Control of selective silicate glass coloration by gold metallic nanoparticles: structural investigation, growth mechanisms, and plasmon resonance modelization

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Abstract Soda lime silicate oxide glasses are studied to perform coloration thanks to gold nanoparticles' crystallization. This precipitation is conducted by chemical reduction of gold ions with stannous or antimony oxides as reducing agents. A control of the rendered coloration between blank to red shades has been obtained using Sb_2O_3 agent and appropriate thermal treatments. The glasses remain colorless while heating up to 450 °C. Structural glasses evolution is studied by MAS NMR spectroscopy of ^{29}Si and ^{23}Na nuclei to investigate the silicate network polymerization change and the modification of sodium/oxygen bond length versus nucleation state and growth of Au nanoparticles. A clear decrease of the Q^2 species part is observed with nanoparticles growth confirmed by the evolution of chemical shift for ^{23}Na resonance. A slight network polymerization is then showed independently of the only thermal treatment. This structural change could be induced by the antimony oxidation and change towards higher coordinations. Finally, the glasses chemical durability has been studied by leaching tests and shows lower alteration for colored glass. The optical spectroscopy applied to colored glasses has given rise to plasmon resonance phenomena at around 600 nm which is the typical surface plasmon resonance of gold for a refractive medium index of 1.5, with a shift of the resonance towards the higher wavelengths with increasing thermal treatment temperature. This shift is modeled by

Drude and MIE approaches and confirms the trend observed by UV-visible measurement with an increasing absorption at the SPR correlated to a typical Ostwald growth mechanism according to the increase of the annealing temperature.

Keywords Silicate glass–ceramic · Gold nanoparticles · Plasmonic effect · Drude and Mie Model · Chemical durability · MAS NMR spectroscopy · Structure

Introduction

Cadmium sulfoselenide is currently used as pigment for red glass making [1, 2]. According to the cadmium toxicity, another common way to elaborate ruby glasses is the addition of gold (or copper) and reducing agents as stannous oxide or antimony oxides to promote the gold reduction, according to the method delivered by the cultural heritage whose first historical trace is at the fourth century [1, 3, 4]. Some thermal treatments are then carried out for gold nanoparticles nucleation and growth associated to the color striking. The gold ruby glass is also still used punctually in luxury bottling, for example by Guerlain or Christian Dior for their perfumes, thanks to metallic dispersions of copper, silver, and gold to obtain colored decorative glass. Nonlinear optical properties of Au nanoparticles constitute also a large field of interest considering chemical and biological functionalities and optical and sensing applications [5].

The peculiar optical properties observed in the visible spectral range are explained by the surface plasmon resonance originating an absorption band usually around 530 nm (for gold) produced by these metal particles in the nanometer size range. However, the colors are variable, depending in part on the concentration and sizes of the gold particles dispersed throughout the glass and in another part of the processing parameters like thermal treatments. Typically, about 0.001–0.1 wt% gold is required to provide coloration in silicate

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glasses, and colors are variable between yellow for gold particles less than 5 nm, pink for particles around 10 nm, purple to red between 10 and 20 nm, and finally deep purple hue are observed for gold nanoparticles of 20–50 nm [6].

The glass structure can also be an important parameter if different redox states or coordination sites can exist for the chemical elements responsible of the coloration or if the network fragility can prevent or improve the nanoparticles growth. Wilk and collaborators have developed an example in acetate glasses where gold nanoparticles size can attain large dimensions in the fragile lithium-rich lead–lithium acetate glasses and liquids thanks to their flexibility in the contrary of sodium–potassium–calcium acetate strong samples where the gold nanoparticles are about 10 nm [6]. In the same way, Vosburgh and Doremus have obtained great changes in the kinetics of gold nanoparticles growth in boro-alumino silicate glasses of various viscosities [7].

The goal of this study is to elaborate glasses with a controlled coloration thanks to gold nanoparticles. This constitutes a challenge taking into account the parameters number to optimize the distribution, the size, and the form of the particles and taking into account the difficulties to characterize these nanoparticles. In the present work, conditions are established to get silicate glasses colored or colorless, thanks to reducing agents and specific thermal treatments controlling the color appearance. The nanoparticles formation is studied from optical absorption and couple to Drude and MIE modelization. Moreover, a structural approach is developed, thanks to nuclear magnetic resonance (NMR) spectroscopy to correlate the structure change and the nanoparticles growth.

Material and method

Glass elaboration

Silicate oxide glasses have been synthesized from the base molar composition 70 %SiO₂–10 %CaO–20 %Na₂O called “base glass.” Reducing agents SnO and/or Sb₂O₃ have been added for 1 to 2 wt%, and gold has been introduced as gold chloride (AuCl) for a rate between 0.1 and 0.4 wt%. In the following, glasses would be identified with the nomenclature “reducer wt% Au wt%–T,” T referring to the temperature of the last thermal treatment following the quench.

