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Photon energy dependent irradiation effects in a Cu(I) containing silica glass: The phenomenon and its applications

R Debnath

Central Glass and Ceramic Research Institute, Calcutta 700 032

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Copper(I) ions in a silica glass upon irradiation either with UV (4-5 eV) or with high energy photons like γ-ray are found to produce copper-related electron deficient species in the matrix. In the case of UV irradiation, formation of isolated divalent copper species has been clearly revealed, while in the case of γ-irradiation, generation of a copper related ionized center of the type $[AlO_4^-/Cu^{++}]^+$ is evident. The difference observed in the effect of photons of two different energies on the system has been ascribed to two different modes of electron movement in the matrix under the two different energetic irradiations of the glass. The importance of the phenomenon with reference to its applications in opto-electronics and optical sensing has been discussed.

1 Introduction

Glassy silica is widely used as an ideal material for various special applications such as space optics, laser optics, optical communication, laser lithography and metal oxide semiconductor[1-8] structures, etc. for its good UV transmittance and high thermo-mechanical strength. Use of silica for any such applications however, requires attention to the fact that exposure of silica to deep UV and high energy irradiations such as X-ray, γ-ray, displays defect centers within its structure which degrade its optical as well as opto-electronic properties. In some cases though, these defect centers makes the material useful for some other applications such as radiation dosimetry[3,4] and radiation sensing[4].

It is well known[9-11] that in the case of natural quartz or a silica glass containing small percentage of aluminium and alkali cation, a major fraction of its aluminium impurity exits in the structure as a network former(NWF) and occupies substitutional sites for silicon. For the aluminium ion, being a (3+)-entity in a (4+)-site, local charge compensation is achieved with the location of an unipositive modifier alkali cation at a nearby position resulting in defect units of the type $[AlO_4^-/M^+]^0$, where M = Li^+, Na^+, K^+, etc.

Such monovalent alkali cation compensated substitutional Al impurity center $[AlO_4^-/M^+]^0$ in a silica glass or in quartz is known[9-17] to act as progenitor to the generation of aluminium ionized hole centers[14] like $[AlO_4/M^+]^0$, under the influence of UV while in the case of high energy irradiations like X-ray or γ-ray these defect units transform into uncompensated or monovalent cation compensated aluminium hole center of the type $[AlO_4]^0$ and $[AlO_4/M^+]^+$, respectively[9-13], depending on the temperature of irradiation as well as the mobility of the associated cation (M^+) of the progenitor. After the first report[9] of discovery of uncompensated aluminium hole center in case of an X-irradiated quartz, various cation compensated Al-hole centers[12,13] have been reported.

One of the important effects of radiation induced generation of such non-equilibrious charge carrier formation in case of a glass is that, these charge carriers under suitable situation can exchange electrons with the nearby interstitial modifier cation, if such ions be present in the glass generating ions of different oxidation states or some cation associated complex of interesting optical and opto-electronic properties.

Here a theoretical interpretation of a phenomenon of photon energy dependent irradiation effect in case of a Cu(I) ion containing silica glass observed earlier by the author, has been presented and the importance of the phenomenon in respect of its various potential applications has been discussed.

2 Experimental Details

The copper(I) activated glass used in these investigations is basically a silica glass of composition (wt% SiO_2 =96- 97, Al_2O_3 = 1-2, Na_2O = 0.05-0.1, rest B_2O_3 to which Cu^+ ions was added, concentration of Cu^+ = 4.2

E mail: rdebnath@cscgcri.ren.nic.in

$\times 10^{-3}$ moles/litre). The method of preparation of the glass has been discussed earlier[18,19].

For UV irradiation, the fourth harmonic (266 nm) of a pulsed Nd YAG laser (spectra physics DCR 11) and for γ-irradiation a ^{60}Co γ-source were used.

All absorption spectra were measured with a Shimadzu UV-VIS-IR absorption spectrophotometer. All EPR spectra were recorded at 300 K using microwave of frequency 9.439 GHz in a JEOL(RE-SERIES) X-band EPR spectrometer with a modulation frequency of 100 kHz. The microwave power was set to 10 mw, considering that it would be sufficient enough to saturate the E_1' centers (if there be any), of the irradiated glass[20].

3 Effect of UV Irradiation (4-5 eV)

3.1 Change in absorption characteristics of the glass

Fig. 1(a) shows the base glass corrected absorption spectrum of UV laser (4th harmonic of a Nd-YAG laser, 266 nm) irradiated copper(I) containing silica glass along with that of the un- irradiated glass. While the un irradiated glass does not show any absorption other than the $3d^{10}$—$3d^{9}$ 4s inter-configurational absorption bands of Cu^{+} ion[18,19] in the UV region, the UV irradiation of the glass causes to develop a set of new weak absorption bands in the VIS (350 nm, 600 nm) and NIR (780 nm) region, which are similar to the d—d absorption properties[21] of divalent copper in such glass both in respect of energy and weakness of transition of the bands.

