

Copper is used in the preparation of some industrial colored glasses, such as red glass hematite, aventurine, and rubies. Copper may exist in glass forming oxide glasses as cupric (Cu^{2+}), cuprous (Cu^{+}) ions, and metallic copper (Cu^{o}) although most glasses melted under ordinary atmospheric condition and with moderate concentration of copper are usually assumed not to contain metallic copper. Most previous studies [4–8] on the oxidation reduction equilibrium of copper in glasses were performed on glasses containing copper as a dopant (less than 2 wt %) in some base composition rather than copper oxide based glasses. Glasses containing copper as the main component are of interest because of their semi-conducting properties.

Colors produced by Cu^{2+} ions have been investigated and interpreted from the viewpoint of ligand field theory [7–10].

In oxide glasses, the transition metal ions form coordination complexes with doubly charged oxygens as the ligands are usually in 4-fold or 6-fold co-ordination. As a general rule, octahedral symmetry is favored over tetrahedral; but other factors, such as ionic radius, polarizability and Jahn–Teller distortion can modify the results. The actual symmetry taken up will also depend on glass composition, and, for example, Ni^{2+} and Co^{2+} have been observed to shift from 6-fold to 4-fold coordination as the alkali content is increased in alkali borate or alkali silicate glasses. [8] In phosphate glasses [11–13] transition metal ions are shown to exist in a reasonable concentration of the reduced state or octahedral coordination.

The present work reports UV-visible spectroscopic measurements of copper ions in sodium phosphate glasses containing increasing concentrations of Cu in different forms and with varying chemical glass composition, and includes the same spectroscopic measurements after successive gamma irradiation. The study also contains the measurements of the infrared absorption spectra of the prepared samples.

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Experimental details

Preparation of the glasses

The glasses were prepared from chemically pure materials. Anhydrous sodium dihydrogen phosphate was taken as the base glass and other glasses were prepared by adding increasing amounts of Cu_2O. Another series was prepared by the addition of either 2%, 4%, or 6% Na_2O or P_2O_5 to the same base sodium phosphate glass containing constant 0.2% Cu_2O.

The weighed batches were melted in porcelain crucibles at the temperature of 900 °C for 1 h. The melts were rotated several times and the homogenized melts were poured in rectangular molds of the dimensions $1 \times 1 \times 4$ cm^3. The prepared samples were carefully transferred to an annealing muffle furnace regulated at 280 °C. The muffle was switched off after $^1/_2$ h and left to cool to room temperature at a rate of 25 °C/h.

UV-visible absorption measurements

Ultraviolet and visible optical absorption spectra were immediately measured for highly polished glass samples of equal thickness (2 mm ± 0.1 mm) before and after each successive gamma irradiation using a recording double beam spectrophotometer, (type JASCO Corp. v-570, Rel-00, Japan) covering the range from 200 to 1,100 nm.

Infrared absorption measurements

The infrared absorption spectra of the undoped and Cu-doped glasses were measured at room temperature in the wave range 400–4,000 cm^{-1} by a Fourier Transform computerized infrared spectrometer type, JASCO, FT/112-43, Japan. The prepared glasses were mixed with KBr in the ratio 2:200 mg glass powder: KBr, respectively. The weighed mixtures were then subjected to a pressure of 5 $tons/cm^2$ to produce clear homogeneous disks. The infrared absorption measurements were measured immediately after preparing the disks.

Gamma irradiation facility

A ^{60}Co gamma cell (2,000 Ci) was used as a γ-ray source with a dose rate of 1.5 Gy/sec. at a temperature of ~30 °C. The investigated glass samples were subjected to the same gamma dose every time. Using a Fricke dosimeter, the absorbed dose in water was utilized in terms of dose in glass. No cavity theory correction was made. Each glass sample was subjected to a total dose of 4MR (4×10^4 Gy).

Results and discussion

UV-visible absorption spectra

UV-visible absorption of base sodium phosphate glass before and after irradiation

The unirradiated undoped parent glass reveals a prominent charge transfer ultraviolet absorption consisting of a main band at about 205 nm and a close neighboring shoulder at about 250 nm with no obvious visible bands (Fig. 1). With first dose of gamma irradiation ($1MR = 1 \times 10^4$ Gy) the ultraviolet absorption band highly increases in the first band and the shoulder grows to a small band at 250 nm together with a marked resolution of a broad intense visible band centered at about 500 nm. With the second dose of irradiation (2MR), the first UV band continues to slightly increase in intensity and the second UV band shifts to larger wavelength to reach 275 nm with obvious increase in intensity while the visible broad band splits into two component peaks at about 430 nm and at 500 nm. With the third dose (3MR), the intensity of the first band seems to approach saturation while the second band continues to increase in intensity accompanied by a resolution of a kink at 310 nm. The same intensity holds with the final dose and the visible spectrum reveals a composite high intense broad band with three peaks at about 450, 500, and 560 nm. It is thus obvious that, by careful inspection of the UV-visible absorption of the unirradiated undoped phosphate glass, the spectrum reveals UV absorption extending from 200 to about 350 nm with two absorption bands, a prominent band at about 205, and a connected small one at about 250 nm. Many authors [14–19] have attributed the occurrence of these charge transfer UV bands to the presence of

