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Journal of the European Ceramic Society 25 (2005) 711–718

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Superficial colouring of lead crystal glass by sol–gel coatings

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Received 15 November 2003; received in revised form 12 February 2004; accepted 25 February 2004

Abstract

Sol–gel silver containing coatings have been prepared and applied upon lead crystal glass. Both undoped and arsenic oxide-doped lead crystal glasses have been used as substrates. Arsenic oxide was introduced with different percentages as a thermoreducing agent, with the aim to favour silver ions reduction and aggregation to form nanosized colloids. Such silver colloids yielded a superficial yellow ruby colouring, due to their known surface plasmon resonance band in the visible range (∼420 nm). The influence of the experimental parameters to obtain yellow ruby colouring (percentage of arsenic oxide in the lead crystal base glass; silver content of the coatings precursor sol; coating thickness; atmosphere, temperature and time for thermal densification; etc.) were investigated. Samples were studied by transmission electron microscopy and optical spectroscopy (absorption and transmission). Colour co-ordinates, dominant wavelength and colour purity percentage were calculated from the corresponding transmission visible spectra. The role of the thermoreducing dopant (arsenic oxide) is essential for obtaining superficial yellow colouring. The higher the percentage of arsenic oxide, the higher is the intensity of the yellow colouring. When the silver content of sols increased, the same tendency is observed. Thermal densification of the sol–gel coatings have to be carried out under oxidising atmosphere, since heat-treatments performed under reducing atmosphere yielded grey-brownish colouring, due to reduction of the lead from the base glass. Optimum conditions for obtaining superficial yellow ruby colouring on lead crystal glass were selected.

Keywords: Sol–gel processes; Electron microscopy; Colour; Optical properties; Glass; Coatings

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1. Introduction

Lead crystal glass with PbO content in the 24–30 wt.% range are commonly used for production of high quality tableware and decorative objects. However, the fabrication of bulk coloured lead crystal glass is less frequent. Colouring of such tableware and decorative articles is performed superficially by both application of a coloured glassy coat (inlayed or "plaqué" glasses)[1] and incorporating small metallic colloids by ion-exchange.[2,3] These two procedures are especially advised when ruby colouring (red or yellow) is the final objective. Particularly, the obtaining of pure red and yellow colourings is difficult to attain since noble metals as copper, silver and gold have to be incorporated in a very controlled conditions of metal concentration, kind of precursors, temperature and time for ion-exchange and thermal development, etc. Since inlayed coloured lead glasses are produced by applying a common glass coat on the lead crystal glass piece, the resulting global quality of such piece is relatively lower than that of lead glasses coloured by ion-exchange. In this latter case the permanent coloured layer is formed in the lead glass bulk, just in the first tens of micrometers from the free surface. Both artistic and marketing reasons aimed the production of high quality coloured lead crystal glass, especially for yellow and red ruby superficial colouring, by means of a reproducible and low investment procedure. In this paper the authors try to give an answer by using the sol–gel technology.

Sol–gel coatings are widely used for different purposes, especially those related with optical, semiconductor, protective and sensing applications.[4–7] This kind of coatings show several advantages: low-temperature processing;[8] good adherence to different substrates (metals, alloys, polymers, ceramics, composites, glasses, etc.); several application procedures (dipping, spinning or spraying) at atmospheric pressure; possibility to prepare multilayered coatings;[9] low-cost equipment, etc.