3.2 EPR properties before and after irradiation

In sharp contrast to the behaviour of the un-irradiated Cu^{+} ($3d^{10}$) containing glass which does not response to EPR, the glass after UV irradiation gives a reasonably strong EPR spectrum [shown in Fig. 1(b)]. The spectrum exhibits two sets of resonances, each of which consists of four hyperfine lines. The principal mean g and the hyperfine tensors of the two sets of resonances are determined[22] respectively as ($g_{\parallel} = 2.14$, $g_{\perp} = 2.05$) and ($A_{\parallel} = -61 \times 10^{-4}$ cm^{-1}, $A_{\perp} = -21 \times 10^{-4}$ cm^{-1}).

The g values and the hyperfine features of the spectrum are found to correlate well with the known values[21,23] of the parallel and perpendicular g tensors and the hyperfine characteristics of divalent copper ($I = 3/2$) in such a glass.

All the above results point to the fact that upon UV (266 nm) irradiation, the interstitial cuprous ions in the glass get slowly oxidized to divalent copper — a phenomenon similar to that known in case of a copper containing silver halide photochromic glasses[24].

Calculations of the bonding parameters of the photogenerated divalent copper with the oxygen atoms of its coordination structure showed[22] that the UV induced oxidation of the precursor cuprous ion has also brought about a change in its coordination from an elongated octahedron to a square planar structure. The irradiated glass on thermal annealing at 150-200 °C for half an hour in an inert atmosphere reverts to its pre-irradiation

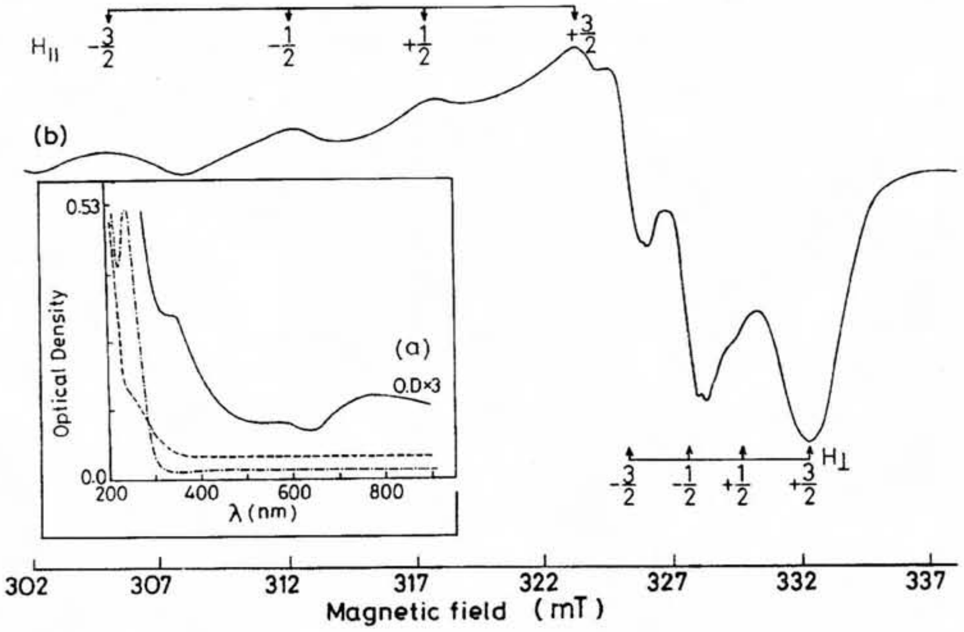

Fig. 1 — (a) Base glass corrected absorption spectra of the Cu(I) containing silica glass at room temperature before (-o-o-o-), and after (——), the UV laser irradiation along with that of the base glass (- - -), sample thickness l = 2.92 mm in all cases; (b) EPR spectrum of copper(I) containing glass after laser irradiation (4.66 eV), [ν(MW) = 9.442 GHz]

stage and hence does neither show absorption in the VIS and NIR region nor it gives any EPR signal due to divalent copper.

3.3 Probable mechanism of formation of divalent copper

Observed phenomenon of UV light induced oxidation of Cu(I) in the glass into divalent copper suggests that there must exist some sort of centers in the neighbouring site of Cu(I) ions in the system which can act as an acceptor of the electrons released from the copper(I) ions by the action of UV photons. Leyderman *et al.*[14] recently observed that UV irradiation of quartz or silica containing substitutional tetrahedral aluminium in their network as $[\mathrm{AlO_4^-/M^+}]^0$ defect center (where $M^+ = Na^+$, Li^+, etc.), causes ionization of the latter generating aluminium related charged center of the type $[\mathrm{AlO_4/M^+}]^+$.

The glass under study is basically a silica glass containing small percentage of aluminium and alkali, e.g. Na^+. So it is very much likely that the glass does have defect units like $[\mathrm{AlO_4^-/Na^+}]^0$ in its structure. According to Leyderman *et al.* UV irradiation of this glass should generate ionized center of the type $[\mathrm{AlO_4/Na^+}]^+$, from its precursor defect unit $[\mathrm{AlO_4^-/Na^+}]^0$. These ionized aluminium centers should act as a potential electron acceptor in the system under favourable situation. In the case of Cu(I) activated sample, the glass contains cuprous ions in its interstitial. These ions of the glass are also expected to be simultaneously photo excited at the time of UV irradiation, because the cuprous ions are known to absorb in the UV region (4-5 eV) because of its ($3d^{10} \rightarrow 3d^9\,4s$) transition.

