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Site-dependent thermoluminescence of copper(I) ions in silica glass

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Abstract. Similar to our earlier observations of site-dependent photoluminescence of Cu^+ ions in a silica glass a phenomenon of site-sensitive copper(I)-related thermoluminescence has been observed in the glass after γ -irradiation.

The results have been interpreted in terms of a process of site-to-site direct recombination of different copper-associated aluminium hole centres with their respective electrons.

1. Introduction

It is known from our previous work [1,3] that cuprous ions in silica glass occupy a distribution of sites of which the luminescence properties of two predominant Cu^+ sites having, respectively, tetragonal and eight-coordinated cubic field structure of oxygen atoms can be distinguished [1] through site-selective UV excitations. The ions in the cubic site emit at around 430 nm with a shoulder around 417 nm and have an excitation maximum at 270 nm, while those in the tetragonal site show emission at around 490 nm and peak excitation at 260 and 244 nm.

The existence of a third group of cuprous ions which have no well characterized oxygen field structure, is however, revealed [3] when the glass is excited with a broad band in the range of 260–270 nm. Under such excitation the sharp 430 nm band loses its distinct identity and instead a new intense broad band peaking at around 450 nm appears. The 490 nm band in this case appears as a shoulder.

In this report we show that such site-sensitive behaviour of Cu^+ ions in the glass is also manifested in the copper(I)-related thermoluminescence (TL) of the glass and suggest that activator-related TL of a solid sometimes may act as a potential probe for identifying the nature of the activator sites in the matrix.

2. Experimental details

The methods of preparation of the Cu(I)-activated glass and estimation of its copper ion concentration have been discussed in our earlier work [1–3]. The copper ion concentration in the glass is of the order of 2.528×10^{18} ions cm^{-3} . A ^{60}Co γ source (0.72×10^5 rad h^{-1}) was used for irradiation of the glass. Irradiations were done at room temperature for 1 h. The TL glow curves of the irradiated glass were recorded in a nitrogen atmosphere using an indigenously built TL set-up of the Bhabha Atomic Research Centre, Bombay, India [4]. In this technique, 5 mg of the powdered irradiated sample were dispersed each time on a super kanthal dish of the set-up and was heated electrically at a constant heating rate

(13.15 K s⁻¹). The glow spectra were studied in a Perkin-Elmer 22B spectrofluorometer with an appropriate arrangement in the sample chamber for heating the sample under investigation at any desired constant temperature. Here, each time 10 mg of the powdered irradiated sample were dispersed on a super kanthal dish previously electrically heated to a desired constant temperature and the luminescence flux from the sample was directed towards the monochromator by a mirror. For selective thermal cleaning of the various thermal traps of the irradiated glass, different glass samples were used. The glass sample in each case was annealed at the appropriate constant temperature required for bleaching the desired trap for a suitable period of time in an inert atmosphere in an annealing furnace equipped with a temperature controller.

3. Experimental results

3.1. Thermoluminescence glow curve

the TL glow curve of the as-irradiated glass is shown in figure 1, curve (a). It exhibits two distinct thermal peaks at 414.5 and 530 K and a shoulder at around 450 K for a heating rate of 13.15 K s⁻¹. The peak positions are independent of the irradiation dose within the saturation limit of the glass. The glow curve of this glass recorded for the same heating rate after thermal cleaning of the 414.5 K thermal peak is shown in figure 1, curve (b). In this spectrum, only two distinct thermal peaks at 450 and 530 K are obtained. The TL glow curve of a sample of the same glass from which both the first two 414.5 and 450 K thermal peaks had previously been bleached by appropriate thermal annealing, however, shows only one peak at 530 K. This glow curve is given in figure 1, curve (c). The trap depth E for the 530 K thermal peak was determined by the peak shape method [5] utilizing τ (width at half-height on the low-temperature side), δ (width at half-height on the high-temperature side) and ω (full width at half-height) of the glow curve in figure 1, curve (c). Those for the 414.5 K and 450 K thermal peaks were, however, calculated by the initial rise method [5], utilizing the glow curves in figure 1, curves (a) and (b), respectively. The E -values obtained for different traps are given in table 1.

Table 1. Trap parameters of the thermal peaks of the glow curves of the Cu⁺-activated silica glass. The heating rate β is 13.15 K s⁻¹.

