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Electron microscopy and EDX-microanalysis of photochromic silver halide glasses of the composition systems Al_2O_3–B_2O_3–SiO_2 and Na_2O–CaO–SiO_2

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The microstructure and microanalysis study of two glasses containing AgCl precipitated particles have been carried out by transmission electron microscopy (TEM, replica method), scanning electron microscopy (SEM) and SEM/EDX (energy dispersive X-ray spectrometry). The composition of these glasses doped with silver halide and CuO was formulated from the Al_2O_3–B_2O_3–SiO_2 and Na_2O–CaO–SiO_2 systems respectively. In both glasses the seeds, nuclei, crystals and matrix were analysed, and the mean size and number of crystals were evaluated from the TEM and SEM observations. The microstructure in both glasses is different because of the different shape of the silver halide particles; the particles of the Al_2O_3–B_2O_3–SiO_2 glass are rounded while Na_2O–CaO–SiO_2 shows square precipitated particles. Likewise, the darkening behaviour is basically different; the Al_2O_3–B_2O_3–SiO_2 glass shows a higher darkening velocity than the Na_2O–CaO–SiO_2 glass, showing for this glass a very small slope value.

1. Introduction

The photochromic materials and/or glasses operate reversibly in their transmittance of light, unlike the photographic process, which acts irreversibly [1]. There are different types of photochromic glasses, but those containing a small dispersion of silver halide crystals must contain AgCl precipitated crystals of between 5 and 30 nm [2]. If the size is smaller than 5 nm the material obtained is not photochromic, and if the size is larger than 30 nm the glass is made opaque by the crystals [3].

The photochromic glasses contain also several sensor agents such as Ag^+, Br^-, F^-, Cl^- and Cu_2O which facilitate the photochemical dissociation of the AgCl crystals giving rise to the metallic silver according to the reaction [4]

$$Ag^+ + Cu^+ \underset{IR}{\overset{UV}{\rightleftharpoons}} Ag^0 + Cu^{++}$$

It is thought these agents produce photolytic silver, which formed in crystals of Ag(HAL)–Cu^+. This is unstable and is easily decomposed through heating and illumination with red light. It is a redox pair sensitive to sunlight [5, 6].

The effect of copper on the AgCl crystal structure and the general microstructure of the precipitated crystals in the Na_2O–CaO–SiO_2 and Al_2O_3–B_2O_3–SiO_2 glassy matrices has not yet been established. Therefore, the aim of this paper is to study the microstructure and microanalytical composition of two photochromic glasses obtained in a previous study at the Departamento de Optica del CICESE, Mexico [7]. The photochromic glasses in the Al_2O_3–B_2O_3–SiO_2 system have been widely investigated in the past [1, 3, 4], though the darkening mechanism and CuO effect are not yet well understood [5, 6]. However, the effect of dopant agents in the Na_2O–CaO–SiO_2 system photochromic glasses has not previously been studied.

2. Materials and methods

Two types of photochromic glasses have been prepared whose compositions are shown in Table I. Silver was introduced from $AgNO_3$ and halides were added as cryolite (Na_3AlF_6), NaBr and NaCl. These oxides were weighed on a precision balance, mixed in a porcelain ball miller for 30 min and melted in platinum crucibles at 1450 °C. After two hours' stirring they form the glass, so the angular velocity of the stirrer was decreased as the stirring time increased. After pouring and cooling, both glasses were submitted at 650 °C thermal treatment in order to precipitate the AgCl crystals. This treatment takes two hours for the 1-glass and 6.5 hours for 2-glass. The viscosity variation with temperature has been measured in both photochromic glasses by using a hot stage microscope (II-A-P, Leitz).

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TABLE I Composition of the two photochromic glasses (wt %)

Oxide	Glass 1 Al_2O_3–B_2O_3–SiO_2	Glass 2 Na_2O–CaO–SiO_2
SiO_2	50.50	64.85
B_2O_3	19.32	2.47
Al_2O_3	6.73	0.97
Na_2O	1.68	13.63
CaO	–	8.35
Li_2O	2.51	–
K_2O	–	2.32
BaO	7.92	–
CdO	–	3.82
ZrO_2	4.46	–
PbO	4.65	–
Ag	0.32	0.43
F^-	–	0.33
Cl^-	0.69	1.15
Br^-	0.11	0.33
As_2O_3	0.29	0.18
Sb_2O_3	0.81	1.11
Cu_2O	0.01	–
CuO	–	0.01

The electron microscopy characterization of the resulting photochromic glasses has been carried out by: (a) transmission electron microscopy (TEM), which is performed using the triafol–carbon replica method on the poured surfaces and on the fresh fracture surface of the samples [8]. In both cases the surfaces have been etched with 2% HF/15 sec. For the TEM observation a JEOL 100-B operating at 100 kV accelerating voltage has been used. (b) Scanning electron microscopy (SEM) and the energy dispersive X-ray microanalysis (EDX) have been performed on fresh fracture surfaces etched with 2% HF/15 sec and coated with Au–Pd by sputtering in an Emscope sputter operating at 20 mA for 1.5 min. A SEM (Etec Corp.)