In the present experiment the Cu^+–containing glass was irradiated with the 4th harmonic of a Nd YAG laser, i.e. with a light of energy 4.66 eV. So under such irradiation, the cuprous ion of the glass are also excited. The excited cuprous ion ($3d^9\,4s$) thus formed should be more vulnerable to donate its outermost electron to an electron acceptor if such species be available nearby. As mentioned earlier, the UV irradiation of the glass generates ionized center $[\mathrm{AlO_4/Na^+}]^+$ in the glass structure. A phenomenon like the excited cuprous ion of the glass, the moment it is formed, donates its outermost electron to a neighbouring $[\mathrm{AlO_4/Na^+}]^+$ center. Oxidizing itself to divalent ion' therefore seems to be the most probable thing to occur.

The sequential steps of the reaction may be written as:

$$[\mathrm{AlO_4^-/Na^+}]^0 \xrightarrow{UV} [\mathrm{AlO_4/Na^+}]^+ + e$$

$$\mathrm{T\ (unidentified\ trap)} + e \rightarrow [\mathrm{T+e}]$$

$$\mathrm{Cu(I)} \xrightarrow{UV} \mathrm{Cu(I)^*}$$

$$\mathrm{Cu(I)^*} + [\mathrm{AlO_4/Na^+}]^+ \rightarrow \mathrm{Cu(II)}\ [\mathrm{AlO_4^-/Na^+}]^0$$

The phenomenon of complete electron transfer from copper(I) to the nearby $[\mathrm{AlO_4/Na^+}]^+$ ionized centre in the present case is facilitated by the UV induced excitation of cuprous ions.

On thermal annealing of the glass, the traps which are not very deep in this case, release their electrons to the matrix which in turn, are immediately captured by the irradiation generated metastable divalent copper, reverting themselves to their monovalent state. No thermoluminescence phenomenon is however, observed in this annealing process of the glass.

4 Effect of γ-irradiation

4.1 Absorption properties

Both the base glass (i.e. glass devoid of copper) and the copper(I) activated glass attain a purple colouration upon γ-irradiation; but the absorption characteristics of the irradiated copper(I) containing glass differs from that of the irradiated base glass. These are shown in Fig. 2 along with the absorption spectra of both the un-irradiated base glass and the Cu(I) containing glass.

A study of the spectrum of the irradiated base glass *vis a vis* that of the un-irradiated glass reveals that the γ- irradiation causes to develop two distinct new absorption bands in the glass one around 295 nm (4.2 eV) and

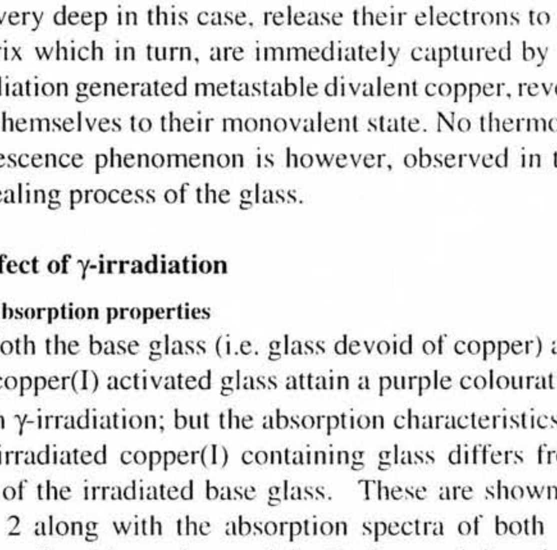

Fig. 2 — Base glass corrected absorption spectra: (——), γ-irradiated Cu(I) containing glass; (-.-.-.), γ-irradiated base glass; (-----), un-irradiated Cu(I) containing glass and (-••-••-) un-irradiated base glass. [sample thickness l = 2.80 mm in all cases]

the other around 500 nm (2.33 eV). In the case of copper(I) containing glass, γ- irradiation however, produces a complex spectrum, where in addition to the above mentioned two bands two more new adsorptions, one as a broad band around 390-400 nm and the other as an absorption profile covering the region 600-800 nm are noted. The absorption band at 244 nm (due to $3d^{10}$–$3d^{9}4s^{1}$ transition) of Cu(I) ions of the glass also suffers a significant loss in intensity.

Observation of 295 nm and 500 nm bands in both the cases of irradiated base glass and the copper(I) containing glass is quite in agreement with the earlier reports[15-17] on the absorption properties of γ-irradiated silica, containing trace alumina and alkali as impurities. Such glass upon γ-irradiation at room temperature is known to generate hole center of the type $[AlO_4]^0$, from the precursor defect unit $[AlO_4/Na^+]^+$ of the glass. This hole center absorbs[15-17] around 300 nm and 500-550 nm.

The energies and the weak transition probabilities of the two additional absorption bands around 390-400 nm and 600-800 nm of the irradiated copper(I) containing glass on the other hand, indicate that the electronic transitions associated with these bands are most likely d--d in nature and are comparable to those of divalent copper ions in such glass[21,22].

Moreover, since the phenomenon of decrease in intensity of the 244 nm band of Cu(I) and the appearance of the additional two VIS and NIR absorption bands occur simultaneously as a result of γ-irradiation, it seems reasonable that the two new adsorptions observed exclusively in the case of the irradiated copper activated glass are associated with some higher valent copper related species which are generated in the glass at the cost of its Cu(I) ions, by the action of γ-ray.