A solid phase mixing of high purity powders is prepared from SiO₂ (Acros Organics, France, Ultra Pure), CaCO₃ (Acros Organics, France, 99 %), Na₂CO₃ (Acros Organics, France, 99.95 %), Sb₂O₃ (Chempur, Deutschland, 99.9 %), and AuCl (Alpha, 99.9 %) to obtain 30 g of glass. Oxides are put in a 10 % RhPt crucible of 10 cm³ of volume and melted under air in an electric glass furnace. A temperature of 1,350 °C is applied during 3 h to assure the melting and homogenization, and then the melt is casted in vitreous carbon

crucible (Sigradur®) to obtain glass cylinder of 15 mm high and 10 mm of diameter. Finally, each vitreous sample is annealed at 450 °C during 16 h to relax the residual constraints. It is important to follow a precise and equal protocol as variation of cooling rate modifies the glass structure, and consequently, generates broadening of ²⁹Si NMR spectra [8]. Finally, the cylinder is cut to form slides of 1 mm thickness that are optically polished.

DSC analysis

The glass transition temperatures (T_g) have been measured by differential scanning calorimetry (DSC, SETARAM multi-HTC) on a small amount of glass powder (about 0.7 g) in a platinum crucible. The powder is heated in argon with a rate of 10 °C/min up to 1,400 °C. Accuracy obtained for T_g determination is ±2 °C.

TEM study

Samples for transmission electron microscopy (TEM) were prepared from crushed powder, dispersed in absolute ethanol, and deposited onto a holey carbon film supported by a copper grid. Bright or dark field images and electron diffraction patterns were carried out with a TEM (Philips CM20) operating at 200 kV and equipped with an EDX probe.

UV visible measurements

UV visible measurements have been performed with a dual beam spectrophotometer Jasco V530 in transmission mode in the range 200 to 1,000 nm in order to follow the glass transmission evolution and particularly to detect the surface plasmon resonance appearance and evolution during the annealing treatment.

Infrared spectroscopy measurements

The measurements were performed with a homemade spectrometer able to measure reflectance and emittance spectra. The device is built around two spectrometers, an air-purged Bruker 70 and a Bruker 80 v working under vacuum. The system is equipped with a set of beam splitters and detectors allowing to acquire spectra in the whole infrared range that is from 50 to 12,500 cm^{−1}. A CO₂ laser is used to heat the sample at temperatures up to 2,500 K. The laser beam (11 mm of diameter) is divided into two parts by a beam splitter which allows to heat both sides of the sample ensuring a good axial temperature homogeneity. Furthermore, the acquisition of the sample flux is limited to a small area 2 mm of diameter to avoid radial gradients.

NMR spectroscopy

The ^{29}Si magic angle spinning (MAS) NMR experiments are performed on a Bruker Avance WB 300 MHz (field of 7 T) operating at 59.63 MHz with a 4 mm Bruker MAS probe and ZrO_2 rotor. The excitation pulse duration (for a $\pi/2$ pulse angle) was 5.5 μs for a recycle time of 900 s, 192 scans accumulation, and a spinning rate of 10 kHz. The chemical shift of ^{29}Si spectra is referenced to tetra-methyl-silane at 0 ppm.

In the case of ^{23}Na ($I=3/2$), MAS NMR spectra are collected on Bruker Avance 750 MHz (17.6 T) spectrometer using a 2.5 mm rotor. Spectra are acquired with a $\pi/18$ pulse to ensure a quantitative excitation of the central transition and a recycle time of 1 s for a spinning rate of 30 kHz. Chemical shifts are reported with respect to NaCl aqueous solution (0.1 mol/L).

The calculation of NMR spectra was carried out using DM-FIT software [9] from Gaussian-Lorentzian lines in the case of silicon and sodium, the quadrupolar coupling constant being very low at this field for ^{23}Na nuclei.

Leaching experiment and ESEM analysis

The alteration behavior of the colored glasses has been studied in deionized water (pH 7.6) by static leaching experiments at 90 °C in an oven. The experiments are driven in Teflon® vessel of 50 ml, on monoliths, during 44 days. Two samples have been studied, a colorless glass Sb1Au0.1-450 treated at 450 °C during 16 h and a red colored glass Sb2Au0.2-550 treated at 550 °C during 16 h.