Parameter	Thermal peak temperatures T_m		
	414.5 K	450 K	530 K
Width, low- T side τ (K)	52.5	36	34
Full width ω (K)	—	—	73
Width, high- T side δ (K)	—	—	39
Geometry factor μ_g	—	—	0.53
Activation energy E (eV)	0.43	0.74	1.11

3.2. Thermoluminescence emission spectra

To identify the origin of the glow of the irradiated glass the TL emission spectra corresponding to the glows of both the bleached samples and the unbleached samples were recorded.

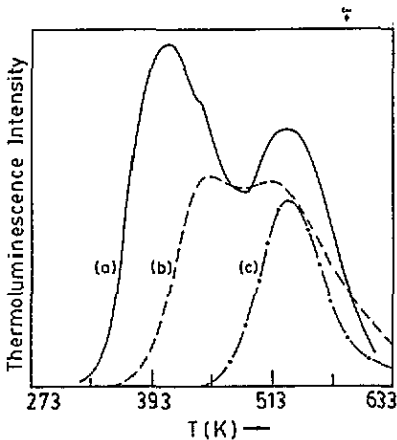


Figure 1. TL glow curves of room-temperature γ -irradiated Cu^+ -activated silica glass (dose, 0.72×10^5 rad) before and after various stages of bleaching: curve (a), as-irradiated sample; curve (b), the sample from which the 414.5 K thermal trap had previously been bleached by annealing at 413 K for 40 min; curve (c), the sample from which both the 414.5 and 450 K thermal traps had previously been bleached out by annealing at 473 K for 30 min.

The TL emission spectrum of the as-irradiated glass measured by heating at a constant temperature of 473 K is shown in figure 2. Under such heating, the first two low-temperature traps (414.5 and 450 K) as well as partially the highest-temperature trap (530 K) observed in the glow curve are expected to be emptied simultaneously. This glow spectrum as shown in figure 2 consists of a broad band at around 450 nm and a shoulder at around 480–490 nm.

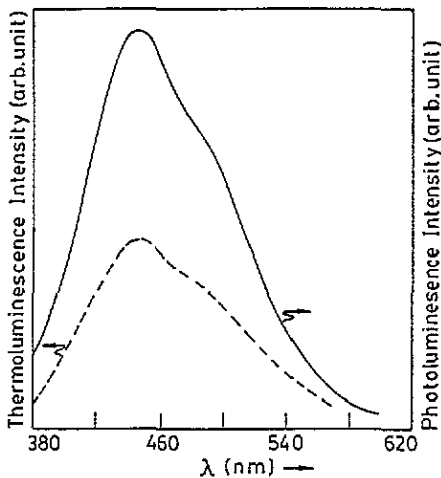


Figure 2. Glow spectrum (---) of the as-irradiated Cu^+ -activated glass together with the photoluminescence spectrum (—) of the unirradiated glass obtained on broad-band excitation in the range 260–270 nm (after [3]).

It is known from our earlier work [3] that cuprous ions in the unirradiated glass on photoexcitation with a broad band of 260–270 nm gives an average emission spectrum due

to $3d^9s \rightarrow 3d^{10}$ triplet transitions of copper(I) ions of different coordination sites in the glass and this spectrum consists of a broad maximum at 450 nm with a shoulder at around 490 nm also shown in figure 2.

Thus the spectrum of the glow that arises as a result of simultaneous recombinations of all the three traps of the as-irradiated glass is found to be identical with the integrated photoluminescence spectrum of copper(I) ions of different sites existing in the glass [1, 3].

The TL emission spectrum of a sample of the glass from which the 414.5 K thermal trap had previously been bleached was recorded by heating the glass at a constant temperature of 503 K. Under this heating, the remaining two traps at 450 and 530 K are expected to be released simultaneously. The glow spectrum obtained with such a sample also exhibits two emission bands: a sharp band at about 435 nm with a shoulder at around 415 nm and a broad band at around 480 nm (figure 3).