4.2 Site sensitive thermoluminescence properties

The colour centers that are generated in both the cases of the γ-irradiated base glass and the Cu(I) activated glass are bleachable[25,26] by annealing in the temperature range 80-300 °C or above. Such bleaching in the case of Cu(I) activated glass is accompanied by a strong blue green thermoluminescence(TL), while no such emission is observed in the case of annealing of the irradiated base glass. The glow curve of the as-irradiated Cu(I) containing glass exhibits[25] thermal peaks at 414.5 K and 530 K and a shoulder at around 450 K. This is shown in Fig. 3 along with the glow curves 3(b) and 3(c), obtained respectively for samples from which selectively first and both first and second low temperature traps had previously been bleached out. The glow curve parameters and the activation energies E calculated for different thermal peaks are given in Table 1.

The thermoluminescence emission spectrum corresponding to the selective release of each of these thermal traps of the irradiated glass recorded by using previously selectively bleached different samples are shown in Fig. 4 where TL emission spectrum of the as-irradiated sample is also shown.

Although the spectral pattern of the glow of each of such samples varies from that of the other, all the observed spectra are very much similar to the known[18,27] photo-luminescence spectra of cuprous ions of different sites of the glass.

It is therefore, evident from the above results that the luminescence centers involved in all the cases of observed TL are in fact, the cuprous ions of different sites existing in the glass and these ions are selectively ex-

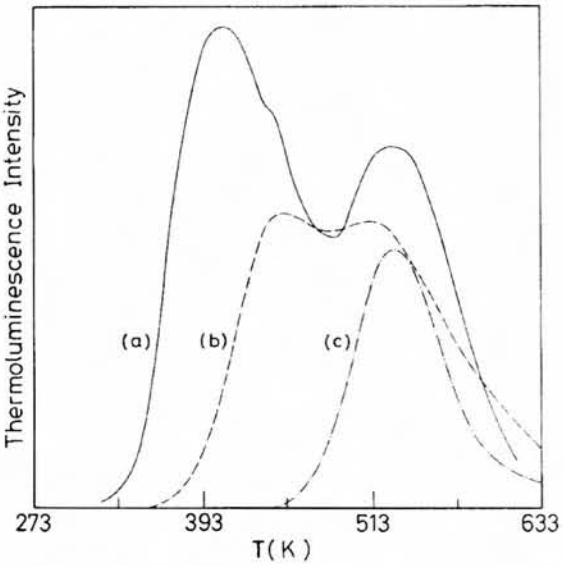

Fig. 3 — TL-glow curves of the γ-irradiated Cu activated silica glass before (a), and after (b, c), step wise selective bleaching of 1st and 2nd low temperature peaks, respectively

Table 1 — Trap parameters of the thermal peaks of glow curves of the Cu(I)-activated silica glass

Parameters	Thermal peak temperatures T_m		
	414.5 K	450 K	530K
Width, low temperature side T(K)	52.5	36	34
Activation Energy E(eV)	0.43	0.74	1.11

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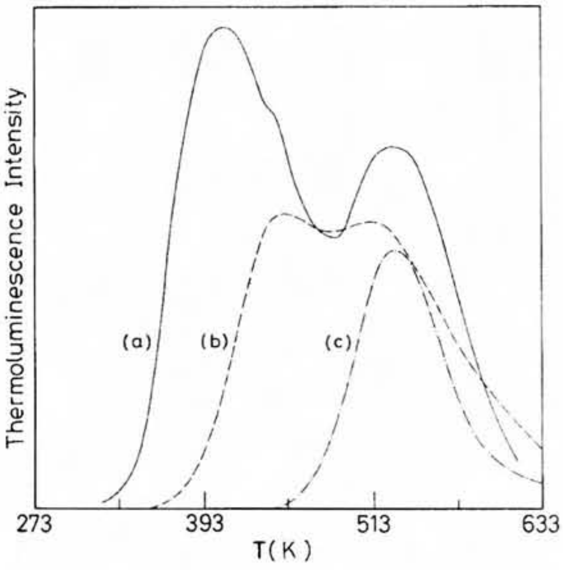

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cited as a result of selective recombination of the thermally released traps with their holes. It is also clear from the emission study that the cuprous ions themselves are not the holes, because in that case recombination of the traps would have given rise to excited copper atoms and as a consequence, a different luminescence. The possible ways by which cuprous ions in the glass can get excited due to recombination of the traps with the holes are :

(1) through transfer of the recombination-energy to the neighbouring cuprous ions through phonon or some other channel;

(2) through direct receipt of the recombination energy as a result of association of the cuprous ions with the hole sites.

In the case of situation (1), there should not arise any selectivity in the process of excitation of cuprous ions of different sites because, surrounding a hole, cuprous ions of all types of coordination may exist and the transfer of recombination energy to each of the surrounding copper sites is equally possible. As the experimental result shows that the cuprous ions of a particular site are excited for a particular type of hole trap recombination,the proposition (2) seems to be the most reasonable, i.e. the cuprous ions are directly related to the holes. It is therefore, concluded that the cuprous ions in the glass become associated with the holes that are generated in the glass when it is irradiated with γ-ray.