After leaching, the cationic concentrations have been determined by inductively coupled plasma–atomic emission spectroscopy (ICP-AES) (Thermo). Three aliquots of 2 ml are taken off during the experiment for each sample. The normalized mass loss $NL(X)$ (in grams per square meter) is given by [10]:

$$NL(X) = \frac{[X]}{f_m(X)} \times \frac{S}{V}$$

Where $[X]$ is the element concentration in the solution (grams per cubic meter), $f_m(X)$ is the mass rate of the element X in the glass (without unity), S/V the ratio of the glass surface area to the solution volume (per meter).

The calculation of the normalized mass losses allows comparing the releasing of the various elements each other in the same matrix or between different glasses. An accuracy of 2 % is retained for Si, Na, and Ca normalized mass losses, 4 % for Sb, and 10 % for Au. The S/V ratio is of the order of 10 m^{-1} for both samples. At the end of the test, the samples are rinsed and dried for observations by environmental scanning electron

microscope (ESEM Philips XL40) and qualitative chemical analysis performed by energy dispersive X-ray spectroscopy (EDX). The retained accuracy is 1 % for metals.

Results and discussion

The base glass composition 70 % SiO_2 –10 % CaO –20 % Na_2O has allowed to test the red color appearance according to the reducing agents choice and to the thermal treatments performed. In compounds formed with a low amount of gold (0.1 wt%), the stannous oxide is a very efficient reducer for gold cations, and red glass is obtained as soon as the glass quench for 1 wt% of SnO. On the contrary, replacing tin to antimony, glass is kept colorless at the elaboration and after the first thermal treatment at 450 °C performed for the relaxation of the residual constraints. In presence of the both reducer oxides (1 wt% each), the glass is also conserved blank up to the first thermal treatment at 450 °C.

Using antimony, the red coloration appears toward 530 °C, covering only the central part of the slide for a thermal treatment of 16 h (Fig. 1). The increase of the temperature involves a change of the color towards the violet and the extension of the colored region up to the total volume. At a temperature of 590 °C, we have observed the pink color first appearance after 15 mn for a very small area just in the middle of the plate and the extension of the colored area with the duration of the temperature stage. After 1 h, the coloration covers half of the surface, and the total-volume is treated after 5 h. From 3 h, some regions change towards purple coloration. At 650 °C, around 100 °C above the T_g , the glass becomes blue.

A few dispersed nanoparticles have been observed by TEM in the glass heat treated at 590 °C for 3 h 30 min (Fig. 2). The observed particles are very small (5–10 nm mean size) but crystallized as proved by both the electron diffraction pattern matching the cubic structure of gold (4.08 Å, Fm-3 m) and the dark field image. In a sample treated at the same temperature during 16 h, we observe larger spherical nanoparticles with a characteristic size of around 15 nm, along with small ones (3–7 nm). The large ones are unambiguously analyzed by EDX as gold. The dark field images prove the crystalline nature of both size nanoparticles. At 650 °C, in a blue colored glass, the observed particles attain 35 nm in mean but are less spherical. TEM analyses have also been performed on a colorless glass treated at 450 °C. At this stage, no gold nanoparticles have been detected. Furthermore, no demixtion is present in the glasses whatever the stage of the process.

The base-glass structure has been analyzed thanks to MAS NMR spectroscopy. ^{29}Si NMR spectrum shows a broad signal in the region –110, –70 ppm attributed to Q^n species (n : number of bridging oxygen BO) [11] (Fig. 3). The calculation of the spectra is carried out from three lines (Gaussian-

Fig. 1 Gold samples coloration according to annealing temperature

lorentzian type) assigned to Q^2 , Q^3 , and Q^4 species. The major specie is Q^3 (78 %) in agreement with the large part of modifier cations sodium and calcium in the glass. A basic calculation leads to a mean ratio $NBO/Si=0.86$ nonbridging oxygen per silicon, considering the glass composition (one NBO for one Na^+ , 2 NBO for one Ca^{2+}), that can be compared to the ratio $NBO/Si=0.88$ deduced of the NMR calculation (Q^3 : 1 NBO/Si, Q^2 : 2 NBO/Si) (Table 1). The glasses incorporating reducer agents and gold have been analyzed at successive stages of the process. At first, it is important to remark that the NMR spectra changes are low. Figure 4 compares the signals for colored glass obtained after various thermal treatments of the same duration (16 h) to the corresponding colorless glass treated at 450 °C and to the base glass. The signal of the colorless glass Sb1Au0.1-450 is clearly shifted towards the low fields according to the base glass. This is associated to a slight decrease of the T_g from 546 °C for the base glass to 538 °C for the colorless. The spectrum calculation shows a consistent increase of the Q^2 part (Table 1). The colored glass Sb1Au0.1-590 offers a slightly modified signal with a shift

towards the lower frequencies according to the corresponding colorless glass. This tendency is verified with the glass annealed at 650 °C. The spectra calculation highlights a decrease of the Q^2 specie intensity with the annealing temperature increase. A decrease of the T_g is then observed.