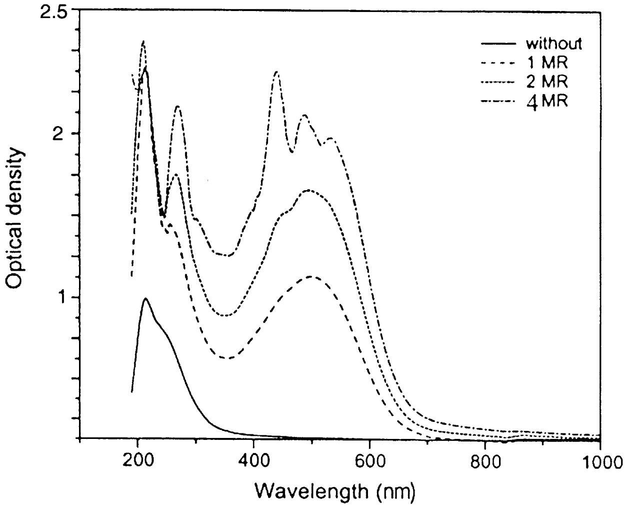
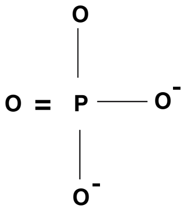


Fig. 1 UV-visible absorption spectra of base undoped sodium metaphosphate glass before and after γ-irradiation

unavoidable trace iron impurities within the raw materials during glass preparation. The broadness of the bands is attributed to the possible presence of more than one site of Fe^{3+} and Fe^{2+} ions [11]. It is also assumed [20–21] that the positions of the UV absorption bands indicate that they belong mostly to Fe^{3+} ions in spite of the reducing behavior of the host base phosphate glass. It is evident that progressive gamma irradiation is observed to finally produce three induced UV bands at 205–210, 260–270, and 310 nm, besides the resolution of three induced visible bands at about 450, 500, and 560 nm.

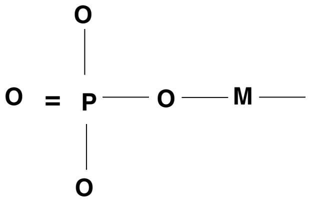
To realize and interpret the effect of progressive gamma irradiation on the base host phosphate glass, the irradiation effect on the host sodium phosphate glass as well as the sharing of the trace iron impurities must be taken into consideration. Previous irradiation studies on alkali and alkaline earth phosphate glasses have been summarized in the review articles by Lell et al. [22], Bishay [23], and Friebele [24]. Bishay [23] shows that the induced optical absorption can be resolved into four bands centered at 2.3 eV (~540 nm), 2.9 eV (~420 nm), 5.5 eV (~225 nm), and 6.0 eV (~200 nm).

The first classification of the radiation induced defect centers that gave rise to these bands was made by Schreurs and Tucker [25], who assumed that the 540 and 420 nm induced bands are due to hole trap centers in the phosphate glass. In their work, the 225 nm band has not been reported and it seems to be correlated with an electron trap. Beekenkamp [26] proposed two models, one for the 2.3 eV (~540 nm) center with a hole trap in alkali phosphate glasses, which consist of a hole trapped in a pair of non-bridging oxygens (NBOs) with the alkali having diffused away (color center I):



$$\mathrm{O{=}\overset{\displaystyle O}{\overset{|}{\underset{\underset{\displaystyle O^-}{|}}{P}}}{-}O^-}$$

The second model was proposed for the 2.9 eV (~420 nm) hole trap center consisting of a hole trapped by an oxygen ion with the alkali covalently bonded to the oxygen (color center II):



$$\mathrm{O{=}\overset{\displaystyle O}{\overset{|}{\underset{\underset{\displaystyle O}{|}}{P}}}{-}O{-}M{-}}$$

Beekenkamp [26] further assumed that the band at 6.0 eV (~200 nm) is due to an oxygen vacancy in a PO_4 tetrahedron which has trapped two electrons. The induced band near 5.1 eV (~245 nm) seems to correlate with the 4.8 eV, (~275 nm) P_2 defect band in p-doped silica [27] which arises from an electron trapped in an antibonding orbital of a PO_4 unit, which has no analog in silicate glasses.

In a recent work by Moncke and Ehrt [19], many irradiation-induced defects are identified in a series of phosphate glasses undoped and doped with a selection of polyvalent ions. They have assumed that the induced defects in glasses are formed in pairs of negative electron centers (EC) and positive hole centers (HC). Moncke and Ehrt [19] utilized optical and electron paramagnetic techniques and were able to detect 6–8 bands due to intrinsic defects which arise from the glass matrix itself and extrinsic defects which are due to dopants or impurities. They assumed that the two iron states even when present as impurities can be affected; Fe^{2+} can be photo-oxidized to $(Fe^{2+})^+$ and Fe^{3+} can be photo-reduced to $(Fe^{3+})^-$. They identified three bands in the visible region which are normally assigned phosphate oxygen hole center (POHC's), those near the UV, to three different phosphate related electron centers (PEC's). Two more defects are also assumed to be present in many irradiated samples. The first is an oxygen related center (OHC) with a band around 300 nm, and the second is the extrinsic $(Fe^{2+})^+$ -HC, which is due to the photo-oxidation of Fe^{2+} ions and has, like Fe^{3+} ions, an ultraviolet band at about 260 nm.