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doi:10.1016/j.jeurceramsoc.2004.02.023

During the last years the incorporation of noble metals particles (especially silver and gold)[10] in sol–gel matrices has been developed with the aim to improve some optical properties, for instance: third order non-linear susceptibility, very intense coloured filters, photochromic and photoluminescent materials, etc. The preparation of noble metals based ruby glasses by the sol–gel method has been a scientific and technical objective as well.[11] In fact some physical and chemical aspects about the incorporation of silver and gold in monolithic sol–gel silica matrices are known.[12,13] Moreover, thin coatings doped with copper, silver and gold upon common soda lime glass have been produced and characterised.[14,15] In this latter case, it has been demonstrated that the initially introduced Au^{3+}-ions are quickly reduced to gold atoms. Then they aggregated to form nanoscaled colloids.[12,16] This kind of nanoparticles is responsible for the characteristic gold ruby colouring (purple and deep pink). As far as for the silver role concerns, it is introduced into the sols as Ag^{+}-ions and after the coating application and thermal densification they are reduced to Ag^{0}, depending on the experimental procedure followed (redox properties of the other compounds in the sol and atmosphere during the heat-treatment, mainly).[17] Further formation of silver nanocolloids occurs, which are the responsible for the characteristic yellow colouring in silver ruby glasses.[18]

The silver ions reduction in common glasses takes place, thanks to the presence of thermoreducing agents, which could be present as glass impurities or as an intentionally added dopant. Usually in common soda lime silicate glasses the residual content of iron oxide is sufficient to reduce the silver ions at the ion-exchange temperature (350–550 °C). Thus, once the silver ions are reduced, they aggregate quickly to form the colloids responsible for the yellow ruby colouring. The open question is: what will be the behaviour of other glasses different from common soda lime silicate glasses in whose composition very low content of impurities is expected? For instance, in sodium borosilicate glasses with impurities content lower than that of common glasses, the colouring due to silver incorporation is not a clear bright yellow but pink-beige. Therefore, the impurities level plays an important role in the reduction and aggregation of silver colloids to display a yellow ruby colouring. In this research it is intended to clarify the relation between the presence of adequate impurities or dopants and the generation of the mentioned colouring. As it was demonstrated,[2] the obtaining of ruby colouring in lead crystal glass (with maximum content of Fe_2O_3 below 0.01 wt.%) by means of silver ions/colloids, is subjected to the presence of some kind of thermoreducing agent in the glass network.

The aim of the present work deals with the study of the potential benefits derived from the application of silver doped sol–gel coatings upon lead crystal glass substrates to obtain superficial yellow ruby colouring. The research performed was planned with the final objective to explore the industrial advantages and/or improvements that could be attained in comparison with other traditional or recent innovative methods to reach such superficial colouring. Concrete objectives were the determination of chemical and physical parameters involved in the formulation and preparation of adequate sols, their deposition upon lead crystal glass substrates and the experimental conditions for densification treatments. Likewise, microstructural and optical characterisation of the samples was undertaken in order to select the optimum parameters that allow the control of the overall procedure in an industrial production environment.

2. Experimental

2.1. Preparation of the lead glass substrates

As colourless substrate, lead crystal glass from the current production at the Fundación Centro Nacional del Vidrio (Royal Glass Manufacture) has been used. Such a glass fits with specifications of the Spanish standard UNE 43-603-79.[19] Bearing in mind the results obtained in recent works on superficial ruby colouring with this base lead crystal glass by ion-exchange,[2] several doped lead glasses were prepared. Arsenic oxide in different amounts (1, 3 and 5 wt.%) was used as a thermoreducing dopant, since its presence can affect redox stability of Ag^{+}-ions incorporated to the sol–gel coating and their further colloidal aggregation. Doped glasses were melted in an electric furnace at about 1500 °C and then they were casted in brass moulds to obtain ingots 50 mm × 30 mm × 12 mm sized. Glass samples were annealed at 485 °C to avoid residual stresses. Slabs (2 mm thickness) were obtained from the ingots and were polished up to total reflection by both sides. Such a kind of lead glass samples, as well as the undoped lead crystal glass as obtained at the Fundación Centro Nacional del Vidrio, was used as substrates for application of sol–gel coatings.