To evaluate the network change with temperature, a further study has been performed on glasses Sb2Au0 without gold and treated in the same conditions (Fig. 4b). We observe a very slight change of the spectra in the temperature range 450–650 °C and an increase of T_g with the temperature annealing. The network polymerization observed in glasses with gold is then relative to the reducing and nanoparticles crystallization processes. The comparison of the spectra for the glasses Sb1Au0.1-450 and Sb2Au0-450 treated at the same temperature shows surprisingly a larger polymerization degree for the second glass with higher antimony content and a lower T_g . This observation shows the change of antimony structural part in these two glasses consequently to the oxidizing state.

Fig. 2 TEM patterns of a colored glass (0.4 wt% AuCl) treated at 590 °C for 3 h 30 min. **a** Bright field mode image showing the presence of nanoparticles. The electron diffraction pattern is embedded. **b** Corresponding dark field mode image showing the crystallinity of the nanoparticles

Fig. 3 ^{29}Si MAS NMR spectrum for the base glass calculation from three Q^n species

A similar approach has been driven by ^{23}Na MAS NMR. The resonance is observed towards 4 ppm that is an usual value for the sodium acting as modifier network cation [12]. The spectra comparison shows (Fig. 5) a shift towards the low fields for the line corresponding to the colorless glass Sb1Au0.1-450 according to the base glass. According to Stebbins and collaborators [13, 14], a shift of ^{23}Na line towards the higher frequencies indicates that the mean bond length Na^+-O is reduced, so Na^+ coordination is also lower and then the part of NBO in the Na^+ neighboring increases. A silicate network depolymerization is then consistent with this ^{23}Na line shift. For the colored glass Sb1Au0.1-590, Fig. 5 shows that the signal is on the contrary slightly shifted towards the lower chemical shifts (around 0.5 ppm). This tendency is confirmed by the glass Sb1Au0.1-650. The thermal treatments could then induce a noticeable decrease of the NBO part in agreement with the

conclusions concerning ^{29}Si spectra. To separate the effect of the temperature and the effect of nanoparticles crystallization, the glasses series without gold (Sb2Au0) have also been studied by ^{23}Na NMR. Here, the spectra are undistinguishable for all thermal treatments. So, we can conclude that the nucleation and growth process for gold nanoparticles induces a slight network polymerization.

The study of chemical durability of glasses has been carried out from leaching tests comparing a non-colored glass (NCG) Sb1Au0.1-450 and a colored Sb2Au0.2-550. The monitoring of leachates pH during time (Table 2) shows an increase relatively similar for the both glasses, independently of the composition differences. This rise indicates the ion-exchange reactions in which modifier cations are replaced by protons and released of the matrix. The pH values of around 10 obtained at the end of the experiment are favorable to hydrolysis phenomenon [15].

Table 1 NMR parameters: chemical shift δ (ppm), width $\Delta\delta$ (ppm), and intensity A (%) of the lines deduced from ^{29}Si NMR spectra calculation and glass transition temperatures T_g ($^{\circ}\text{C}$)

Glass	T_g ($^{\circ}\text{C}$)	Q^4 δ (ppm)/ $\Delta\delta$ (ppm)/ A (%)	Q^3 δ (ppm)/ $\Delta\delta$ (ppm)/ A (%)	Q^2 δ (ppm)/ $\Delta\delta$ (ppm)/ A (%)
Base glass-/	546	-101.7/12.5/16	-90.8/11.4/78	-83.1/11.0/5
Sb1Au0.1-450 (blank)	538	-100.2/12.0/14	-89.8/10.3/71	-82.2/10.7/15
Sb1Au0.1-590 (red)	531	-100.1/12.8/17	-90.0/11.0/71	-82.0/11.0/12
Sb1Au0.1-650 (blue)	527	-101.1/12.5/17	-89.8/11.4/77	-79.5/9.8/6
Sb2Au0-/	539	-101.4/13.5/20	-90.2/11.4/74	-80.9/9.8/6
Sb2Au0-450	529	-100.3/13.5/17	-89.7/11.5/77	-80.0/10.0/6
Sb2Au0-590	536	-100.7/12.3/15	-89.9/11.5/77	-79.7/11.0/8
Sb2Au0-650	540	-101.0/13.0/15	-89.9/11.5/76	-80.2/10.5/9

Fig. 4 ^{29}Si MAS NMR spectra for **a** base glass compared to a colorless and two colored glasses Sb1Au0.1, respectively, treated at 450, 590, and 650 °C. **b** Glasses without gold nonannealed and treated at 450, 590, and 650 °C