The author of the present article, in addition to others in the field, have recently identified that the charge transfer ultraviolet bands observed in various undoped glasses; soda lime phosphate [12], bio-glass [28], cabal [29] glasses, originate mainly from the trace iron impurities in the raw chemical materials used for preparation of these glasses. Besides, they have reached the conclusion that an increase in the intensity of the UV bands with gamma irradiation is correlated partly with the photochemical transformation of Fe^{2+} ions to Fe^{3+} ions by capturing positive holes which generally amount to almost saturation with successive gamma irradiation.

Absorption spectra of Cu-doped glasses

Figure 2 reveals the UV-visible absorption of glasses containing low concentrations of Cu_2O (0.001–0.05%) before and after successive gamma irradiation. The absorption spectra before irradiation markedly show strong charge transfer ultraviolet broad absorption with three resolved peaks at about 230, 270, and 310 nm, followed by a broad

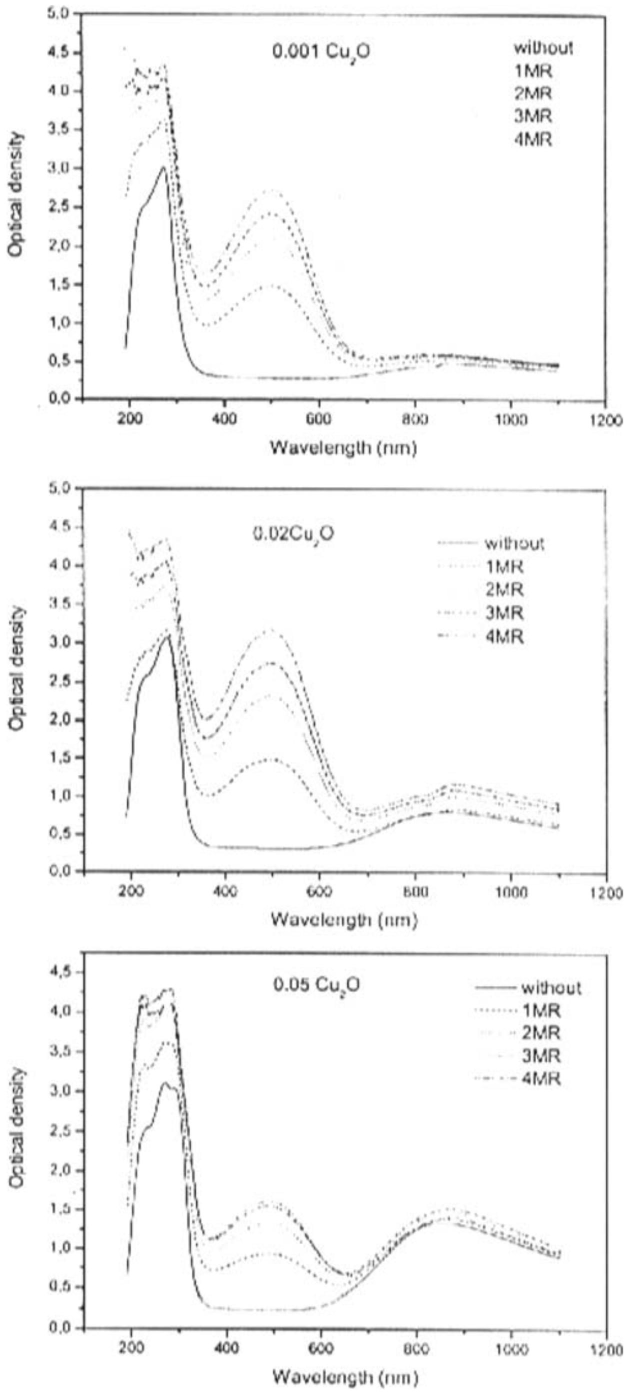


Fig. 2 UV-visible absorption spectra of Cu-doped sodium phosphate glasses (Cu_2O 0.001–0.05% before and after successive gamma irradiation

basin and then by a high-intense visible band with two small peaks at 780 and 810 nm, and finally a broad visible band extending from 850 to 1,100 nm with some minor peaks. With gamma irradiation, the absorption spectra remain almost the same as before irradiation except for the observation of the resolution of a small new peak at about 420 nm and a slight increase in the intensity of the bands.

Figure 3 illustrates the UV-visible absorption spectra of the Cu-doped phosphate glasses containing (1–7.5% Cu_2O). The absorption spectra reveal strong ultraviolet bands at about 205, 275, 310, 350, and 390 nm. The visible spectra show two bands at about 650 and 680 nm, followed by a broad band with four component peaks at about 700, 740, 780, and 820 nm.

