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Photoluminescence from Cu activated glass prepared by spray pyrolysis

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Abstract

Photoluminescent copper activated glass has been prepared by the spray pyrolysis technique at atmospheric pressure using air as carrier gas. The Cu source is an aqueous solution of CuCl_2 sprayed at relatively low substrate temperature, (420–510°C). Rutherford backscattering measurements show that the copper diffuses into the glass substrate. The photoluminescence spectra from these samples show a peak at about 500 nm. The intensity of this peak is strongly dependent on substrate temperature during deposition and on deposition time. This light emission is however, relatively independent of the solution flow rate which determines the amount of Cu reaching the glass surface during the preparation process. A Cu^+ center is suggested as a possible source of the luminescence emission observed in these samples. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Luminescent centers associated with copper impurities introduced in crystalline and glass materials have a wide wavelength range of photoluminescence emissions depending on the host

material and on other dopants introduced simultaneously [1–6]. For example, Cu-doped zinc sulfide crystals emit either a green or a blue emission [1] and a broad emission at 570 nm has been reported for polycrystalline films [2]. More recent work on the luminescent characteristics of $(\text{Ca}_{1-x}\text{Sr}_x)\text{S}:\text{Cu}^+$ powder phosphors reports light emissions in the wavelength range 400–500 nm depending on the relative concentration of calcium and strontium [3]. Also, due to its potential application to obtain tunable laser emissions in the visible range, copper has been incorporated to sapphire, alkaline halide, alkaline earth halides, silica calcium

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phosphate, sodium borate, and β alumina [4–8]. In the case of β alumina crystals, the color of the Cu emission depends on the co-dopant used, ranging from 470 to 700 nm. Among the results reported for Cu incorporation in glass materials, there are a couple of interesting works on the luminescent characteristics of copper-doped alumoborosilicate glass [9] and silica glass [10]. In the case of alumoborosilicate glass, a broad band luminescence emission is observed with a peak intensity located at about 500 nm. Similar emission is reported for silica glass, although in this case an additional band is observed at 433 nm. The 500 nm emission has been associated with a $3d^{10} \rightarrow 3d^9 4s$ ($^3E-^1A$) transitions characteristic of monovalent copper. The 433 nm band observed in silica glass has been associated with a site-dependent effect of the monovalent copper impurity. The glass activation with monovalent copper is however, a complex procedure that requires suitable control of the atmosphere and temperature conditions. The temperatures involved were also relatively high [9,10].

In the present work, the photoluminescence properties and the preparation procedure of copper activated glass by spray pyrolysis at atmospheric pressure and at relatively low substrate temperatures are reported. Rutherford backscattering results, showing that Cu diffuses into the glass at the substrate temperatures used for this work are also presented.

2. Experimental details

The spray pyrolysis system used for the sample preparation process is similar to that reported earlier [2]. In this system an aqueous solution is sprayed by a pneumatic nozzle onto the heated surface of a substrate leaving a solid film and waste volatile products which are removed through an exhaust. The process occurs normally at atmospheric pressure. In this work a solution of $CuCl_2$ is used to deposit a copper oxide film on the surface of the substrate. This spraying solution is 0.1 M solution of $CuCl_2$, AR degree, in a mixture of three parts of isopropyl alcohol and one part of de-ionized water. The samples were prepared under the conditions shown in Table 1. The carrier gas

Table 1
Preparation conditions of Cu activated glass

Sample	Substrate temperature $T_s(^{\circ}C)$	Solution flow rate F_a (cm^3/min)	Spraying time (min)
CUV1	420	8	10
CUV2	450	8	10
CUV3	480	8	10
CUV4	510	8	10
CUV5	510	5	10
CUV6	510	14	10
CUV7	510	8	15
CUV8	510	8	5

flow rate was 10 l/min, this gas being air. The nozzle–substrate distance was 30 cm. The substrates were commercial glass (constituents SiO_2 , Na_2O and CaO).