The presence here of large cations can improve the network alteration because they leave behind larger voids providing larger opening into which water can diffuse. According to the calculations of normalized mass losses thanks to ICP-AES measurements, the modifiers cations are strongly released in the solution, following the order $\text{Ca} > \text{Sb} > \text{Na}$ at the beginning (Fig. 6, Table 2). For all cations, the dissolution rate tends to be reduced with leaching time to a lesser extent for sodium according to its strong diffusion ability. Gold is very few released in particular in colored glasses that can be associated to the nanoparticles

presence. We observe also a slight decreasing of mass loss for sodium and calcium cations in colored glass compared to colorless, but the normalized mass losses behavior for calcium is complex with a decrease, especially in the case of the colored glass and a slow down followed by a releasing resumption in the colorless glass. The leached glasses' surface has been analyzed by ESEM. An alteration film (a few microns depth) commonly named "gel" is formed in the two cases on large areas (Fig. 7b) and regions with some crystals in spherules have also been observed for the NCG glass

Fig. 5 ^{23}Na MAS NMR spectra for base glass compared to a colorless glass (450 °C), a red colored glass treated at 590 °C, and a blue glass (650 °C)

(Fig. 7a). The qualitative mean gel composition has been analyzed by EDX:

CG : 85 mol.% SiO_2 –13 %mol.CaO–2 mol.% Na_2O
 NCG : 83 mol.% SiO_2 –16 %mol.CaO–1 mol.% Na_2O

The gel composition is strongly depleted in sodium according to the glass composition in agreement with its “tracer element” nature that is little retained in the condensed products [16]. In another part, the gel layer is slightly enriched in calcium in the NCG sample that can be due to the presence of crystallites enriched in calcium. Then, the gel formation can explain the reduction of cations releasing rate with time, according to its diffusion barrier role and retention properties [17]. The decrease of the calcium mass loss for the colored glass implies some condensation or precipitation of hydrolyzed elements phenomena. The crystallization observed for

the non-colored glass can explain the dissolution resumption in the case of calcium for the colorless glass. Some authors have shown the important influence of pH in the basic range on the crystallization phenomena and the reduction of the protective properties of the gel that can be induced [16]. This difference of behavior between the two glasses could result in the structure change involves by the growth of gold nanoparticles and highlighted by the NMR structural study. Angeli and coworkers have shown how the glass structure and composition influence the gel properties especially in basic media [18].

UV visible measurements acquired in transmission mode (Fig. 8) clearly show the typical plasmon resonance of gold nanoparticles located around 600 nm with an increase of the maximum of the absorption with the increasing temperature until 600 °C (Fig. 9b). The annealed sample at 650 °C shows a drastically move of the resonance towards the higher wavelengths and a decrease of the absorption. Coloration evolution of the annealed samples (Fig. 1) leads to purple coloration with a color expansion when increasing temperature until a blue coloration for the sample annealed at 650 °C. These hue changes are correlated to the evolution of the SPR position (Fig. 9a). For a better comprehension of the UV visible measurements evolution, we have developed Drude and Mie Modelization.

The Drude model allows from known experimental data such as those of “Palik” to consider the interband electronic transitions and intraband for the determination of the contribution of the electrons participating in the absorption effect due to the surface plasmon resonance [19]. The dielectric function $\varepsilon(\omega)$ of the noble metal can be written as:

$$\varepsilon = \varepsilon_1 + i\varepsilon_2$$

Table 2 Normalized mass losses calculated from ICP-AES for static leaching experiments on colored glass Sb2Au0.2-550 (CG) and non-colored glass Sb1Au0.1-450 (NCG) in g/m^2 versus time of leaching in hours and pH measurements of leachates during leaching test

Glass	Time (h)	pH	Si	Ca	Na	Sb	Au
CG	0	7.6	0.03	6.4	1.0	0.3	0
	24	8.8	3.46	17.8	6.4	10.7	0.4
	576	9.9	25.55	8.8	46.6	38.9	1.4
	1056	9.8	26.83	4.1	77	51.8	0.5
NCG	0	7.6	0.03	6.4	1.0	0.3	0
	24	8.8	3.76	28.2	9.5	14.5	4.7
	576	10.5	22.75	28.0	55.5	37.9	1.9
	1056	10.2	30.84	64	84	50.6	1.8

Fig. 6 Comparison of the normalized mass losses during leaching for cations in a colored glass (CG) Sb2Au0.2-550 and colorless glass (NCG) Sb1Au0.1-450