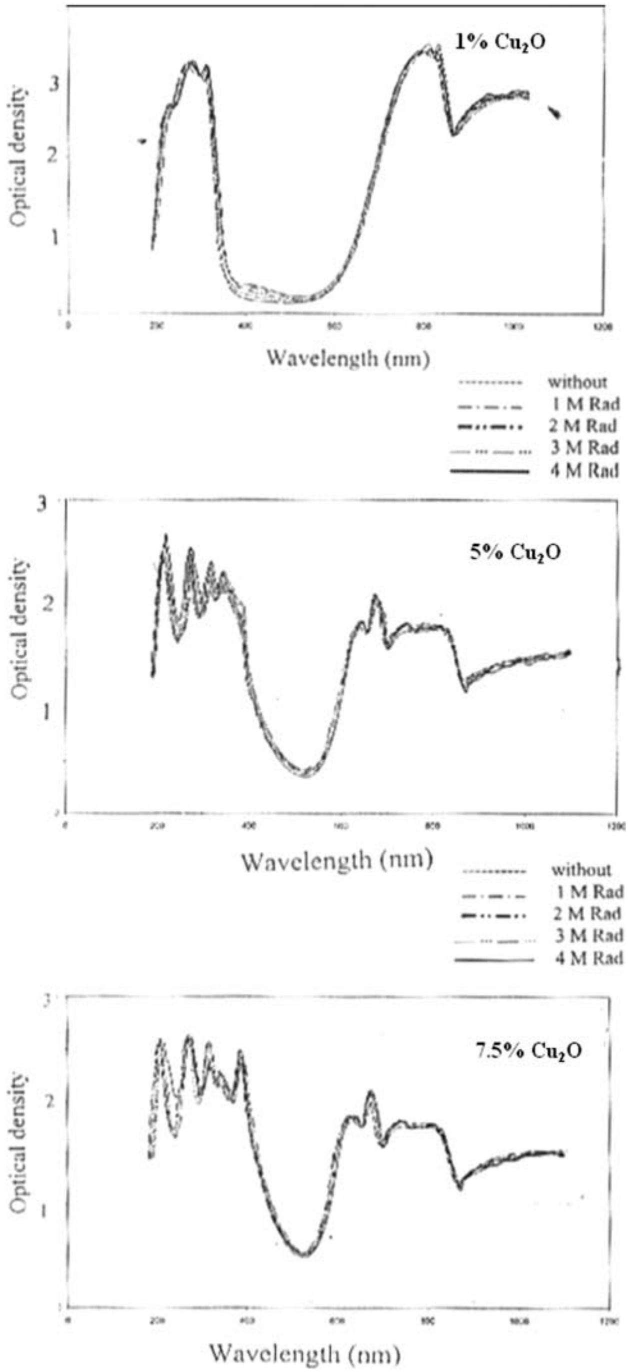


Fig. 3 UV-visible absorption spectra of Cu-doped sodium phosphate glasses (Cu_2O 1–7.5% before and after successive gamma irradiation

Contribution of the UV-Visible spectrum of copper-doped glasses

Copper may be present in glasses as Cu^{2+}, Cu^{+}, and neutral or metallic copper as (Cu^{o}) [5–6]. In glasses containing more than 10 mol% alkali and melted at 1,000 °C with air as the furnace atmosphere, neutral copper is found to be almost absent [5–6]. Cu^{2+} is the only known ion having the 3-d^9 configuration [7]. The energy diagram for d^9 systems in octahedral symmetry is just the inverse of that for octahedral d^1 system. It is well known that the spectra of all glasses containing copper have at least a unique wide, and asymmetrical broad visible band centered near 800 nm [7, 8]. A Comparison with the spectra of aqueous and crystalline cupric complexes shows that the Cu^{2+} must be present in the glass in approximately octahedral coordination [30]. Duran and Fernandez Navarro [31] assume that in Cu^{2+} chemistry there is no crystallographic evidence for a static regular octahedral stereochemistry whose lack of symmetry caused by an electronic hole in the dx^2-y^2 orbital produces the tetragonal distortion known as the Jahn–Teller effect. This effect causes, predominantly, an elongated octahedral stereochemistry with four short in-plane bond lengths and two longer axial bond lengths. This structure corresponds to a ligand field of D_{oh} symmetry (tetragonal bipyramidal). Three absorption bands due to the transitions $2B_{1g} \rightarrow 2B_{2g}$, $2B_{1g} \rightarrow 2A_{1g}$, and $2B_{1g} \rightarrow 2E_{g}$ can appear in the visible and near infrared, their peak frequency depending on the distortion of regular environment.

Duran and Fernandez Navarro [31] further assume that the Cu^{2+} ions are coordinated by the NBOs in silicate glasses and their influence become evident through the effect of the alkali ions. Thus, the increasing distortion with change in chemical composition may thus be related to the change in polarizatility of the oxygen ions surrounding the Cu^{2+}, and to its dependence on the field strength of the network former and modifier ions.

Earlier, Edwards et al. [32] have assumed that the assignment of the presence of a strong tetragonal distortion caused by the Jahn–Teller effect is unlikely upon consideration of the population of energy levels of the split ground state at room temperature. They have introduced another explanation by assuming the presence of spin orbit coupling. The ground state for Cu^{2+} is the E_g level, and the excited state is the T_{2g} level. The T_{2g} level may be split up to 1,000 cm^{-1} by spin obit coupling, which would be sufficient to cause the asymmetry observed in the Cu^{2+} bands.

The broadness and asymmetry of the broad visible (near IR) band is believed [33] to be due to splitting of a low-symmetry ligand field component. Cozar and Aderlean [34] have called this local symmetry of Cu^{2+} as an unusual tetrahedral (T_d) configuration. However, recent studies [33, 35] are favoring the so-called presence of Cu^{2+} in octahedral symmetry with tetragonal distortion by a Jahn–Teller effect.