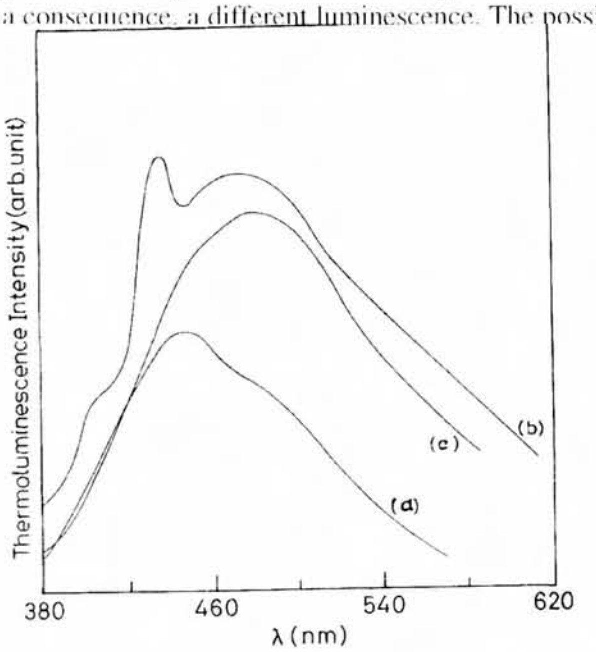

Fig. 4 — TL-emission spectrum of the γ-irradiated Cu(I) activated glass: (a), as irradiated sample, (b), the sample from which first low temperature trap of 414.5 K had previously selectively been cleaned out and (c), the sample from which both the first and the second low temperature traps had previously been cleaned out

4.3 EPR properties

Both the base glass and the Cu(I) containing glass do not show any electron paramagnetic resonance(EPR) spectrum before γ-irradiation but do so after irradiation. The EPR spectrum of the γ-irradiated base glass and that of the γ-irradiated Cu(I) containing glass at 300 K are shown in Fig. 5. The spectrum of the base glass (i.e. glass

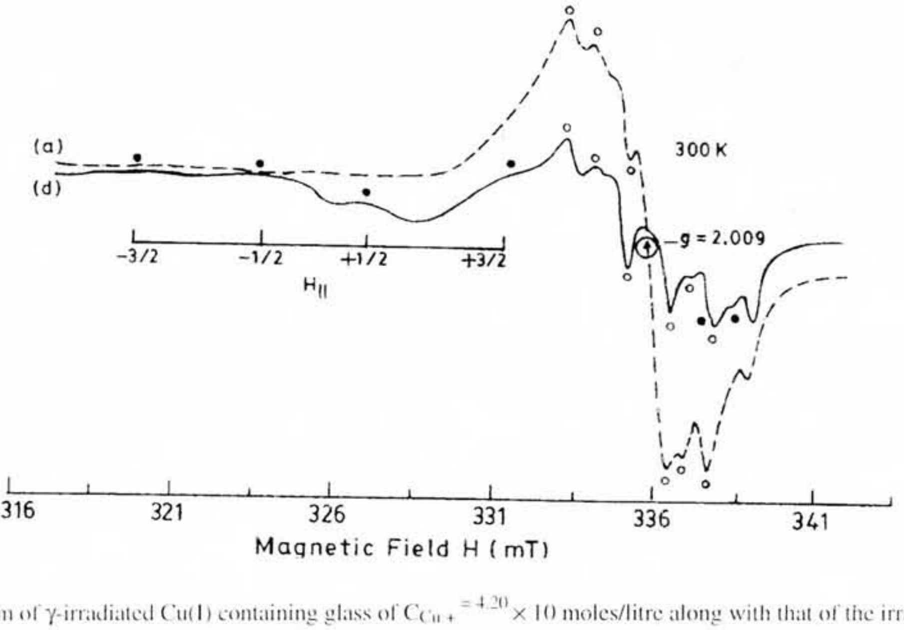

Fig. 5 — EPR spectrum of γ-irradiated Cu(I) containing glass of $C_{Cu^{+}}{}^{=4.20} \times 10$ moles/litre along with that of the irradiated un-activated glass at 300 K [ν(MW) = 9.439 GHz]
["•"indicates copper hyperfine line positions and "•"indicates Al-hyperfine line positions]

devoid of copper) exhibits a resonance of mean g tensor = 2.009 with a six line hyperfine feature of an average separation of 0.89 mT. The observed values of g, the hyperfine characteristics and the total width (ΔH_{full} = 4.44 mT) of the spectrum suggest[9-11] that the resonance owes its origin to a substitutional aluminium impurity hole center of the type $[\mathrm{AlO}_4]^0$ (^{27}Al, 100 % abundance and its nuclear moment $I = 5/2$).

The spectrum of Cu(I) containing glass on the other hand, exhibit resonances wherein addition to the resonance due to the aluminium hole center $[\mathrm{AlO}_4]^0$, two fresh sets of resonance are observed, of which one appears in the field region overlapping with that of $[\mathrm{AlO}_4]^0$ center and the other at a relatively lower field. In the case of the set of lower field, a four-line hyperfine feature of the resonance is clearly revealed, while in the case of the set that occurs overlapping with those of $[\mathrm{AlO}_4]^0$ lines, only two lines are distinguishable. The following are also observed in another EPR study[28]: (1) With the incorporation of cuprous ions in the glass the aluminium hole concentration decreases. More the Cu(I) ion concentration in the glass, more is the decrease of the hole concentration. (2) The two sets of new resonances that are observed only in the case of Cu(I) activated glasses but not in the case of the glass devoid of copper(I), become more and more prominent with the gradual increase of Cu(I) ions in the glass.