The ion beam analysis (IBA) facilities of the Institute of Physics of the National Autonomous University of Mexico based on a 5.5 MeV CN Van de Graff accelerator, were used to obtain the atomic composition of the films [11,12]. The conventional $^4He^+$ Rutherford backscattering technique (RBS), was used to bombard the samples with 2.4 MeV particle energy and the backscattered energy spectra from the targets were measured with a surface barrier detector set at $\Theta = 170^{\circ}$ with a solid angle $\Omega = 2.0$ msr. The concentration depth profiles were determined by fitting the RBS experimental data using the RUMP simulation program [13]. Optical transmission spectra were obtained with a double beam Shimadzu UV-260 spectrophotometer. The measurements were performed with reference to air in the wavelength range of 190 to 850 nm. The photoluminescence spectra (PL) were obtained using the 365 nm wavelength radiation from a mercury lamp coupled to a filter. The emitted light was collected by means of an optical fiber with a filter to eliminate the blue photoluminescent emission from the glass. The spectral resolution was achieved with an optical multichannel analyzer (OMA). The OMA sensor was kept at $-10^{\circ}C$. The spectral response of the whole detection system is flat in the wavelength range analyzed.

3. Experimental results

The RBS analysis of the $^4\text{He}^+$ backscattering energy spectra was performed using the RUMP computer simulation program. Fig. 1a shows the RBS spectrum from a glass substrate with a thin metallic copper layer deposited on it. The solid line corresponds to the computer simulation obtained assuming a 20 Å thick CuO layer and a glass substrate composition of $\text{Si}_1\text{O}_{2.5}\text{Na}_{0.4}\text{Sn}_{0.0001}$. The

line marks in the figure signal the leading energy edges at 0.863, 1.184, 1.346 and 1.599 MeV of alpha particles scattered at the surface layer of the substrate by oxygen, sodium, silicon and calcium, respectively. The peak at 1.853 MeV is due to particles scattered from the Cu atoms on the surface. This isolated peak shape for the copper signal is expected from a thin layer on the substrate surface. The presence of tin is due to surface contamination on the substrate, probably introduced during the fabrication process of the glass sheet (float glass process uses a melted tin bed to spread the glass on a sheet form) since it is present in substrates with and without spray pyrolysis diffusion treatment. Fig. 1b shows the RBS spectrum of one of the copper-diffused samples studied. The constituent elements of the glass substrate are indicated, as in the previous case, but besides the presence of copper, also chlorine is observed as well as a redistribution of the Na signal that presents a small peak. The RUMP simulation (solid line) required, in this case to assume 5 layers. Fig. 2

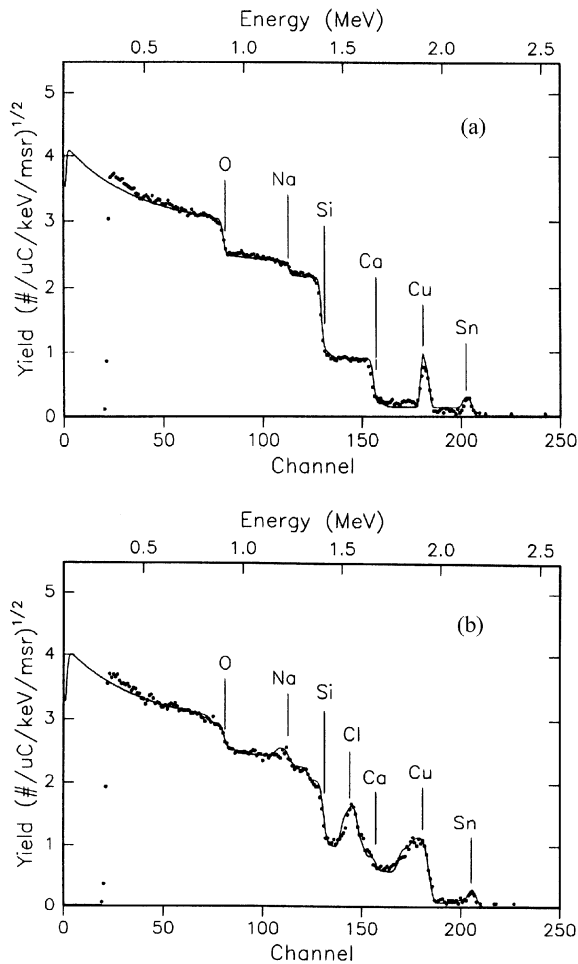


Fig. 1. 2.4 MeV α backscattered energy spectra for normal incidence geometry and laboratory angle of 170° from (a) glass substrate with a metallic copper layer thermally evaporated on it and (b) copper activated glass. The solid line correspond to the computer fitting obtained with RUMP simulation.