Paul [36] has previously assumes that a close study of the asymmetric band around 800 nm in a variety of complexes shows that this broad band is virtually made up of at least two, and possibly of three or four overlapping symmetrical bands [37]. These postulations may explain the observed numerous peaks in the region 770–1,000 nm, in the present study. In the phosphate glass, some authors [38, 39] have identified and confirmed the presence of Cu^{+} ions and assumed their presence in trigonally distorted octahedral coordination and exhibiting ultraviolet bands. Denath et al. [38] have suggested that their position is at 215 and 243 nm while Ehrt and Brettschreider [39] have proposed them to be at 175 and 230 nm.

On the basis of such previous postulations, it is therefore assumed that the observed UV bands are due to the possible sharing of absorption due to the presence of both Cu^{+} ions and trace iron impurities.

It is worth mentioning that because of the relatively low symmetry (i.e., less than cubic) of the environments in which the Cu^{2+} ion is characteristically found, detailed interpretations of the spectral properties are somewhat complicated, even though one is dealing with the equivalent of a 1-electron case [40]. Also, it is evident that the complete assignments of the numerous broad bands extending from 400 to 1,000 nm region of the spectrum with correct locations are obviously difficult [40]. Further work is needed to achieve such a resolution.

Effect of gamma irradiation on UV-vis absorption of Cu-doped glass

The principal effect of ionizing gamma irradiation results from almost purely electronic processes [24]. Specifically, these effects occur because electrons are excited to leave their normal positions and move or travel through the glass network. In particular, the addition or the removal of one or more electrons from intrinsic defects or impurity centers results in the formation of induced color centers which can absorb light. The net radiation damage processes that take place in glasses are generally the same as those that take place in crystals. There are three basic processes [24]:

(i) radiolysis;
(ii) displacement or (knock-on) damage; and
(iii) electron rearrangement.

In glasses containing transition metal ions, there is a marked possibility that most transition metal ions may change their valances through photochemical reactions by accepting or releasing electrons.

On gamma irradiation, the following photochemical reactions are suggested to take place in Cu-doped glasses [12, 41–43]:

$$\text{Defect} + h\nu \rightarrow \text{trapped electron} + \text{free hole} \quad (1)$$

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

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

$$\text{Cu}^{+} + \text{free electron} \rightarrow \text{Cu}^{o} \quad (4)$$

The present experimental spectral data reveal that the Cu-doped glasses reveal numerous induced UV and visible bands. These induced bands indicate exclusively the collective sharing of the combined effects of both intrinsic defects from the base phosphate glass together with the contribution of the added copper ions present in various valencies in the base phosphate glass. The base phosphate glass is accepted to produce ECs mostly in the ultraviolet region while phosphorus positive hole centers are situated in the visible region [19, 26–28, 39].

The experimental observation of the small increase of the intensities of the UV-visible bands followed by almost constancy with progressive irradiation indicates the marked shielding effect of copper ions and the rapid reaching to saturation in glasses containing higher copper contents.

Gamma irradiation is observed to produce a new kink at about 420 nm and a similar band is induced in the base glass with progressive gamma irradiation. This induced band was early attributed by Morsi and Nassar [41] to the formation of metastable elemental copper (Cu^{o}) formed according to the photochemical reaction No. (4). Moreover, Ahmed et al. [43] assume that this induced band is associated with positive holes in the intrinsic defects in both the base and Cu-doped glass.

However, two authors [35, 44] have identified a similar band at 425–428 nm, attributing this band to Cu^{2+} caused by some transitions in tetragonal symmetry [43] or to further splitting of the already distorted octahedral environment [35]. Further work is obviously needed to justify the proper attribution of this band at about 420–440 nm in copper-containing glasses by combined techniques.

Effect of glass composition on the absorption spectra of Cu-doped glasses

Figure 4 illustrates the absorption spectra of two Cu_2O doped (1% Cu_2O) sodium phosphate glasses containing additional (a) 10% P_2O_5 or (b) 10% Na_2O before and after successive gamma irradiation. The absorption spectra reveal three important features which can be summarized as follows:

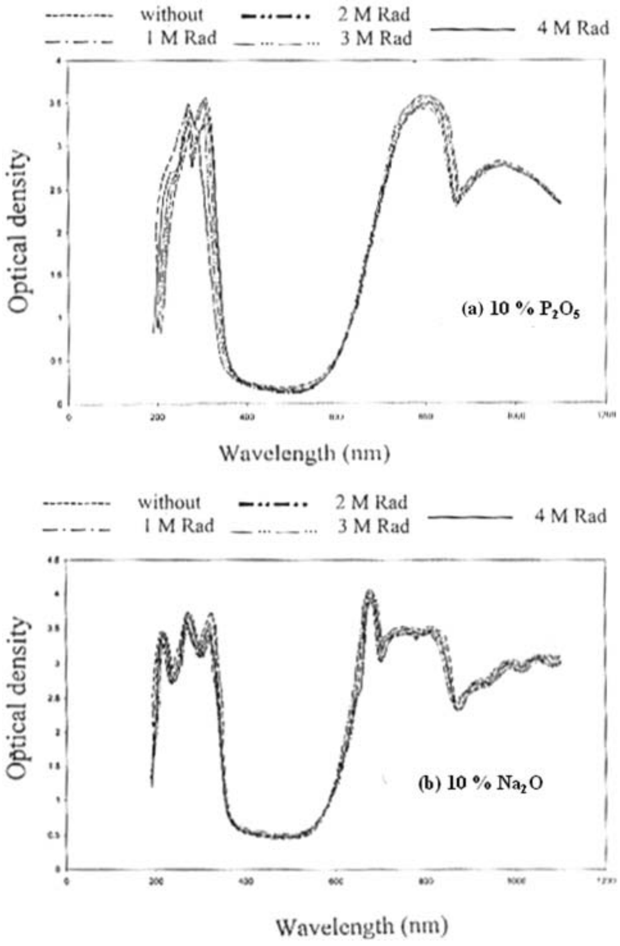


Fig. 4 UV-visible absorption spectra of two Cu_2O (1%)-doped sodium phosphate (**a**) 10 P_2O_5 (**b**) Na_2O before and after successive gamma irradiation