All the above results therefore, suggest that the observed new two sets of resonance of the γ-irradiated Cu(I) containing glass are related to some paramagnetic copper species and represent the parallel and the perpendicular component of the resonance of the latter.

Since the generation of this paramagnetic copper species occurs with the simultaneous annihilation of the aluminium hole center,it seems evident that such species are formed as a result of capturing of the $[\mathrm{AlO}_4]^0$ holes of the γ- irradiated glass by the interstitial Cu(I) ions.

4.4. Possible structure of the γ-generated center

The absorption and the EPR spectra of the irradiated glass show that the hole center which are generated in this glass as a result of γ-irradiation are Al-hole centers of the type $[\mathrm{AlO}_4]^0$.

The phenomenon of annihilation of this hole centers with the incorporation of Cu^+ ions in the glass suggest that the Cu(I) ion captures the hole, or in other words, neutralizes the hole by shifting one of its outermost electron towards the hole.

The thermoluminescence results described above also points to the view that copper ion is directly associated with the Al hole center of the irradiated glass.

Association of a Cu(I) ion with an Al-hole of the type mentioned above may lead to either of the following two structures $[\mathrm{AlO}_4/\mathrm{Cu}^+]^+$ or $[\mathrm{AlO}_4^-/\mathrm{Cu}^{++}]^+$. Considering the absorption and the EPR characteristics of such center which show the presence of higher valent copper ion in the system, the reasonable structure of the copper associated Al-center observed in the γ-irradiated glass should be $[\mathrm{AlO}_4^-/\mathrm{Cu}^{++}]^+$.

Theoretically, the EPR spectrum of such an ionized center should exhibit hyperfine interactions, both from the copper and the aluminium nucleus. But the experimental spectrum of the center shows no detectable hyperfine coupling to the aluminium nucleus of the center. The result indicates that after the capture of the hole by the Cu^+ ion, the hole becomes neutralized by sharing an electron from the copper and consequently enforcing on the latter a partial divalent character.

Accounting the observed two sets of resonance of the copper related center for the anisotropy of the Zeeman and the hyperfine terms of the oxidized copper, the magnetic parameters of the center can roughly be estimated from the experimental line positions and using an approximate spin Hamiltonian.

$$H = \bar{g}\,\beta\,\hat{S}\,\hat{H} + \bar{A}\,\hat{S}\,\hat{I} \qquad \ldots(1)$$

where nuclear moment I only for the copper nucleus (3/2) has been taken into consideration.

Such an estimation of the parameters corresponding to the low field resonance of the spectrum yields $g_{\parallel}$ = 2.061 and $^{\mathrm{Cu}}A_{\parallel} = -25.72 \times 10^{-4}\ \mathrm{cm}^{-1}$.

The observed unusually low values of g and the hyperfine tensor of the resonance suggest that the paramagnetic copper species which is generated in the glass due to the capture of the hole differs greatly in its spin density from that of an isolated divalent copper ion in such glass[21,22].

5 Action of UV and γ-photons

The observed difference between the nature of interaction of γ-radiation and that of the UV radiation on the copper(I) containing glass is note worthy. While γ-irradiation of the copper(I)-containing glass results in the generation of a copper associated aluminium hole center of the type $[\mathrm{AlO}_4^-/\mathrm{Cu}^{++}]^+$, irradiation of the same glass by the 266 nm UV light generates isolated divalent copper ion.

To understand the reason for such difference of action of photons of different energies, one has to first look into the structure of the glass containing cuprous ions in its interstitial and Al^{+3} in the substitutional silicon sites.

The concentration of the Cu(I) ions in the glass is 0.005-0.0125 %, i.e. almost ten times less than that of Na(I) ions (0.05-0.1 %). The ratio of silicon atoms to aluminium atoms in the glass network is also very very high. So Cu(I) ions of the glass in most cases, are expected to exist as charge compensator to the non-bridging oxygen of silicon atoms rather than to those of aluminium atoms. Again the glass being a nearly pure silica, majority of the oxygen atoms of the network is bridging oxygen. Now, if one assumes that at least one of the six surrounding oxygen atoms of the octahedral Cu(I) ions of the glass[18,27] is linked with an aluminium ion, the chemical picture of such an octahedral Cu(I) site in the glass before UV or γ-irradiation will be similar to the one shown in Fig. 6.

UV irradiation of this glass generates compensated aluminium ionized center $[AlO_4/Na^+]^+$, while γ-irradiation at room temperature generates[9-11] uncompensated aluminium hole center $[AlO_4]^0$, by dislodging both the non-bonding electron on oxygen as well as the compensating cation (the Na^+ ion in the present case) of the precursor defect unit $[AlO_4^-/Na^+]^0$.

The UV generated $[AlO_4/Na^+]$ center does not allow the hole to move away from the Na^+ cation site, but in the case of γ-generated $[AlO_4]^0$ hole center, the hole is free to move over the four oxygen atoms of the tetrahedra.