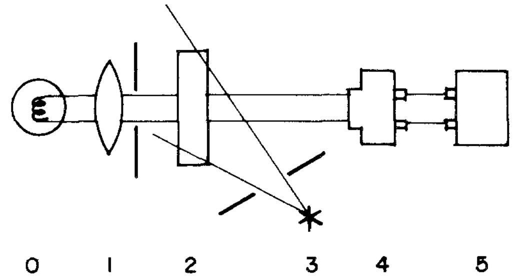


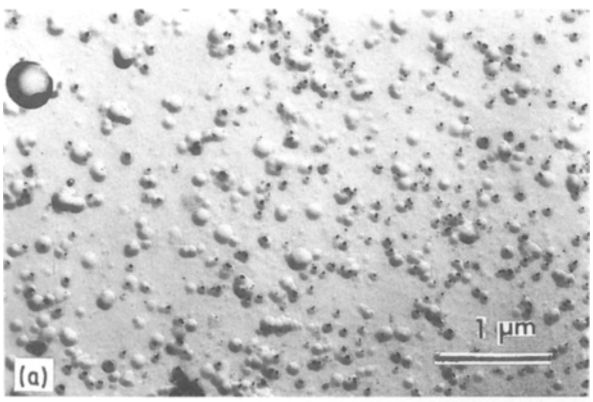
Figure 1 Optical system for taking time–transmission optical spectra in the photochromic glasses considered here. 0, tungsten lamp; 1, convergent lens; 2, photochromic glass specimen (3 mm thickness); 3, Silvania UV 275 W sunlamp; 4, Oriel 7070 detector; 5, linear plotter.

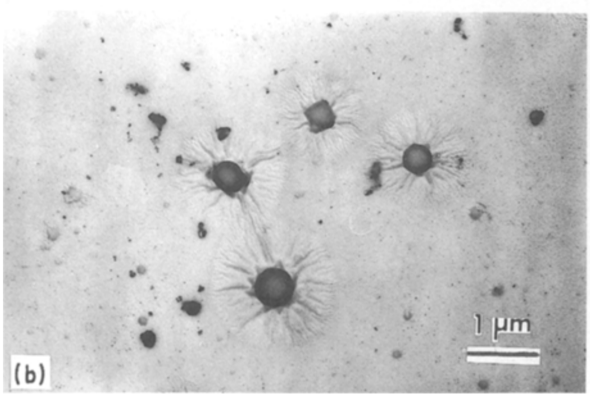
operating at 20 kV accelerating voltage with an EDX Kevex spectrometer with 7077 microcomputer was used to perform the SEM observations and microanalysis. An additional observation by TEM on a thin foil of the 1-glass has been performed. This thin foil was prepared by grinding and argon ion thinning as is usual for TEM [9]. The darkening rate of glasses investigated here has been carried out in an optical system with two channels, as indicated in Fig. 1. The first irradiation channel contains a 275 W Silvania UV Sunlamp and the second channel allows us to obtain the transmittance changes via a tungsten lamp and an Ariel 7070 detection system coupled to a linear plotter.

3. Results and discussion

Fig. 2a–c show the general microstructure observed by TEM (replica method) of 1-photochromic glass formulated in the Al_2O_3–B_2O_3–SiO_2 system. This glass shows three types of particles dispersed in the glassy phase: droplets of glass-in-glass phase separation, droplets or crystalline nuclei of larger size, irregularly distributed, and dark and rounded crystals, which could be silver halide, which have a halo around them.

The occurrence of liquid immiscibility or glass-in-glass phase separation on the 1-glass is possibly due to the extent of the miscibility gap in the Al_2O_3–B_2O_3–SiO_2 system [10]. The mean size of the droplets is approximately 200 nm with an irregular distribution in different areas. Thus, some areas show an average number of particles per unit area of $N_a \approx 27 \times 10^6$ particles/mm^2 and in other areas the





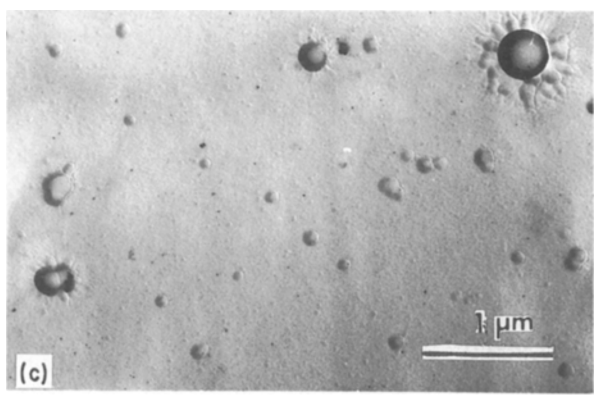


Figure 2 (a)–(c) General microstructure observed by TEM of 1-photochromic glass formulated in the Al_2O_3–B_2O_3–SiO_2 system.