Where ε_1 and ε_2 are, respectively, the real and imaginary parts of the dielectric function. In the noble metals, the contributions of s and d electrons of $\varepsilon(\omega)$ (respectively the band and interband contributions) can be separated:

$$\varepsilon(\omega) = 1 + \chi^s(\omega) + \chi^d(\omega)$$

With:

$$\varepsilon^s(\omega) = 1 + \chi^s(\omega)$$

$$\varepsilon^d(\omega) = 1 + \chi^d(\omega)$$

$$\varepsilon(\omega) = \varepsilon^s(\omega) - 1 + \varepsilon^d(\omega)$$

Where $\chi^s(\omega)$ is the Drude part of the dielectric susceptibility and $\chi^d(\omega)$ the interband part (electrons). Consequently, the dielectric function is given by:

$$\varepsilon^s(\omega) = 1 - \frac{\omega_p^2}{\omega[\omega + i\Gamma(R)]}$$

In many theoretical models using Mie theory, a size effect is introduced by the radius parameter R of a particle in the dielectric function associated with conduction electrons:

$$\Gamma(R) = \Gamma(\infty) + \frac{Av_F}{R}$$

Where $\Gamma(\infty)$ (collision coefficient) and v_F (Fermi velocity) are given in Table 3 for different noble metals, and $A=1$ is an arbitrary parameter depending on the model. ω_p is the bulk plasmon frequency Drude given by:

$$\omega_p = \sqrt{\frac{ne^2}{m_e\varepsilon_0}}$$

Fig. 7 ESEM micrographs obtained in BSE mode of leached glass surface. **a** Non-colored glass. **b** Colored glass. As comparison, **c** ESEM micrograph of the non-colored glass where the alteration film has been removed

Fig. 8 Extinction spectra versus wavelength according to annealing temperature (T) for Sb1Au0.1-T glasses

Where n is the electron density of the s electrons, e the elementary electric charge, m_e their effective mass, and ε_0 the vacuum permittivity.

$$\frac{1}{n} = \frac{4\pi r_s^3}{3}$$

Where r_s is the Wigner-Seitz radius (WS). It remains to include the interband contribution from data “Palik.” Knowing the imaginary part of the interband contribution and taking into account the interband threshold (minimum energy for which the transition occurs more), the determination of the interband contribution is made by the Kramers-Kronig relationship with P representing the main part of the integral. The integration is performed to values up to 9,000 eV.

$$\varepsilon_{re}^d(\omega) = 1 + \frac{2}{\pi} P \int_{\omega_{IB}}^{\infty} \frac{\Omega \varepsilon_{im}^d(\Omega)}{\Omega^2 - \omega^2} d\Omega$$

We use the “focus” software developed by Meneses [20] including interpolation type Fritsch-Carlson in order to rebuild the real part. Necessary relations are:

Fig. 9 **a** and **b** SPR position evolution and maximum extinction value according to annealing temperature

Table 3 Main characteristics of gold

Metal	Au
Electronic structure	[Xe]5d ¹⁰ 6s ¹
Interband Value (eV)	1.85
r_s (WS) u.a.	3.01
m_e u.a.	1.01
$\hbar\omega_p$ (eV)	8.98
$\Gamma(\infty)$ (eV)	0.14
v_F (10 ⁸ cm/s)	1.38

$$\varepsilon_1(\omega) = \varepsilon_1^{(d)}(\omega) - \frac{\omega_p^2}{\omega^2 + \Gamma^2}$$

$$\varepsilon_2(\omega) = \varepsilon_2^{(d)}(\omega) + \frac{\Gamma\omega_p^2}{\omega(\omega^2 + \Gamma^2)}$$

According to Mie’s theory [21], we consider a metal sphere of radius R exposed to an external electromagnetic field of wavelength λ . If the radius is in the nanometer range, we use the quasi-static approach and the effects of delays can be neglected ($R/\lambda \ll 1$). Thus, in the dipole approximation, the absorption cross-section of a metal sphere embedded in a matrix is written:

$$C_{abs}(\omega) = \frac{\omega}{c\varepsilon_0\varepsilon_m^{1/2}} \text{Im}[\alpha(\omega)]$$

Where $\alpha(\omega)$ is the dynamic polarizability of the particle, c is the speed of light, and ε_m is the dielectric function of the matrix. In the case of a homogeneous sphere of dielectric function ε , $\alpha(\omega)$ is written:

$$\alpha(\omega) = 3V\varepsilon_0\varepsilon_m \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}$$

$$\text{With } V = \frac{4\pi}{3}R^3$$

The contribution of the diffusion is given by (in the case of a spherical particle):

$$C_{diff}(\omega) = \frac{3V^2\omega^4}{2\pi c^4} \varepsilon_m^2 \left(\frac{(\varepsilon_1 - \varepsilon_m)^2 + \varepsilon_2^2}{(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^2} \right)$$

The sum of absorption and diffusion cross-section corresponds to the total extinction with:

$$C_{abs} + C_{diff} = C_{ext}$$

As seen in Fig. 10 which gives absorption and diffusion cross-section according to increasing particles size for a refractive medium index of 1.5, we can notice that absorption dominates for particles under 80 nm and diffusion cross-section becomes effective above this size value. We can then conclude from the TEM observations which give a particle estimation between 15 to 35 nm, that absorption is in our case the dominant phenomenon for these temperature ranges below 600 °C. To conclude, according to the modelization and coupled to the UV visible and TEM measurements, the increase of the absorption at the SPR with the annealing temperature is attributed to nanoparticles growth certainly governed by an Ostwald process.