(a) With the introduction of 10% P_2O_5, the UV spectrum reveals a prominent and strong absorption with three peaks at about 210, 275, and 310 nm followed by a sharp broad shallow basin and the visible spectrum shows two broad bands centered at about 780 and 950 nm.

(b) With the introduction of 10% Na_2O, the UV spectrum reveals the characteristic three charge transfer bands at about 210, 275, and 310 nm followed by a shallow broad basin and then the visible spectrum shows a high-intense band at about 680 nm, a broad band with two peaks at about 750 and 810 nm, and finally three peaks at about 930, 970, and 1,030 nm.

(c) It is obvious that with successive gamma irradiation in both the two cases, the absorption curves remain very close. This indicates that the two studied glasses show obvious resistance to the effect of gamma irradiation.

(d) The observed variation of the UV-visible absorption with the change in the glass composition can be realized and interpreted by considering the acid-base concept of the glass constituents or the structural response by composition variation as follows:

(a) The addition of 10% P_2O_5 increases the acidic character of the host glass and the spectrum reveals the UV charge bands due to trace iron impurities and the two visible broad bands due to Cu^{2+} ions in distorted octahedral coordination [5–8].

(b) The addition of 10% Na_2O increases the basic character of the host glass and the spectrum shows the UV bands which are known to be due to trace iron impurities. The visible spectrum shows about six component peaks. The observed split visible peaks indicate that the host glass assumes more disorder or disrupted structure due to the increase of alkali modifier oxide (Na_2O). This situation seems to initiate the splitting of the broad visible bands due to Cu^{2+} ions and with the resolution of about six component distorted peaks.

(c) The spectra of the two glasses reveal marked resistance to gamma irradiation as their compositions contain 1% Cu_2O. Glasses containing copper ions were previously assumed [12, 13, 33] to show obvious resistance to gamma irradiation

Infrared absorption spectra

Effect of the Cu content

The infrared absorption spectra of undoped and Cu-doped sodium phosphate glasses are illustrated in Figs. 5–7. The IR spectrum of the base sodium phosphate glass is characterized by the following features (Fig. 5):

(a) A doublet strong band with two peaks at about 485 and 505 cm^{-1}.
(b) A doublet medium band with two peaks at about 725 and 755 cm^{-1}.
(c) A doublet strong band with two peaks at about 800 and 1,060 cm^{-1}.
(d) A sharp band with a peak at about 1,120 cm^{-1} showing a small kink at about 1,170 cm^{-1} at the descending lobe.
(e) A sharp band with a peak at about 1,270 cm^{-1}.
(f) A medium band at about 1,640 cm^{-1}.
(g) Three kinks at about 2,420, 2,800, and 2,940 cm^{-1}.
(h) A near IR broad band centered at about 3,418 cm^{-1}.

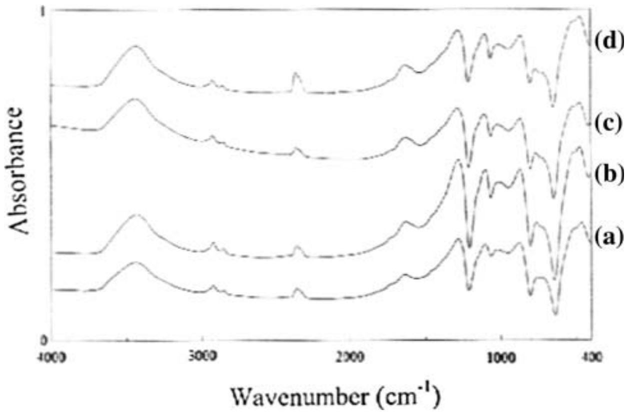


Fig. 5 Infrared absorption spectra of base and Cu_2O-doped sodium phosphate Glasses (**a**) base (**b**) 1% Cu_2O (**c**) 2% Cu_2O (**d**) 7.5% Cu_2O

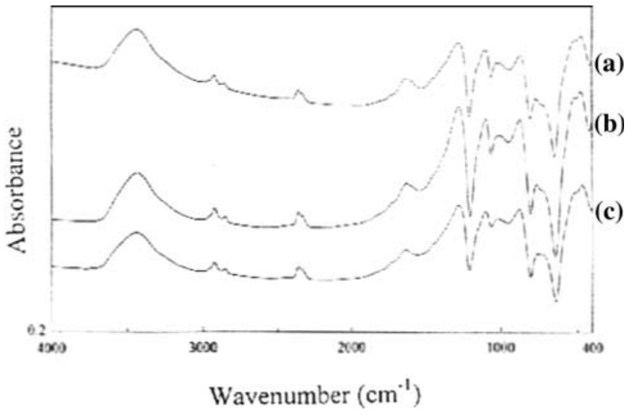


Fig. 6 Infrared absorption spectra of %Cu_2O-doped phosphate glasses with varying added P_2O_5 content (**a**) 2.5% P_2O_5 (**b**) 5% P_2O_5 (**c**) 10% P_2O_5