2.2. Sols formulation and preparation

Silica-based sols containing variable amounts of silver (in the 0.1–5 mol% range) were prepared starting from the following precursors: tetraethoxysilane ($Si(OC_2H_5)_4$, TEOS), anhydrous methanol (MeOH), nitric acid (0.5 M HNO_3), oxygen peroxide (110 vol.% H_2O_2) and silver nitrate ($AgNO_3$). Such precursors were selected bearing in mind their compatibility and adequate redox properties, with the aim to preserve the oxidation state of silver ions in the sol, i.e. to avoid a much as possible sol ingredients with reducing properties, which could prematurely reduce the silver ions. All reagents (analytical grade) were used as received without any further purification. Molar ratio TEOS/MeOH/HNO_3/H_2O_2 was 1/14/5/1 for all the coatings prepared. The sols elaboration was as follows: the TEOS amount was firstly diluted with MeOH and then pre-hydrolysed by adding the aqueous solution of HNO_3. After 15 min stirring, H_2O_2 was added to preserve silver as Ag^{+}-ions, avoiding reduction and precipitation as metallic silver that could not be incorporated to the sol–gel silica glassy network. During preparation, light and especially ultraviolet light were prevented to discard photochemical reduction of silver ions. Finally, $AgNO_3$ was added and the stirring was maintained during 20 min to accomplish the $AgNO_3$ dissolution and hydrolysis, as well as the homogenisation of all the organic and inorganic components.

2.3. Application of coatings and treatments

Coatings were applied upon all the lead glass substrates by dipping them into the corresponding sols. A home-made dip-coater was used at drawing rates in the 0.68–5.54 $mm\,s^{-1}$ range.

With the aim to investigate the influence of the redox conditions on the reduction of silver ions in the coatings, two kinds of thermal treatment were carried out: under oxidising atmosphere (air) and under reducing atmosphere (N_2–H_2 mixture, 90–10 vol.%). Temperature was ranging between 450 and 525 °C, because of the thermal limit imposed by the lead crystal base glass, whose transition temperature $T_g = 449.6\,°C$ was determined by dilatometry.[20] Stabilisation time at each treatment temperature was varied between 15 and 60 min. Table 1 summarises the experimental parameters for the tests performed. Coatings thickness was evaluated from the reflection visible spectra of samples by means of the interference fringe method.[21] The measured thicknesses of coatings were: 380, 423, 430 and 445 nm, for drawing rates of 0.68, 2.36, 3.35 and 5.54 $mm\,s^{-1}$, respectively.

2.4. Characterisation techniques

Absorbance and transmission optical spectra of samples were recorded with a Perkin-Elmer model Lambda 19 spectrophotometer in the 320–800 nm range. Colour parameters of samples were calculated from the corresponding transmission spectra: colour co-ordinates, position in the chromaticity chart, dominant or complementary wavelength and colour purity percentage.[22]

After aggregation of silver atoms, the resulting nanosized colloids were directly observed by transmission electron microscopy (TEM) by using a Philips EM 300 and a Hitachi 7000 microscopes. Simple replicas from the samples surfaces were obtained by conventional carbon deposits upon the surface of the coatings previously attacked with diluted HF during 15 s.

Table 1
Experimental conditions for preparation and thermal densification of silver containing sol–gel coatings upon lead crystal glass

Thermal densification				
Temperature (°C)	450	480	500	
Time (min)	30	45	60	
Coatings preparation				
Silver content (mol%)	0.1	1	5	
Drawing rate ($mm\,s^{-1}$)	0.68	2.36	3.35	5.54

All possible combinations of variables were tested.

3. Results and discussion

3.1. Transmission electron microscopy

The influence of the lead crystal glass dopant concentration (arsenic oxide) can be observed in Fig. 1. The silver colloids size (∼20–40 nm) directly increased with the percentage of arsenic oxide in the base glass. Lead crystal glass doped with 3 wt.% As_2O_5 showed a very clear background with very few colloids. These appeared aggregated and, in general, they are scarce and very small. In turns, in the glass doped with 5 wt.% As_2O_5, silver colloids are well-distributed, both isolated and aggregated with rounded shape.