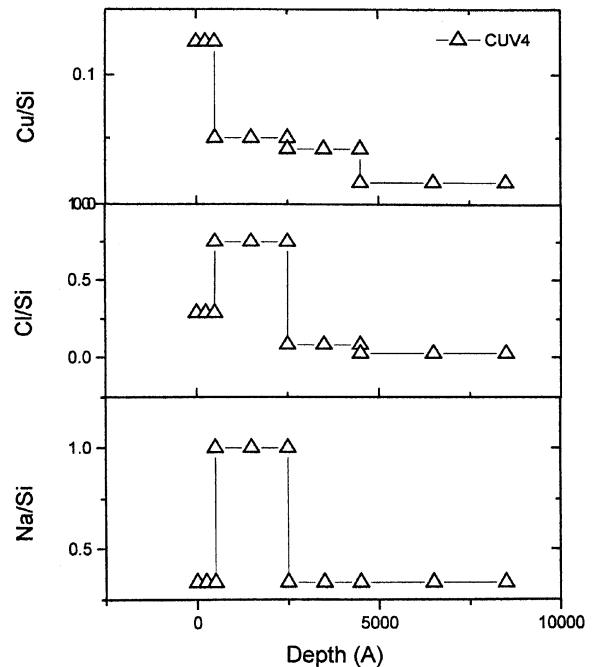


Fig. 2. Cu, Cl and Na profiles normalized to the Si content as determined by the RUMP simulation program fitted to the experimental data shown in Fig. 1b.

shows the profile distribution for the Cu, Cl and Na ratios to Si content. From these profiles it is possible to see that Cu diffuses into the glass to a depth of about 5000 Å from the surface, while the Cl and Na have a maximum distribution within 2500 Å from the substrate surface. It is interesting to note that the similarity of the Cl and Na profiles was characteristic of all the samples analyzed. The total copper incorporation was larger with longer deposition times and the profile extended more into the substrate, but no farther than 10 000 Å.

Fig. 3 shows the optical transmission spectra from a glass substrate and for sample CUV7. The curve for the Cu activated sample shows an overall optical transmission smaller than that shown by the glass substrate alone. This attenuation of the transmitted light is due to a combined effect of the copper and chlorine incorporation to the glass substrate and possibly a copper oxide layer deposited on the glass. It should be pointed out however that no interference effects due to multiple reflection of a thin layer on top of the glass substrate were observed on the transmission spectra of this sample nor for any of the other samples studied. Also a slight shift of the absorption edge is observed on the samples with respect to the glass substrate. These effects could be originated by the overall

attenuation of the transmitted light. The attenuation of light is a result of the incorporation of Cu to the glass since it is larger as the amount of copper incorporated increases. The case presented in this figure corresponds to the sample with the largest amount of copper incorporated (as estimated from the RBS measurements). A similar behavior has been observed in Cu activated alumoborosilicate [9].

A typical room temperature photoluminescence spectrum from Cu activated glass samples is shown in Fig. 4. This spectrum shows a single broad peak centered at ~ 500 nm. Pure silica glass and alumoborosilicate glass present similar photoluminescence emission when doped with Cu^+ ions [9,10]. This emission is due to interconfigurational transitions $3d^{10} \rightarrow 3d^9 4s$, of the Cu^+ ion and the exact location of the peak in wavelength as well as the presence of additional peaks depend on dopant concentration and site location within the glass. In our case, no significant variations in the photoluminescence spectra shape or location of the peak intensity in wavelength were observed for the different preparation conditions studied. However, the luminescence intensity as a whole, was strongly dependent on the substrate temperature during the deposition (T_s) and on the deposition time (t_D) at