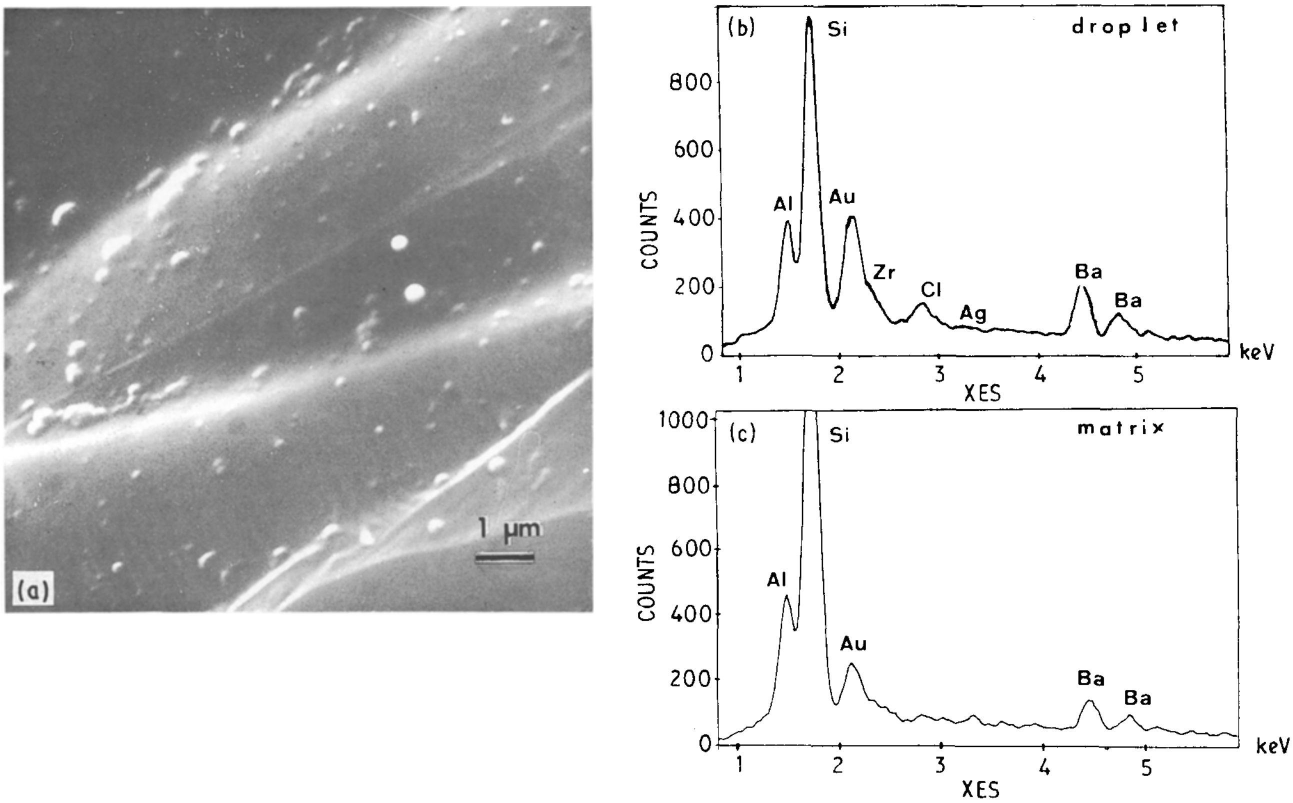
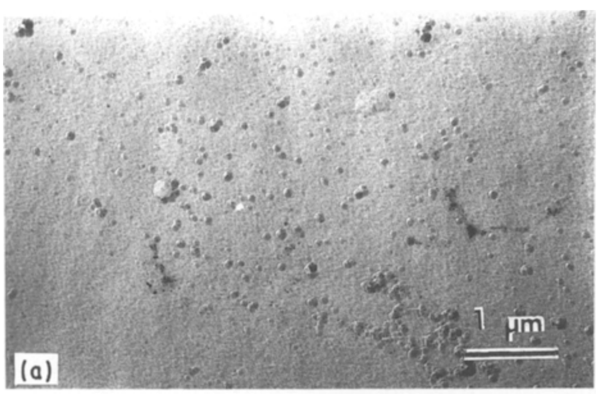


Figure 3 Micrograph of AgCl crystals in 1-glass by SEM. (a) Crystals showing white contrast; (b) and (c) EDX microanalysis on larger rounded particles (AgCl crystals).

particle density is very low, with $N_a \approx 3 \times 10^6$ particles/mm^2.