Silver amount in the sol is an important parameter that can affect the colloids formation. Fig. 2 show the TEM images from samples coated with sols containing 0.1 and 5 mol% of silver (compare with the sample containing 3 mol% silver from Fig. 1b). The coating with the lowest silver content (Fig. 2a) showed very small isolated col-

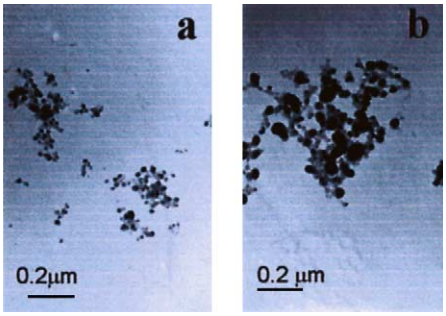

Fig. 1. TEM micrographs of lead crystal base glass doped with: (a) 3 wt.% As_2O_5 and (b) 5 wt.% As_2O_5. Coating parameters: composition $3Ag{\cdot}97SiO_2$ (mol%), drawing rate 2.36 $mm\,s^{-1}$, densification at 500 °C for 60 min.

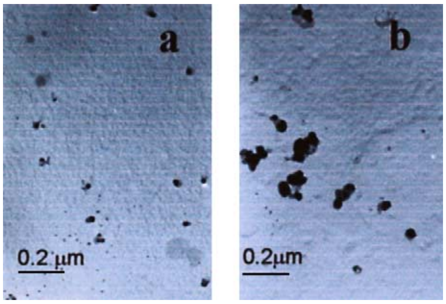

Fig. 2. TEM micrographs of lead crystal base glass doped with 5 wt.% As_2O_5, coated with different sols: (a) $0.1Ag{\cdot}99.9SiO_2$ and (b) $5Ag{\cdot}95SiO_2$ (mol%). Coating parameters: drawing rate 2.36 $mm\,s^{-1}$, densification at 500 °C for 60 min.

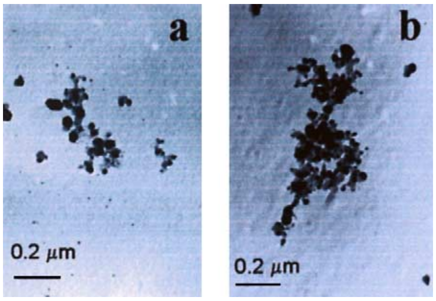

Fig. 3. TEM micrographs of lead crystal base glass doped with 5 wt.% As_2O_5, coated and densified under oxidising atmosphere at different temperatures: (a) 470 °C and (b) 525 °C. Coatings parameters: composition $3Ag{\cdot}97SiO_2$ (mol%), drawing rate $2.36\,mm\,s^{-1}$, densification time 60 min.

loids (∼20 nm), while for higher silver content the colloids appeared bigger (∼80 nm) and interconnected, especially in the sample coated with the 3 mol% silver sol (Fig. 1b).

The coating densification temperature determines the colour reached by the sample. In Fig. 3 several TEM images of samples coated with the $3Ag{\cdot}97SiO_2$ (mol%) sol and treated at different temperatures are shown (compare with the sample treated at 500 °C from Fig. 1b). For the lowest thermal densification (470 °C, Fig. 3a) silver colloids appeared as small aggregates. When the temperature was raised up to 500 °C (see Fig. 1b), both the aggregates size (∼40–80 nm) and the interconnections increased. Finally, after the 525 °C treatment (Fig. 3b) the aggregates of colloids were more compact.

The coating thickness also affected the aggregation degree of silver colloids in such coatings. The lowest is the drawing rate during the dip-coating process, the lowest the coating thickness. Silver colloids size (∼40–100 nm) increased for the thicker coatings; while the colloids aggregation appeared more intense for the thinner coatings (compare Figs. 1b and 4).