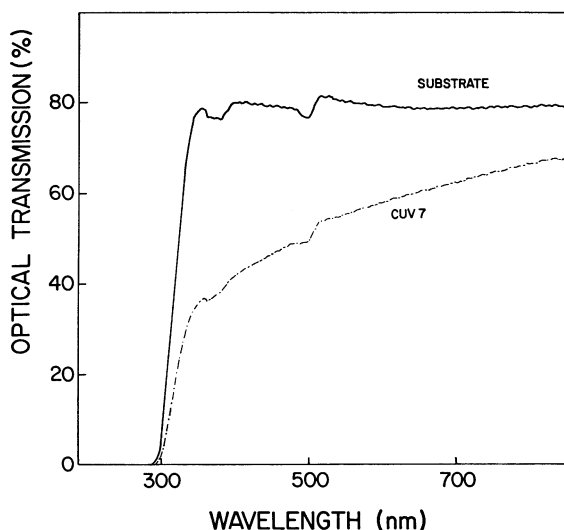


Fig. 3. % Transmission spectra for a clean glass substrate and for a Cu activated sample (CUV7).

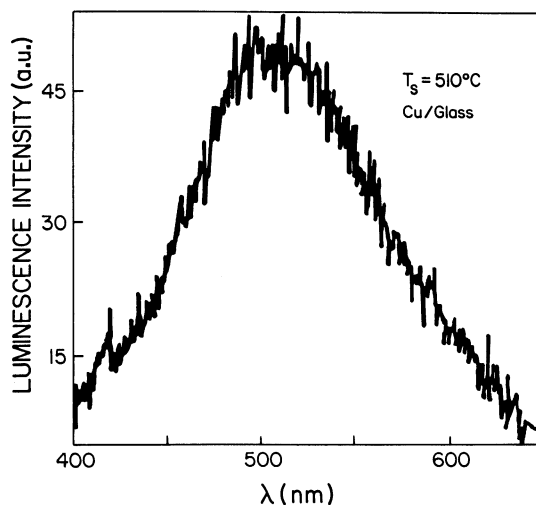


Fig. 4. Photoluminescence spectrum from a copper activated sample (CUV4). The luminescence emission from all the samples studied presented similar spectral characteristics.

a given temperature. Fig. 5 shows the behavior on the peak luminescence intensity as a function of T_s in the range of temperatures studied while the rest of the parameters were fixed. The luminescence intensity shows an initial linear increase with temperature, but presents a saturation effect at temperatures above 480°C. The luminescence peak intensity also increases with deposition time, as shown in Fig. 6. In this case no saturation effect was observed up to 15 min of deposition time at a fixed substrate temperature of 510°C.

4. Discussion and conclusion

The incorporation of copper in the glass substrate is clearly observed from RBS results shown in Figs. 1 and 2. The Cu diffuses into a depth of about 5000 Å from the substrate surface and certainly no more than 10 000 Å. Since the luminescence and the total amount of copper in the samples are relatively independent of the spraying solution flow, which determines the amount of Cu reaching the substrate during the preparation of the samples, it is assumed that the introduction of copper into the substrate is limited by the speed of the diffusion process of the copper in glass. The presence of Cl is

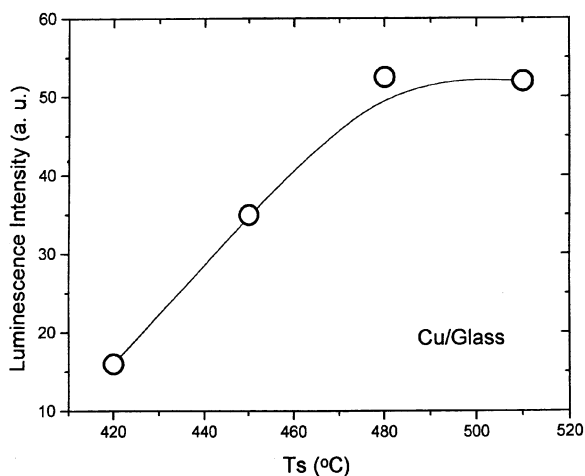


Fig. 5. Luminescence intensity at the peak as a function of the substrate temperature during sample preparation. A saturation type of effect is observed on the light emission intensity at temperatures above 480°C.