The particles larger than the immiscibility droplets have a mean size of approximately 300 to 500 nm, showing an irregular distribution in different areas – either very concentrated (Fig. 2a) or very dispersed (Fig. 2c). It could be the silver halide crystallization nuclei which are the main agents responsible for the photochromic effect. The dark rounded particles must be the AgCl crystals precipitated and grown by thermal treatment at 650 °C from the original glass. These crystals are larger than those reported by Pascova and Gutzow [11] in similar glasses. These authors precipitate AgCl crystals (30 to 50 nm) with a good distribution by thermal treatment of the original glass at 640 °C for one hour. The observation and measurement of crystal size were carried out in that case by transmission electron microscopy of thin foils [11]. On the other hand, the crystals observed here (Fig. 2c) show haloes or areas around them indicating the existence of diffusion or coprecipitated particles, as can be seen in Fig. 2b. Moreover, these crystals showing a dark contrast by TEM are white by SEM (Fig. 3a) due to the atomic number contrast given by the secondary and backscattered electrons. The SEM



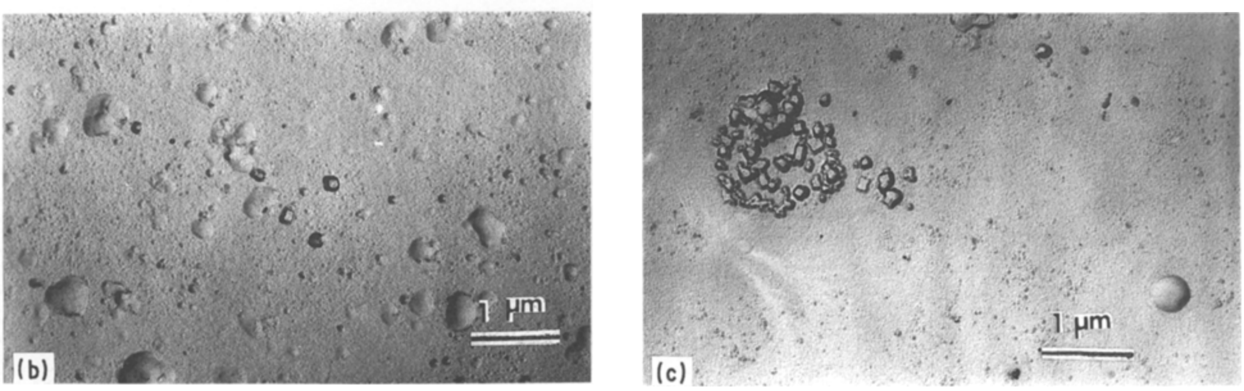


Figure 4 General microstructure observed by TEM of 2-photochromic glass formulated in the Na_2O–CaO–SiO_2 system.

observation agrees well with the TEM replica observations and allow us to confirm with the EDX microanalysis that larger rounded particles are AgCl crystals (Fig. 3b).

Fig. 4 shows the microstructure observed by TEM replica in the 2-glass. As in the 1-glass, three types of particles can be observed: (a) immiscibility droplets irregularly dispersed with a mean diameter of around 100 nm; (b) pseudo-rounded particles of larger size than the droplets and with a lower sodium concentration; and (c) small cubic crystals which are either isolated (Fig. 4b) or grouped forming clusters (Fig. 4c) with an approximate mean size of 300 nm. The observed TEM "heterogeneity" in 1- and 2-glasses (Figs 2 and 4) can be due to insufficient stirring or mixture of the raw materials, or uncontrolled features of the glass-forming technique because of large composition of these glasses (18 components, as can be seen in Table I). However this "heterogeneity" does not affect the appearance or properties of these glasses and was only detected by electron microscopy.

Fig. 5a shows the general microstructure of the poured surface on 2-glass observed by SEM with the EDX spectra corresponding to droplets (approximate mean size 500 nm) and matrix. There is no difference between the spectra, although when the same glass is etched by 2% HF for one minute it can be observed (Fig. 6a–c) that the rounded droplets (white contrast with the secondary plus backscattered electron image) are enriched in chloride with respect to the matrix (Fig. 6b). The EDX microanalysis carried out in etched areas of the matrix show the leaching of sodium and the decreasing ratio of Ca/Si (Fig. 6c). This sodium leaching allows us to detect the silver halide particles by EDX (Fig. 6b) due to the improvement of the AgCl content with respect to the matrix elements.