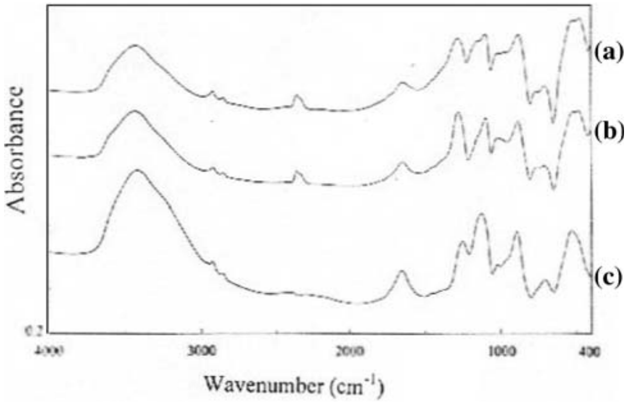


Fig. 7 Infrared absorption spectra of 1%Cu_2O-doped sodium phosphate glasses with varying added Na_2O content (**a**) 2.5% Na_2O (**b**) 5% Na_2O (**c**) 10% Na_2O

With increasing Cu_2O concentrations (1%, 5%, 7.5%) the IR spectra reveal no obvious changes in the number of all the mentioned IR absorption peaks in the undoped glass.

It is obvious that the addition of Cu_2O until this maximum concentration reaches (7.5%) does not cause any major influence on the main characteristic phosphate groups in the studied base sodium phosphate glass, but only minor effects are observed in the intensities or positions of some of the IR bands.

At first addition of Cu_2O, the entire absorption band reveals slight increase in their intensities. The absorption band at about 1,280 cm^{-1} progressively shifts to longer wavelengths reaching about 1,290 cm^{-1} in the high Cu_2O content glass. Also, the small shoulder observed at about 1,230 cm^{-1} is progressively resolved to a separate small peak at about 1,250 cm^{-1} in the high Cu_2O content glass.

Effect of change in glass composition

The infrared absorption spectra of sodium phosphate glasses of varying chemical compositions but containing constant 1% Cu_2O are illustrated in Figs. 6 and 7 from which it can be seen that:

(1) The progressive increase of Na_2O content 2.5%, 5.0%, or 10% causes obvious changes in the IR absorption spectra. All the doublet bands with two peaks are changed to be singlet sharp bands and the second peak in each case is vanished. Hence, the IR spectrum for high Na_2O content glass consists of the following absorption bands:

  (a) A strong IR band at about 530 cm^{-1}.
  (b) A medium band at about 750 cm^{-1}.
  (c) A strong band at about 930 cm^{-1}.
  (d) A small band at about 1,060 cm^{-1}.
  (e) A strong band at about 1,150 cm^{-1}.
  (f) A quite strong band at about 1,250 cm^{-1}.
  (g) A medium band about 1,640 cm^{-1}.
  (h) A very broad strong band centered at about 3,430 cm^{-1}.

(2) The progressive increase of P_2O_5 content 2.5%, 5%, or 10% causes no marked changes in the IR spectra already observed with the base glass keeping the same doublet bands and the same relative intensities of all the IR bands in the limits of glass compositions studied.

Infrared spectra of phosphate glasses in relation to their structure

The network structure of phosphate glass is accepted to contain a polymeric arrangement that is controlled by the predictions and postulations of Zachariasen [45], Van Wazer [46], Martin [47], and Brow et al. [48].

This network is dominated by linkages between PO_4 tetrahedral. In the case of vitreous P_2O_5, the PO_4 groups are connected to adjacent units by three of their four vertices; one place is occupied by a terminal, double-bonded oxygen atom. Although the structure of P_2O_5 glass is modified with the addition of alkali oxides, the phosphorus retains 4-fold coordination throughout the full composition range from pure P_2O_5 to the fully alkali oxide saturated orthophosphate MPO_4 [47]. As alkali oxide is added to P_2O_5, the phosphate structural group passes [49] from Q_3 to Q_2 to Q_1 to Q_o as the molar ratio of alkali oxide to P_2O_5, $R = M_2O/ P_2O_5$, passes from O, to 1 to 2 and finally to 3. These modifications are similar to those taking place in a silicate network upon the addition of alkali oxide. Kordes et al. [50] consider the formation of NBOs in phosphate glasses and they propose the formation of different phosphate structural groups during the reorganization processes accompanying the continuous addition of modifier oxide. They assume that the doubly bonded oxygens remain and a one-to-one correspondence exists between the number of alkali added and the number of NBOs created. The first addition of alkali or alkaline earth oxides, such as Na_2O or CaO to P_2O_5 glass, results in conversion of the three-dimensional network, to linear phosphate chains [51, 52]. This linear chain structure results in cleavage of P–O–P linkages and the creation of NBOs in the glass.