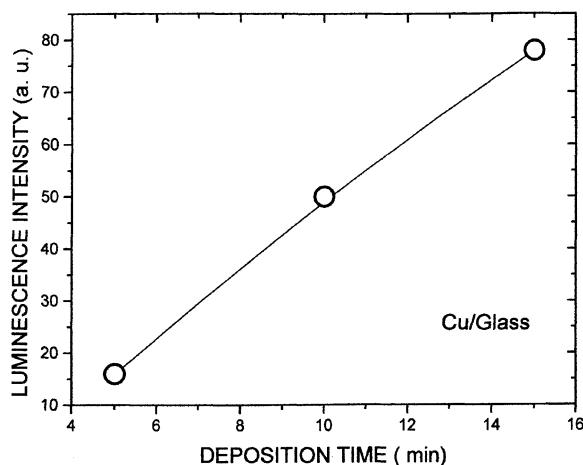


Fig. 6. Luminescence intensity at the peak as a function of the deposition time. A linear behavior is observed in the range of times studied.

not completely unexpected since the spraying solution is made with CuCl_2 . Whether the chlorine remains bonded to the Cu or to Na ions or by itself is not possible to determine with the present data, however, the Cl profile is remarkably similar to the Na profile in all cases, indicating that if any it would have linked to Na. The optical transmission spectra (Fig. 3) show lower transmission values for the Cu diffused sample, however there is no significant variation in shape other than a tendency for a larger absorption at low wavelength values and a small shift for the cut-off of the transmission signal which could be a result of the overall attenuation of the transmitted light. The samples showed a slight coloration with copper diffusion, however they remain clear (e.g. no milking or whitish appearance was observed). Therefore, bulk scattering seems to be no problem for these samples.

The photoluminescence spectra for the copper diffused samples show a striking resemblance to luminescence emissions reported for monovalent Cu ions in both silica and alumoborosilicate glass. In these two cases a broad-band peak located around 500 nm has been observed, although some variations are present depending on the ion site within the glass in the case of silica glass and on the concentration in the case of alumoborosilicate glass. Therefore, it is suggested that the luminescence

observed in the present case is related to this type of centers. There are cases however in which a dopant introduced in the form of chloride remains in molecular form giving rise to a luminescent emission associated with radiative transitions within molecular energy states [14]. The luminescence intensity in such cases follows the temperature dependence of the chlorine presence in the sample, which tends to escape as the deposition temperature is increased in the range of 250–480°C. Fig. 5 shows that these samples present the opposite behavior, increasing the intensity of the luminescence as the deposition temperature is increased up to 480°C. Besides the copper and Cl profiles shown by the RBS data analysis are rather different reinforcing the idea that they might not remain bonded. The possibility that the luminescence observed is generated at a copper oxide layer on the surface of the substrate is less likely, since no luminescence emission has been reported for copper oxide at wavelengths below 700 nm [15].

The increase of the luminescence intensity with deposition time is consistent with an incorporation of the copper limited by the speed of the diffusion of copper in glass as suggested by the RBS results, since longer deposition times at a given temperature will mean more chances for copper incorporation into the glass, increasing the amount of copper related luminescent centers that contribute to light emission observed.

In summary, Cu activated luminescent glass has been prepared by the spray pyrolysis technique at atmospheric pressure, at low temperatures and using air as carrier gas. This process requires short times and no further annealing. The RBS analysis shows that copper ions are diffused into the glass most likely by a thermally activated mechanism which seems to be limited by speed of the diffusion process. The photoluminescence spectra present a broad-band emission with a peak intensity located at about 500 nm for all the samples studied.

The similarities with luminescence spectra reported by other authors for Cu-doped silica and aluminoborosilicate glasses strongly suggest that as in those cases, the luminescence observed in these samples is associated to interconfigurational transitions $3d^{10} \rightarrow 3d^9 4s$ in Cu^+ ions incorporated in the glass substrate.

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