Fig. 7 shows the darkening and fading curves with time for both the glasses investigated here. It can be seen that in the Al_2O_3–B_2O_3–SiO_2 glass the photochromic sensitivity is in the darkening range 61 to 85%, where the time to reach these values is approximately 3 min. For the Na_2O–CaO–SiO_2 glass the photochromic sensitivity decreases to 75% darkening in 10 min.

The variation of viscosity with temperature in these photochromic glasses is very similar in both, between $\log \eta = 6$ to 10, but at lower viscosity values the slope of η with $1/T$ is steeper for the 2-glass (Fig. 8) than for the 1-glass. As is well known, the crystallization rate depends on the viscosity according to the general expression

$$I_0 = \text{const}\frac{1}{\eta}\exp\left(\frac{K}{T\Delta T^2}\right)$$

Therefore, a higher variation of viscosity with temperature implies large values of I_0 for 2-glass (Na_2O–CaO–SiO_2 matrix), favouring the full crystallization of silver halide crystals, as is observed in Fig. 4c.

The glasses considered here are photochromic due to the silver halide photochemical dissociation catalysed by the addition of copper. It is well known that the addition of copper also increases the degree of darkening and the velocity of dissociation [12]; the Cu^{2+} ions inhibit the release of halide from crystals increasing the quantum efficiency of the photolytic silver formation [7]. The photolysis of silver chloride, sensitized with copper, can be expressed as

$$Ag^+Cl^- + Cu^+Cl^- \rightleftharpoons Ag^0 + Cu^{++}Cl_2^-$$

Therefore, the copper not only affects the photochromic process but also the AgCl crystalline structure. Though the analytical resolution obtained by SEM does not allow us to analyse the boundaries between the rounded crystals and the matrix, it is

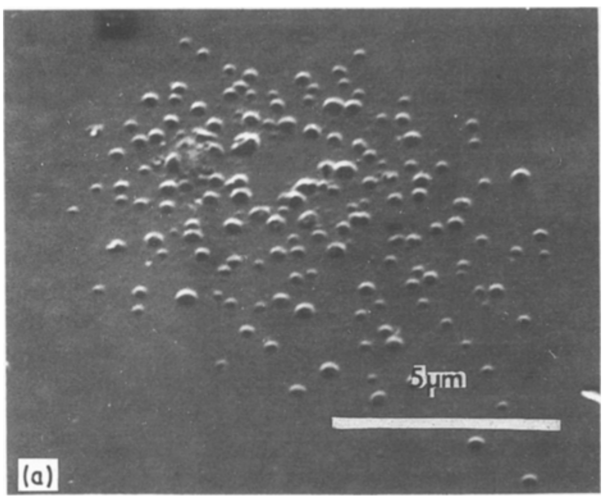
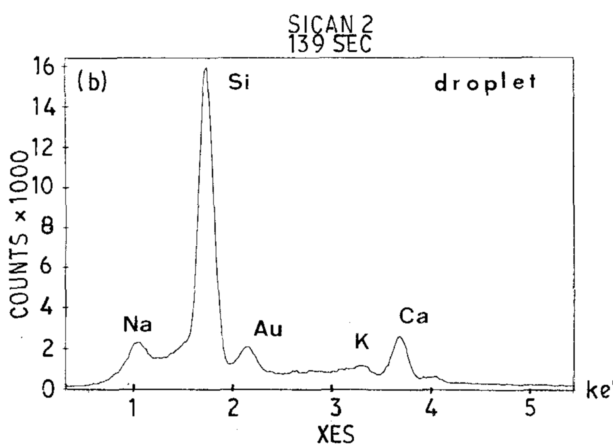
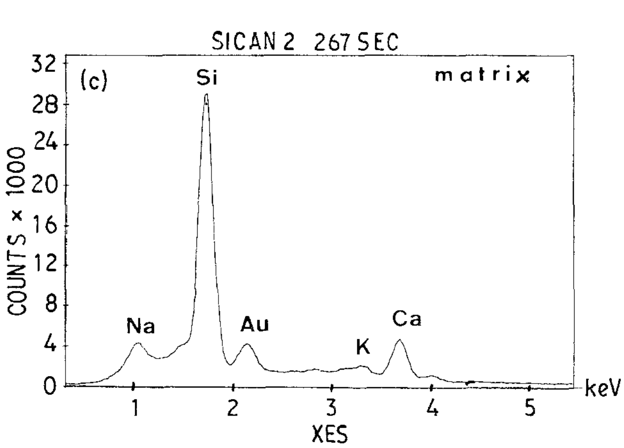


Figure 5 (a) General microstructure of the poured surface on 2-glass observed by SEM with EDX spectra corresponding to: (b) droplets, (c) matrix.





assumed that the interface or halo observed by TEM replica (Fig. 9) is related to the CuCl effect on the AgCl crystals according to the above reaction. Hence, the observation and microanalysis performed by HREM (high resolution electron microscopy) and AEM (analytical electron microscopy, that is to say TEM/STEM/EDX) should facilitate the confirmation of the photolysis reaction at the grain boundary.