It is also remarkable the occasional presence of crystals prints in the surface of the coatings obtained with the highest drawing rate. However, the background of the samples surface obtained with medium and low drawing rate appeared very clean. This could be attributed to the accumulation of sol in such coatings and hence of silver that, after reduction and aggregation, can precipitate as small silver crystalline nuclei.

Fig. 4. TEM micrograph of lead crystal base glass doped with 5 wt.% As_2O_5, coated at $5.54\,mm\,s^{-1}$. Coatings parameters: composition $3Ag{\cdot}97SiO_2$ (mol%), densification at 500 °C for 60 min.

The results indicated that all parameters studied influenced on both the size and the aggregation degree of the silver colloids. The size is proportional to: (i) the dopant content in the lead crystal base glass; (ii) the molar percentage of silver in the coating precursor sol; (iii) the coating densification temperature; and (iv) the drawing rate from the sol during the coating application. The colloids aggregation degree increases with the following parameters: (i) the dopant content in the lead crystal base glass; and (ii) the coating densification temperature. The increasing of silver molar percentage gives rise to more homogeneous colloids aggregation in the entire coating surface.

3.2. Optical spectroscopy

3.2.1. Samples treated under oxidising atmosphere

In the first experiment carried out, undoped lead crystal glass substrates were coated with the silver doped silica sols. The samples were thermally treated under oxidising atmosphere (air). After densification at the different temperatures, transparent and colourless samples were obtained, as was confirmed by the absence of absorption bands in the visible range of the corresponding spectra. This means that silver ions remain in the coatings and no silver metallic colloids were formed. Thus, the presence of a thermoreducing agent in the lead crystal base glass is necessary to favour the silver ions reduction and aggregation to form silver colloids, responsible for the yellow ruby colouring. This behaviour is similar to that observed for silver ion-exchanged lead crystal glass[2] and for silver ion-exchanged soda lime glass,[23] i.e. silver ions need a thermoreducing agent to be reduced, aggregated and distributed as small colloids by the glass surface to generate yellow colouring.

Such thermoreducing polyvalent ions are present in the glass with their two main oxidation states. For instance, the redox pairs Sn^{2+}/Sn^{4+}, Fe^{2+}/Fe^{3+}, As^{3+}/As^{5+}, Sb^{3+}/Sb^{5+}, etc. will be displaced to the reduced or to the oxidised state depending on the presence and redox potential of other ions (in this case, Ag^+-ions) capable to react according to Eq. (1):

$$\begin{aligned} &Ag^+ + M^{n+} \leftrightarrow Ag^0 + M^{(n+1)+} \\ &M^{n+} = Fe^{2+},\ As^{3+},\ Sb^{3+},\ Sn^{2+},\ \text{etc.} \end{aligned} \tag{1}$$

On the basis of former results[2], in the present work the redox pair As^{3+}/As^{5+} was selected as the most adequate dopant to promote and enhance the generation of silver nanoparticles.

In Fig. 5 the visible absorption spectra of three lead crystal base glasses doped with different arsenic oxide amounts and coated with silver containing silica sol are shown. As can be seen, the influence of the dopant concentration is very important: the intensity of the characteristic surface plasmon resonance band of silver colloids at about 420 nm increased as the arsenic oxide content in the base glass increased. The corresponding samples showed a typical yel-