For the particular case of the annealed sample at 650 °C, we observe a broadening of the absorption curve and a red shift of the SPR. Two hypotheses can be proposed to explain this result. The first one comes from the TEM observations which evidence some non-spherical particles leading to a nonhomogeneous field over the extension of the particle and consequently a decay of the SPR. Moreover, we observe for this sample a drastic increase in the FWHM of the transmission curve which is linked to a broadening of the size particles distribution.

The second hypothesis is illustrated in Fig. 11 where the absorption cross-section is plotted for an increasing refractive medium index and a particle size of 8 nm where absorption dominates and lead to a red shift of the SPR. Infrared measurements in reflectivity mode have been driven according to an annealing temperature of the Sb1Au0.1 glass sample from 440 to 1,150 K and for wavenumber from 150 to 2,750 cm⁻¹. These measurements are plotted in Fig. 12 according to the annealing temperature and illustrate the increase of the medium refractive index which is visible above 2,500 cm⁻¹. However, these two associated hypothesis can explain the behavior of the 650 °C annealed sample.

Gold is known for its low solubility in glasses. Experiments by ¹⁹⁷Au Mössbauer have proved the Au⁺ state of gold in the quenched colorless glass and the presence of nondissolved metallic gold at this stage [3]. Complementary experiments by ¹¹⁹Sn Mössbauer spectroscopy are consistent with mainly Sn²⁺ component in the quenched colorless glass and Sn⁴⁺ in

the red glass [3]. Schreiber and collaborators have established a relative electromotive force series (E' values) of redox couples in soda–lime–silicate melts at 1,400 °C through an indirect procedure by experimentally measuring the equilibrium redox ratios of the individual elements as a function of the imposed oxygen fugacity. E' is deduced of the equation $\log(X) = (n/4)(-\log f_{O_2}) + E'$, where X is the ratio of the concentrations of the element in the reduced state to the oxidized state, n is the number of electrons transferred in the redox couple, and f_{O₂} is the imposed oxygen fugacity [22]. Thanks to this method the authors proposed the following values (±0.3 units) for E': Au³⁺/Au⁰ > 3.6, Sn⁴⁺/Sn²⁺: -4.9 (estimation), Sb⁵⁺/Sb³⁺: +0.3 [23]. Otherwise, they show the good correlation between the relative electromotive force series established in the melt and the series of standard reduction potentials in aqueous solution. No value has been proposed for the redox couple Au⁺/Au⁰, but considering the correspondence between the two series (melt/aqueous solution), we can also suppose a positive value for this couple, superior or close to the estimated value given for the couple Au³⁺/Au⁰ by Schreiber et al.

Stannous and antimony oxides are then convenient reducing agents with a stronger power for Sn²⁺ compared to Sb³⁺ following the probable redox equations:

However, considering the gold nanoparticles redox potential, it is now well established that the values vary with the nuclearity (atoms number), and that clusters (a few atoms) present a redox potential much more negative than the bulk metal, but this value increases with the nanoparticle formation [24]. Then, the redox mechanism implied during the nucleation and growth process is complex and certainly requires to consider a row of redox couples Au⁺/Au_n⁰ according to the gold aggregates size (n).

Tin has been found to speed the formation of the metallic nanoparticles by a catalyst role during annealing and an alloy could be formed between tin and gold [3]. In this case, highly dispersed tin seems to provide the presence of many condensation nuclei and the low total amount of gold will then prevent the formation of large gold particles (few nanometers). In the same way, nanocrystalline phases Cu_ySb_{2-x}(O, OH)₆₋₇ have been highlighted with copper and Cu₂O phases in ruby colored cuprous oxide glasses [25]. In our case, no alloy has been detected between gold and antimony and the stronger releasing of Sb compared to Au in our leaching tests favors the hypothesis of alloy absence. However, antimony is most likely involved in the gold nucleation. The TEM observations of two nanoparticles size populations are in agreement with an Ostwald ripening mechanism for particles growth. The color appearance is easier to control using antimony as reducing agent, and colorless glass can be prepared in this case for

Fig. 10 Theoretical absorption and diffusion cross-section for gold nanoparticles between 1 to 80 nm

annealing up to 450–500 °C. Local treatments by laser or in a thermal gradient furnace could then be applied for decorative functions or specific marking. First promising results have been obtained by CO₂ laser treatment, with local coloration without additional annealing.