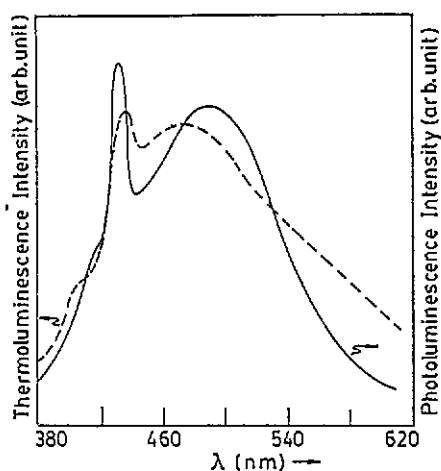


Figure 3. Glow spectrum (---) of an irradiated glass sample from which the 414.5 K thermal trap had previously been bleached out together with the photoluminescence spectrum (—) of the unirradiated glass obtained on selective excitation at 270 nm (after [1]).

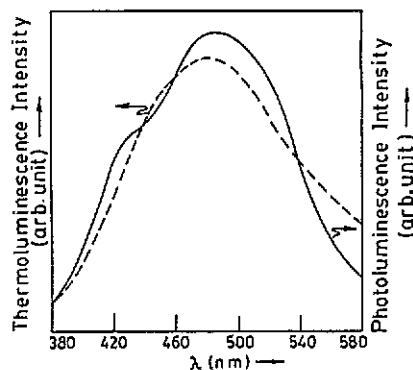


Figure 4. Glow spectrum (---) of an irradiated glass sample from which both the 414.5 K and the 450 K thermal traps had previously been bleached out together with the photoluminescence spectrum of the unirradiated glass obtained on selective excitation at 260 nm or 244 nm (after [1]).

This spectrum is, however, also known [1] to occur in the case of a photoluminescence study when the unirradiated glass is photoexcited with a narrow band of 270 nm (also shown in figure 3). In the case of photoluminescence the sharp 430 nm band together with the 417 nm shoulder are ascribed to the $3d^94s \rightarrow 3d^{10}$ triplet transition of Cu^+ ions in eight-coordinated cubic sites [1] and the 490 nm broad band to a similar transition of Cu^+ ions in tetragonal sites [1].

Finally the TL emission spectrum of a sample of glass from which both the 414.5 K and the 450 K traps had previously been bleached was recorded by keeping the sample at a constant temperature of 523 K. This spectrum (figure 4) consists of only one broad band at around 480 nm and correlates well with the spectrum of $3d^94s \rightarrow 3d^{10}$ triplet photoluminescence of Cu^+ ions of the tetragonal sites in the glass (also depicted in figure 4).

4. Discussion

It is shown in the preceding section that previous bleaching of the 414.5 K thermal trap makes the TL emission spectrum of the glass free from the 450 nm band. Now, since the 450 nm emission band in this glass is known [3] to originate from the Cu^+ ions of unspecified field structure, it is logical to assume that the 414.5 K thermal traps observed in the glow curve of the irradiated glass are related to those recombination sites which are associated with Cu^+ ions having an unspecified field structure. Again the TL emission spectrum of a sample of the irradiated glass in which only the 530 K thermal trap has been left after thermally cleaning out of 414.5 K and 450 K traps shows only one emission band maximizing at 480 nm. Since the photoluminescence spectrum of Cu^+ ions of tetragonal sites of the unirradiated glass are known to exhibit a single maximum at around 490 nm [1], it may be considered that the recombination sites of the 530 K thermal traps are associated with the Cu^+ ions of the tetragonal sites. From similar arguments it can easily be shown that the group of Cu^+ ions belonging to the eight-coordinated cubic field site which shows photoluminescence at around 430 nm is related to the recombination sites of the 450 K thermal trap of the irradiated glass. Thus, similar to our previous photoluminescence observation, site-dependent TL of Cu(I) ions in silica glass is also observed.

Such site-sensitive TL of activator ions in solids is, however, not unknown. Postel'nikov and Shuranova [6] reported that manganese ions in γ -irradiated phosphate glass exhibit site-sensitive behaviour in its TL. Very recently Meijerink and Blasse [7] also noted the existence of two types of photostimulated luminescence centre related to two different sites of Eu^{2+} ions in an x-irradiated barium bromoborate crystal.

Selective deactivation characteristics of the traps and non-dependence of their thermal peak positions on the irradiation dose suggest [8,9] that a centre-to-centre direct electron-hole recombination is involved in the bleaching process of the defects in the irradiated glass. Now a direct electron-hole recombination process requires [8,10] that the electron (trap) and the hole be located within a distance over which tunnelling can occur.