In order to precipitate the AgCl crystals in the 1-glass a thermal treatment of two hours has been used, as compared with the 6.5 hour thermal treatment used in 2-glass of the Na_2O–CaO–SiO_2 composition system. The nucleation time seems to be too short in the 1-glass, producing rounded silver halide colloidal particles, whilst with a longer thermal treatment cubic crystals are precipitated which follow fcc AgCl crystallization ($a_0 = 0.555$ nm). According to the classical theory of nucleation and growth [11, 13], the AgCl crystals are formed following the next stages:

GERM → NUCLEUS → COLLOID → CRYSTAL

⟶ PHASE SEPARATION DROPLETS

Pascova and Gutzow [11] suggest that AgCl is formed by a phase separation in the binary AgCl–glassy matrix system followed by an Ostwald ripening mechanism. Thus, the germination depends on the glass viscosity, and therefore the crystal distribution is more homogeneous in the 1-glass (Al_2O_3–B_2O_3–SiO_2) composition system than in the 2-glass (Na_2O–CaO–SiO_2) composition system due to the lower viscosities over similar temperature ranges for the 1-glass [2].

Otherwise, the liquid immiscibility is lower in the 2-glass than in the 1-glass containing the boron oxide [10], but is strongly increased by the CdO, BaO and B_2O_3 additions.

Finally, the AgCl crystals from the 2-glass show under TEM a cubic shape, forming heterogeneously distributed clusters. This is also due to the lower extension of the phase separation affecting the crystalline microstructure. A TEM thin foil micrograph of the 1-glass droplets (Fig. 10) shows evidence of their polycrystalline morphology, which can be identified as silver halide on the basis of the electron diffraction patterns, while the 2-glass droplets have monocrystalline appearance.