Most research on the vibrational spectroscopy of phosphate crystals [53] and glasses [54, 55], treat information on their structure obtained in terms of the oxygen bridges and terminal groups rather than in terms of polyhedra, or Q^n species. Among various phosphate polyhedra, the isolated $(PO_2)^{3-}$ orthophosphate anion is the only one inseparable into dynamically independent groups and therefore its vibrations can be treated as a whole. Notably, it is the $(PO_2)^-$, $(PO_3)^{2-}$, and $(PO_4)^{3-}$ groups, rather than separate P=O and P–O–groups, that manifest themselves in the vibrational spectra of meta-, pyro-, and orthophosphate and also of phosphate glasses related to the corresponding composition ranges. Based on such a view, the vibrational spectrum characteristic of pyrophosphate anion comprises bands related to the stretching vibrations of $(PO_3)^{2-}$ groups and the P–O–P bridges, the same phosphorus atoms participating in the vibrations of both these fragments. The spectral characteristic of metaphosphate chains comprises bands related to the stretching vibrations of the $(PO_2)^-$ terminal groups, and the P–O–P bridge. Therefore, the spectral characteristic of any anions intermediate in chain length comprises bands related to the stretching vibrations of both the above-terminal groups and the P–O–P bridge [55].

Interpretation of the IR spectra

Typical infrared spectra of undoped and Cu-doped sodium metaphosphate glasses are shown in Fig. (5). The mid-region of the IR spectrum is seen to be consisted of three doublet bands at 485–505, 725–755, and 800–1,060 cm^{-1} followed by three subsequent singlet bands at about 1,120, 1,270, and 1,640 cm^{-1}.

The near infrared spectrum comprises three small kinks at 2,400, 2,950 cm^{-1}, and a broad band centered at about 3,420 cm^{-1}. It is reported [56] that the band at about 466–475 cm^{-1} is assigned to the bending vibration of O–P–O units, δ (PO$_2$) modes of (PO$_2$)^n chain groups, and the band at $\sim$500 cm^{-1} is related as a fundamental frequency of (PO$_4^3$) [57] or as harmonics of P=O bending vibration [58]. The peak at about 725 cm^{-1} may be attributed to the symmetric stretching vibration of P–O–P rings [59–61]. The IR absorption in the region 800–1,000 cm^{-1} was found to be sensitive to the different metaphosphate groups in the form of chain-, ring -, and terminal group [62]. The strong feature at about 1,060 cm^{-1} is attributed to asymmetric stretching of P–O–P groups, v_{as} (P–O–P) modes, linked with small metaphosphate rings as cycoltriphosphate [P$_3$O$_9$]$^{3-}$ or smaller rings [62, 63].The small peak at about 1,120 cm^{-1} is assigned to asymmetric stretching of PO$_2$ groups, as (PO$_2^-$) modes [60, 61]. The IR band at about 1,270 cm^{-1} is attributed to the PO$_2$ asymmetric stretching of the doubly bonded oxygen vibration, v_{as} (P=O) modes [64, 65]. The band at about 1,640 cm^{-1} is related to the P–O–H bridges [64–67]. The IR broad band centered at about 3,420 cm^{-1} can be related to H$_2$O or POH vibrations [64–67].

Effect of change in the Na$_2$O or Cu$_2$O content on the IR spectra

The experimental IR results are visualized by resolving the doublet bands due to phosphate network and the slight increase of the band due to P–OH vibration. These results can be realized and interpreted by considering that the addition of more Na$_2$O leads to the continuous breakdown of the ring type structure of the phosphate glass through the formation of more NBOs and the depolymerization or reorganization of the network.

The inspection of the IR spectra of glasses containing high Na$_2$O contents reveals the decrease of the intensity of the band at (880–1,020) cm^{-1}, which indicates that the relative total content of P–O–P bridges with ring structure decreases. This behavior is a good indication of, and support for the formation of terminal PO$_3^{2-}$ groups vibrating at about (1,130–1,200 cm^{-1}). This trend also confirms the previous assumption of Shih et al. [67] that the infrared spectra of P$_2$O$_5$–Na$_2$O–CuO glasses are strongly composition-dependent and they show significant changes with the change of any one of the component oxide contents; and the conclusion that the IR spectra of glasses of the mentioned system mostly represent characteristics from all metaphosphate glasses.

The observed shift of the bands as the Cu$_2$O content increases can be correlated with the increase in covalent character of P–O–O bonds by the increase of the Cu$_2$O content [67]. Another postulation is that these changes are due to the decrease of the average phosphate chain length [65]. The depolymerization effect of the sodium metaphosphate glass by the addition of copper leads to the formation of short chains. Chahine et al. [65] have concluded that when copper oxide is added to a metaphosphate (NaPO$_3$) glass, the skeleton of (P$_2$O$_6$)$^{2-}$ chains is gradually broken into short phosphate groups, such as (P$_4$O$_{13}$)$^{6-}$, (P$_3$ O$_{10}$)$^{5-}$, and (P$_2$O$_7$)$^{4-}$.

Conclusion

Induced coloration of prepared undoped and Cu-doped sodium phosphate glasses by gamma-ray irradiation was investigated. UV-visible and infrared spectroscopic studies were measured for the prepared samples before and after gamma-ray irradiation. At low Cu$_2$O contents gamma irradiation produces numerous induced uv and visible defects from collective combination of trace iron impurities and copper ions beside the sharing of the host sodium phosphate glass. At high Cu$_2$O contents, the doped glasses show marked resistance to gamma irradiation. Infrared absorption spectra indicate the presence of metaphosphate groups exhibiting their characteristic vibrational bands. The structural phosphate groups and their arrangement are observed to change with the change of glass composition and with the Cu$_2$O content.

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