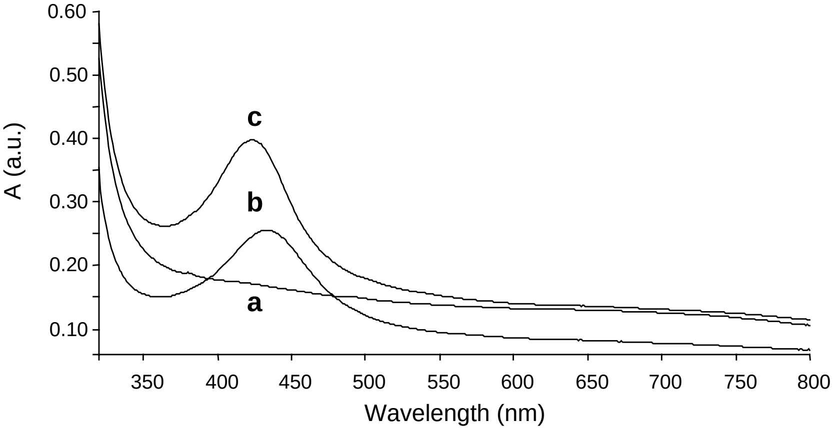

Fig. 5. Visible absorption spectra of lead crystal base glass doped with: (a) 1 wt.% As_2O_5, (b) 3 wt.% As_2O_5 and (c) 5 wt.% As_2O_5. Coatings parameters: composition $3Ag{\cdot}97SiO_2$ (mol%), drawing rate 2.36 mm s^{-1}, densification at 500 °C for 60 min.

low ruby colouring that appeared more intense for the highest dopant percentage. Since 5 wt.% As_2O_5 yielded the best result, this dopant percentage was maintained and all the other experimental parameters were varied in subsequent tests.

The influence of the coating densification temperature can be analysed in Fig. 6. The intensity of the silver colloids absorption band increased with the treatment temperature. The samples obtained after the different heat-treatments showed different yellow colouring, from a very pale yellow hue for the sample treated up to 450 °C, to a very deep yellow for the sample treated up to 525 °C. From the point of view of a visual observation, both samples densified at 500 and at 525 °C showed the same intense yellow colouring. For this reason and taking into account a further application to an industrial process in which the saving of energy is an important factor, the densification temperature of 500 °C was taken as the optimum.

Fig. 7 shows the absorption visible spectra of coated samples densified at 500 °C for different times, ranging from 15 to 60 min. The intensity of the silver colloids band increased with treatment time. Once again, the visual observation of both the 45 min and the 60 min-treated samples demonstrated that no important colouring differences are present. Therefore, due to the same reasons as for the densification temperature, the 45 min heat-treatment was selected as the most adequate.

The influence of the silver molar percentage in the coating precursor sol is shown in Fig. 8. The highest intensity of the silver colloids band corresponded to the sample coated with the 5 mol% containing sol, while the samples coated with 0.1 and 1 mol% containing sols did not show such a band and, hence, the yellow ruby colouring. According to these results, the optimum silver content in the coating precursor sol is 5 mol%, though samples coated with the 3 mol% silver containing sol showed a relative intense yellow colouring. The use of 3 or 5 mol% silver containing sols will depend on the final colour intensity required.

Finally, the coating thickness parameter was studied. Thickness was varied by changing the drawing rate during

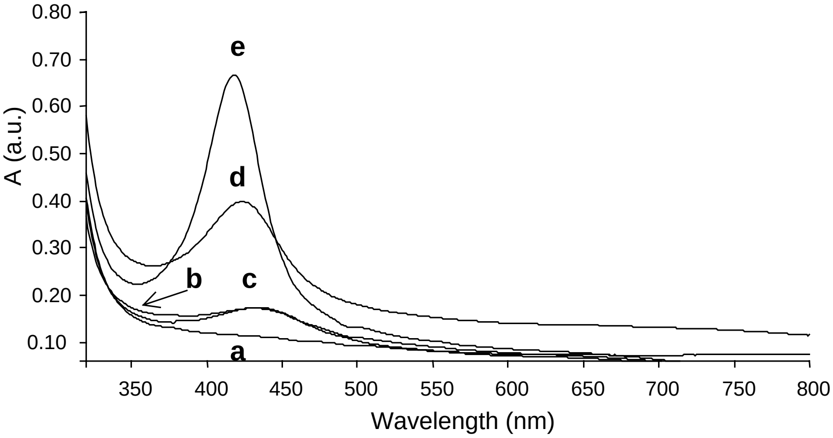

Fig. 6. Visible absorption spectra of lead crystal base glass doped with 5 wt.% As_2O_5, coated and densified under oxidising atmosphere at different temperatures: (a) 450 °C, (b) 470 °C, (c) 485 °C, (d) 500 °C and (e) 525 °C. Coatings parameters: composition $3Ag{\cdot}97SiO_2$ (mol%), drawing rate 2.36 mm s^{-1}, densification time 60 min.