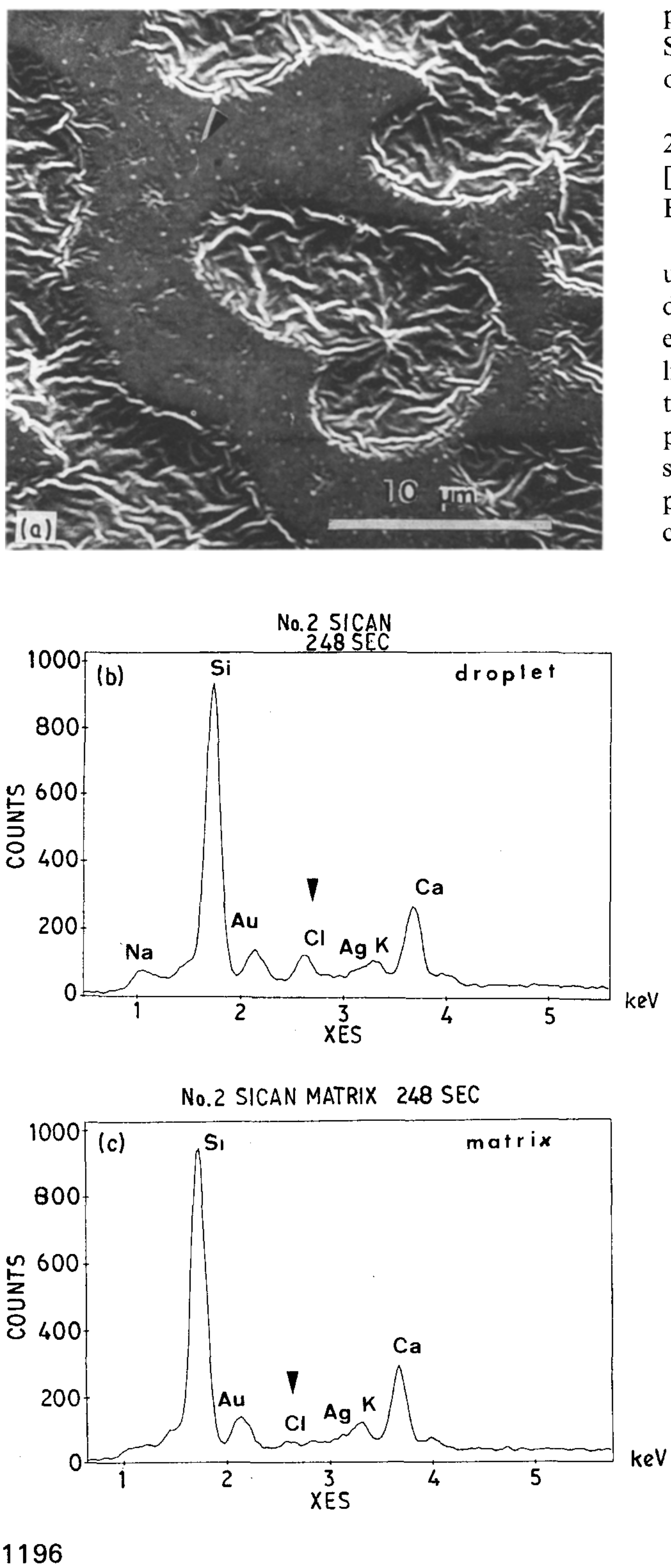


Figure 6 (a) General microstructure observed by SEM of the 2-glass etched by 2% HF for one minute. (b)–(c) EDX microanalysis carried out in etched areas (droplet and matrix).

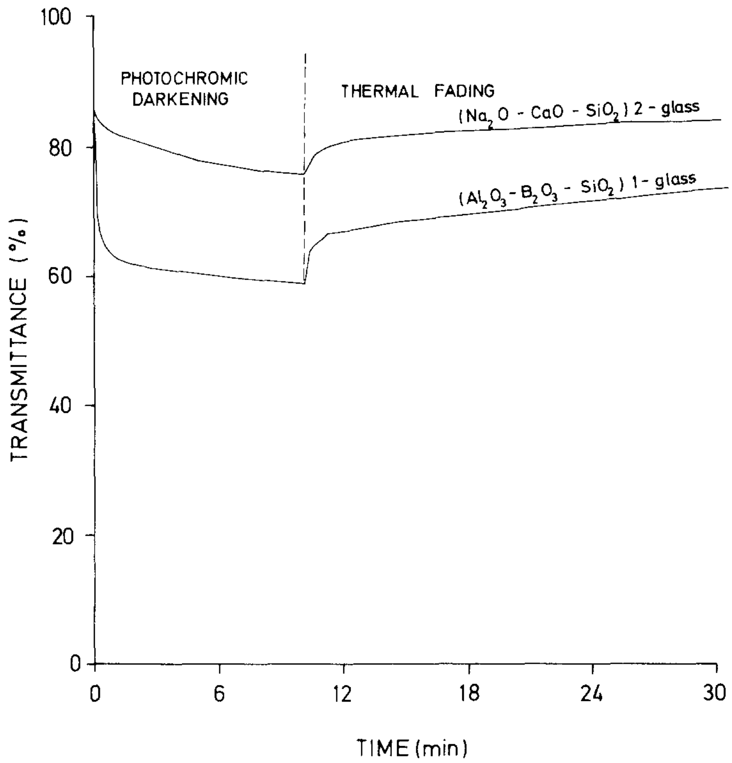


Figure 7 Curves of optical transmittance versus time for 1- and 2-glasses showing the photochromic darkening and the thermal fading.

4. Conclusions

The general microstructure of the silver halide particles precipitated in a glassy matrix in order to obtain photochromic glasses is strongly dependent on the glass composition considered. Thus, with an Al_2O_3–B_2O_3–SiO_2 glassy matrix, rounded crystals (approximately 0.3 µm mean diameter) nucleated by glass-in-glass phase separation are obtained, while in a Na_2O–CaO–SiO_2 glassy matrix at the same 650 °C thermal treatment temperature, smaller and cubic crystals (approximately 0.1 µm) are precipitated. The degree and rate of darkening of the Al_2O_3–B_2O_3–SiO_2 glass is greater than in the Na_2O–CaO–SiO_2 glass, due to homogeneous distribution and more colloidal texture of droplet particles of silver halide in the vitreous matrix. The photochromic effect is limited in both glasses, because the droplet mean diameter is greater than the size required for a good photosensitive material.

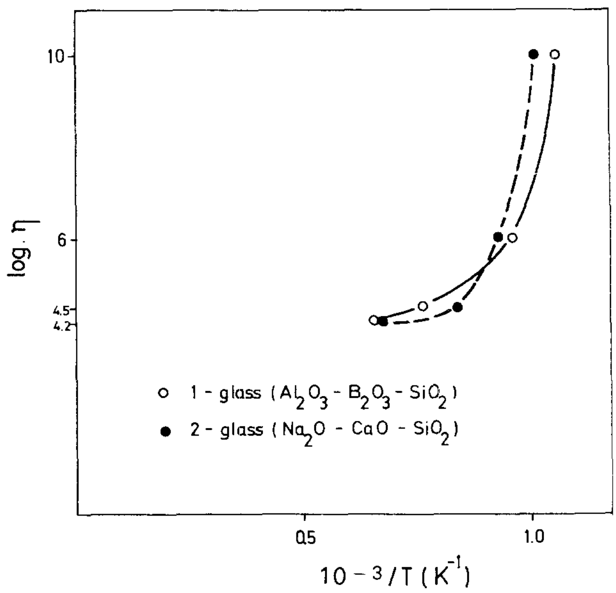


Figure 8 Variation of viscosity against temperature for the 1-glass and the 2-glass determined by hot stage microscopy.