In another study [11] we observed from our EPR results on the system that a new class of aluminium hole centre compensated with copper, of the type $[\text{AlO}_4/\text{Cu}^+\text{O}_n]^+$, is generated in this glass upon γ -irradiation. With that knowledge in mind we propose the following tentative mechanism for the observed site-selective TL behaviour of the irradiated glass.

Since the glass itself contains a significant percentage of aluminium (about 1%) [2], upon γ -irradiation at ambient temperature, uncompensated aluminium hole centres of the type $[\text{AlO}_4]^0$ are generated [12,13] in the glass. Amongst these hole centres those located at the neighbouring sites of Cu(I) ions are immediately captured by the copper(I) ions to form copper-compensated aluminium hole centres of the type $[\text{AlO}_4/\text{Cu}^+\text{O}_n]^+$ which differ in their energies depending on the oxygen field structure associated with the copper(I) ion. The electrons released from the aluminium site by the high-energy photons (γ -ray) during the irradiation do not move very far from the aluminium site but remain possibly on some nearby four-coordinated silicon sites stabilized by either sodium or lithium ions like those described by Jani *et al* [14].

Thus different copper-compensated aluminium hole centres in conjunction with their respective nearby electron traps form different types of localized defect unit in the irradiated glass each of which is characterized by a definite activation energy. On selective stepwise thermal stimulation, electrons corresponding to a certain type of hole are released, directly tunnel to the latter and transfer their energy to the associated cuprous ions. The excited cuprous ions in a subsequent stage become dissociated from the complexes $[\text{AlO}_4/\text{Cu}^+\text{O}_n]^0$ and relax to the ground state with the emission of radiation energy according to their associated field structure.

A proposed scheme of the electron-hole direct recombination process of the γ -irradiation Cu^+ -activated glass under thermal stimulation is given in figure 5.

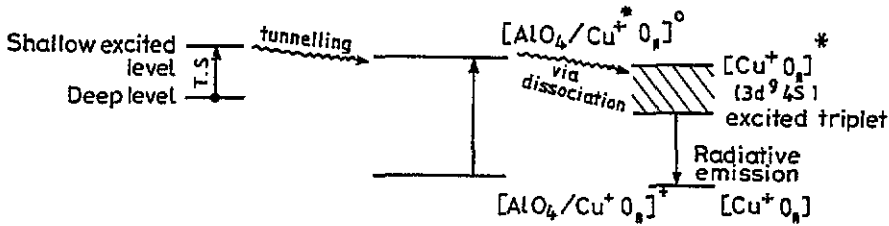


Figure 5. A proposed scheme of thermally stimulated electron-hole direct recombination process of the γ -irradiated Cu^+ -ion-activated glass: TS, thermal stimulation. The emission energy of copper is dependent on its associated field structure.

Acknowledgments

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References

- [1] Debnath R and Das S K 1989 *Chem. Phys. Lett.* **155** 52
- [2] Debnath R 1992 Indian Patent Application 618/DEL,92
- [3] Debnath R and Kumar S 1990 *J. Non-Cryst. Solids* **23** 271
- [4] Gupta N M and Thatte S B 1970 *Bhabha Atomic Research Centre Report* BARC 462
- [5] Chen R 1969 *J. Appl. Phys.* **40** 570
- [6] Postel'nikov S A and Shuranova N G 1989 *Sov. J. Glass Phys. Chem.* **15** 388
- [7] Meijerink A and Blasse G 1991 *J. Phys. D: Appl. Phys.* **24** 626
- [8] McKeever S W S 1985 *Thermoluminescence of Solids* (Cambridge: Cambridge University Press)
- [9] Avouris P and Morgan T N 1981 *J. Chem. Phys.* **74** 4347
- [10] Bull R K 1989 *J. Phys. D: Appl. Phys.* **22** 1375
- [11] Chaudhuri J and Debnath R to be published
- [12] Griffiths J H E, Owen J and Ward I M 1954 *Nature* **173** 439
- [13] Lee S and Bray P J 1962 *Phys. Chem. Glasses* **3** 37
- [14] Jani M G, Halliburton L E and Halperin A 1986 *Phys. Rev. Lett.* **56** 1392