As highlighted by the optical measurements (Fig. 9), the coloration process is largely favored by the temperature because it contributes to the species diffusion but also because in

this temperature range close or upper the T_g, it contributes to change the network, slightly reducing the rigidity. Then, small particles (15 nm) are observed with treatments up to T_g, but nonspherical larger particles have been obtained with thermal

Fig. 11 Absorption cross-section for increasing the value of the medium refractive index from 1.3 to 1.8

Fig. 12 Infrared reflectivity measurement of the Sb1Au0.1 glass according to the annealing temperature

treatment above T_g (particles of 35 nm for the treatment 110 °C above T_g). These larger particles are certainly responsible of the SPR red shift promote by a nonconstant electric field over his axis associated to refractive index change due to glass structural change for treatment above T_g . This medium refractive index increases versus the glass temperature has been evidenced by in situ Fourier transform infrared spectroscopy measurements in reflectivity mode.

NMR results show clearly a silicon network change during coloration process with a polymerization tendency. Taking into account the very low gold content, we suppose that these observations result essentially of antimony part. In crystals, Sb_2O_3 exists in a cubic form (senarmontite) and an orthorhombic form (valentinite—more stable form at high temperature) with SbO_3 trigonal pyramids forming chains in valentinite [26]. The orthorhombic cervantite Sb_2O_4 crystals incorporate Sb^{3+} in $Sb^{3+}O_4$ pseudo trigonal bipyramids and Sb^{5+} in $Sb^{5+}O_6$ octahedra [27]. Sb_2O_5 antimony oxide is found in monoclinic structure consisting exclusively in $Sb^{5+}O_6$ octahedra. In glasses, there are few studies concerning the structural part of antimony, but authors are often agree to consider the former role of Sb^{3+} according to its field strength. The studies on amorphous systems Sb_2O_3 , $(1-x) B_2O_3-x Sb_2O_3$ and $(1-x) SiO_2-x Sb_2O_3$ conclude to a former role of antimony with the presence of mainly $Sb^{3+}O_3$ trigonal pyramids (as in valentinite) but also in a low amount of higher coordinated antimony $Sb^{3+}O_4$ pseudo trigonal bipyramid units and $Sb^{5+}O_6$ octahedra [28]. The Mössbauer spectroscopy has proved the Sb^{5+} presence in these glasses in low amount [29]. The structural part of SbO_6 octahedra is not clear, but the two structures SbO_4 and SbO_6 could be paired and serve to connect the network. Also, Wood et al. show the increase of silicon network polymerization when low amounts of antimony are added in an alumino borosilicate glass [30].

During coloration process, Sb^{3+} is expected to oxidize in Sb^{5+} and the annealing treatments lead to the gold nanoparticles nucleation and growth, inducing slight changes in linkages and atomic arrangements. Here, the network polymerization change could be connected to the relative amount of $Sb^{3+}O_4$ and $Sb^{5+}O_6$ units. NMR analyses for ^{29}Si and ^{23}Na provide these changes attesting a slight polymerization development with a decrease of Q^2 units after treatments at higher temperature, but ^{23}Na resonance shift could also evidence of a charge balance part of sodium in the antimony environment. Mössbauer spectroscopy studies are in progress to attest and quantify the Sb^{5+} valence.

Conclusion

Soda lime silicate glasses have been used as a matrix for chemical reduction of gold and nanoparticles crystallization to obtain pink to purple “ruby” glasses type. The reducing

chemical agent choice and thermal treatments allow a good control of the coloration appearance and consequently to possible selective volume and surface coloration with local laser heating. The mechanisms have been characterized by complementary analyses. Optical UV-visible analyses and Drude and Mie modelization performed show the distinct part for absorption and diffusion according to the particle size. Absorption is dominant and increase in the range size 15 to 35 nm obtained with annealing carried out between 590 and 650 °C and correlated to Ostwald mechanisms growth. Larger and less spherical particles obtained with treatments well above T_g are associated to the red shift of the SPR with a typical blue coloration, larger size distribution, and change in the refractive medium index evidenced by infrared spectroscopy measurements. The structure analysis by NMR spectroscopy gives indirect information of gold nanoparticles formation thanks to the silicon network changes. Coloration induces a slight increasing of the network polymerization. The signal is very sensitive to antimony presence that is suspected to adopt a tetrahedrally and octahedrally coordinated environment with oxygen. The chemical durability is also slightly increased after coloration with a very low releasing of gold for the colored glass.

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