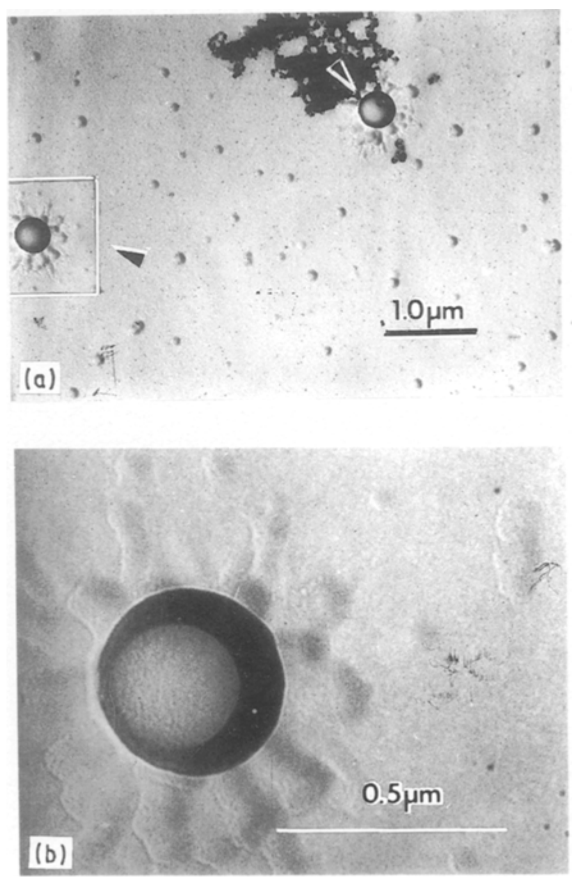


Figure 9 Micrograph of the boundary between rounded crystal and matrix observed by TEM in 1-glass.

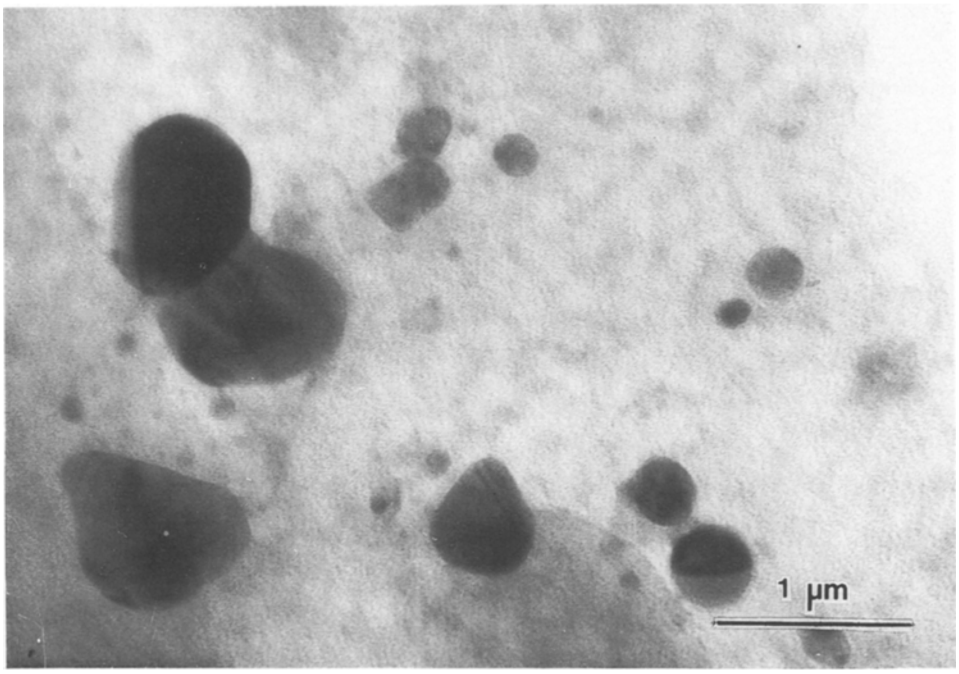


Figure 10 Droplet morphology observed by thin foil TEM in 1-glass.

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