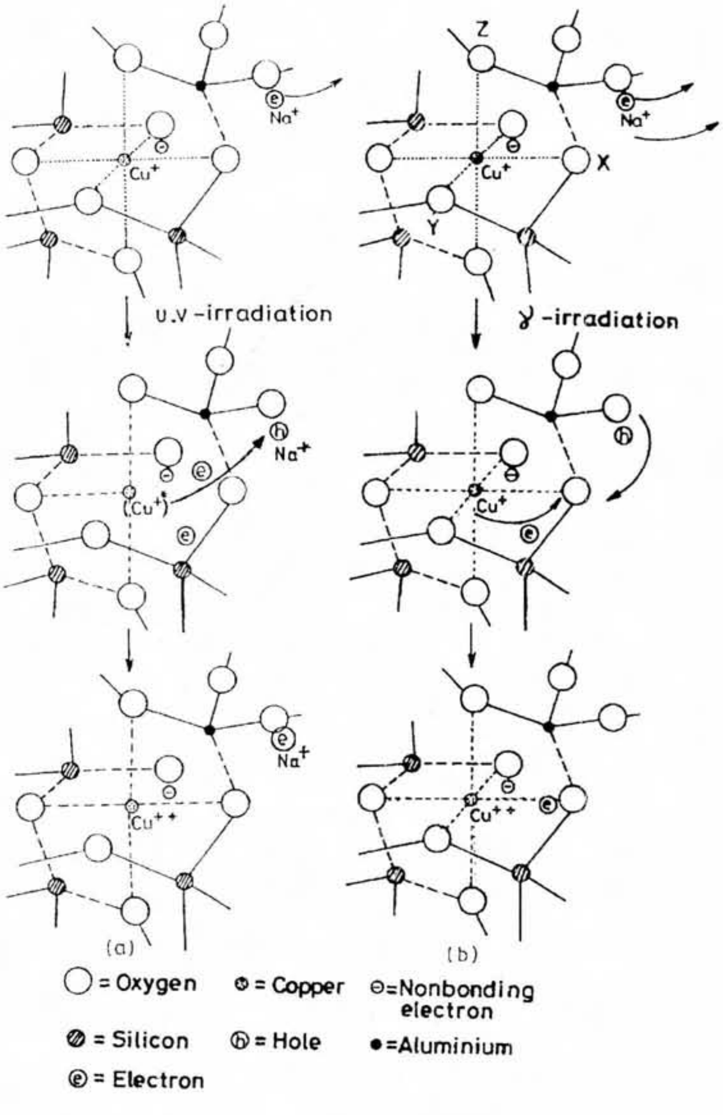

Fig. 6 — Proposed model of electron dynamics (a) in the case of UV irradiation, (b) in the case of γ-irradiation of the glass

Thus in the case of γ-irradiation, once the uncompensated hole is generated on the aluminium tetrahedra (AlO_4), it starts hopping from one oxygen to the other. In this process,the moment the hole reaches the oxygen atom nearest to the Cu^+, it gets captured by the cation receiving a share of an electron of the latter. The net result is a virtual oxidation of the Cu(I) ion. However, because of the fact that the electron donated by the Cu(I) ion is not totally transferred to the $[AlO_4]^0$–hole but only remains shifted towards one of the oxygens of the (AlO_4) tetrahedra, the Cu(I) ion can not become absolutely free of this electron and hence attains a character in between monovalent and divalent state showing unusually low values of *g* and hyperfine tensor. The structure of such a composite species should be $[AlO_4/Cu^{++}]^+$. The related excited state dynamics of the process of the hole capturing process is shown in Fig. 6(b).

In the case of 266 nm UV irradiation, an additional effect of excitation of the cuprous ions of the glass occurs simultaneously with the creation of ionized aluminium center of the type $[AlO_4/Na^+]^+$. This ionized aluminium center being already compensated by sodium cation is not expected to capture further any other cation, but is very much expected to capture an electron whenever available from some source nearby. An excited cuprous ion (Cu)* on the other hand, being more vulnerable to give up an electron than the ground state ion, in a situation where both the $[AlO_4/Na^+]^+$ ionized centers and the excited cuprous ion (Cu)* are generated side by side, a complete transfer of electron from copper to aluminium ionized center becomes possible resulting in the formation of divalent copper. The related dynamics of electron movement is shown in Fig. 6(a).

6 Practical Applications of the Phenomenon

The observed phenomenon of photon energy dependent formation of different copper-related oxidation products can successfully be applied to various useful technologies. For example, since the monovalent copper ($3d^{10}$) is diamagnetic and divalent copper ($3d^9$) is paramagnetic, the phenomenon of UV light induced oxidation of copper in the glass can be detected quantitatively by EPR or by absorption measurements and hence can be used in UV radiometry[29]. Again since the UV induced generation of divalent copper gives a photochromic effect in the glass, it can be successfully used as an UV sensor[30].

Similarly, thermoluminescence properties of the X- or γ-irradiated glass can be used respectively in X- or γ-ray dosimetry[31,32]. Fig. 7 shows a γ-ray dose versus TL intensity plot of such glass. It is seen from the curve that the glass gives a linear response to the γ-ray dose up to 400 Gy and can sense radiation dose as low as 5 Gy. The

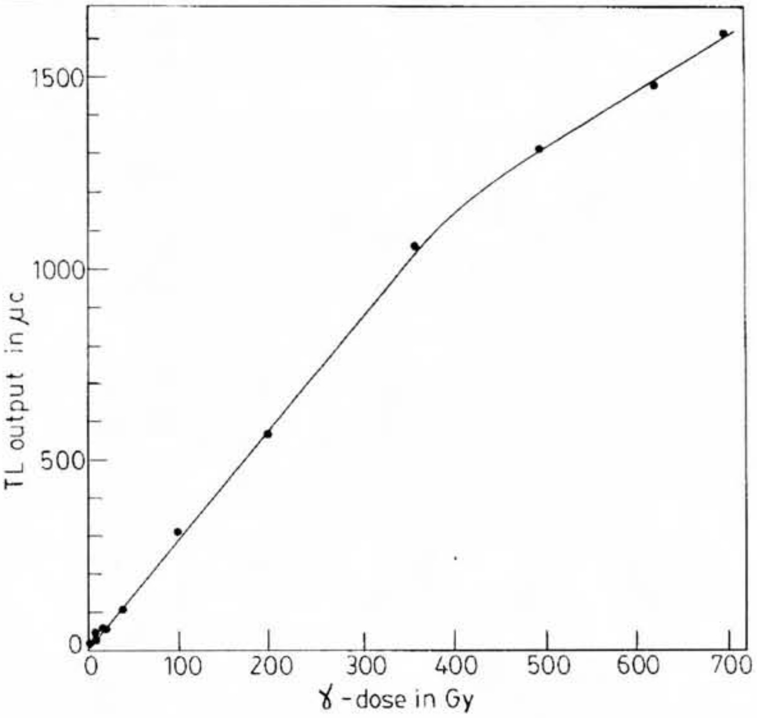

Fig. 7 — A plot of thermoluminescence intensity versus γ-ray dose of the Cu^+– containing silica glass

observed values of trap depth of the traps of the γ-irradiated glass show[25] that these traps are stimulable by near IR radiation of energy 1.2 eV. The glass therefore, could also be successfully used for IR sensing and two- dimensional X-ray or γ-ray imaging using appropriate IR laser for stimulating the traps.

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References

1 Krajnovich D J, Pour I K, Tam A C, Leung W P & Kulkarni M V, *SPIE Glass*, 1848 (1992) 544.

2 Huges R C, *Phys Rev Lett*, 30 (1973) 133.

3 Goksu H Y, Wieser A, Stoneham D, Bailiff I K & Figel M, *Appl Radiat Isot*, 47 (1996) 1369.

4 Ranjbar A H, Charles M W, Durrani S A & Randle K, *Rad Prot Dosimetry*, 65 (1996) 351.

5 Harai E, Wang S & Royce B S H, *J Appl Phys*, 46 (1975) 1310.

6 Brower K L, Lenahan P M & Dressendorfer P V, *Appl Phys Lett*, 41 (1982) 251.

7 Griscom D L, *J Non-Cryst Solids*, 149 (1992) 137.

8 Griscom D L & Cook M, *J Non-Cryst Solids*, 182 (1995) 119.

9 Griffiths J H E, Owen J & Ward I M, *Nature*, 173 (1954) 439.

10 Lee S & Bray P G, *Phys Chem Glasses*, 3 (1962) 37.

11 Mackey Jr J H, *J Chem Phys*, 39 (1963) 74.

12 Davis P H, Huang C Y & Weil J A, *J Phys Chem Solids*, 39 (1978) 897.

13 Weil J A, Huang C Y & Davis P H, *Solid State Commun*, 27 (1978) 1263.

14 Leyderman A, Weil J A & Williams J A S, *J Phys Chem Solids*, 46 (1985) 519.

15 Halperin A & Ralph J E, *J Chem Phys*, 39 (1963) 63.

16 Lell E, *Phys Chem Glasses*, 3 (1962) 84.

17 Lell E, Kreidl N J & Hensler J K, *Progress in ceramic science*, Ed J E Burke, (Pergamon Press, Oxford), 1986.

18 Debnath R & Das S K, *Chem Phys Lett*, 155 (1989) 52.

19 Debnath R, *J Lumin*, 43 (1989) 375.

20 Brower K L, *Phys Rev B*, 20 (1979) 1799.

21 Imagawa H, *Phys Status Solidi*, 30 (1968) 469.

22 Debnath R & Chaudhuri J, *Chem Phys Lett*, 217 (1994) 357.

23 Sands R H, *Phys Rev*, 99 (1955) 1222.

24 Courant D & Gourier D, *J Appl Phys*, 71 (1992) 1081.

25 Chaudhuri J & Debnath R, *J Phys Condensed Matter*, 6 (1994) 3987.

26 Debnath R, Chaudhuri A K, Luthra J M, Vaijapurkar S G & Bhatnagar P K, *J Lumin*, 65 (1995) 279.

27 Debnath R & Kumar S, *J Non-Cryst Solids*, 123 (1990) 271.

28 Debnath R, *J Mater Res*, (Communicated).

29 Debnath R, Indian Patent Application, No. 1225/DEL/94.

30 Debnath R, *Annual Report*, Central Glass & Ceramic Research Institute, 1993-94, p. 15.

31 Debnath R, Indian Patent Application, No.618/DEL/92.

32 Debnath R, US Patent No. 5651804 dated July 29, 1997 and US patent application No.08/393,936.