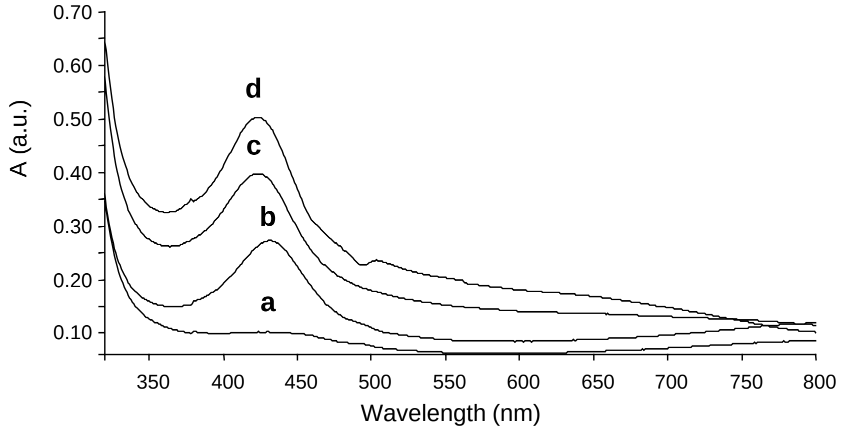

Fig. 7. Visible absorption spectra of lead crystal base glass doped with 5 wt.% As_2O_5, coated and densified for different times: (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min. Coatings parameters: composition $3Ag{\cdot}97SiO_2$ (mol%), drawing rate 2.36 mm s^{-1}, densification at 500 °C.

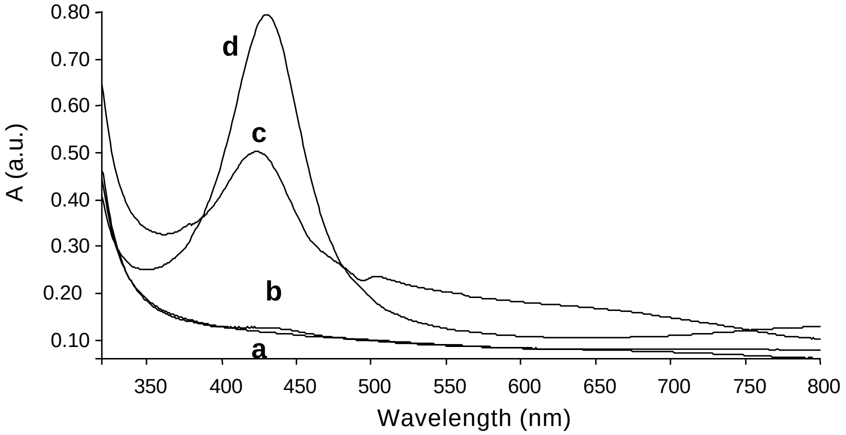

Fig. 8. Visible absorption spectra of lead crystal base glass doped with 5 wt.% As_2O_5, coated with different sols: (a) $0.1Ag{\cdot}99.9SiO_2$, (b) $1Ag{\cdot}99SiO_2$, (c) $3Ag{\cdot}97SiO_2$ and (d) $5Ag{\cdot}95SiO_2$ (mol%). Coatings parameters: drawing rate 2.36 mm s^{-1}, densification at 500 °C for 45 min.

the coatings obtaining by dipping. Fig. 9 shows the optical absorption spectra of coated samples obtained with different drawing rates. The intensity of the silver colloids band proportionally increased with the drawing rate. This confirms the empirical relationship between the coating thickness (d) and the drawing rate (v), following the expression:

$$d \approx k(v)^{2/3} \tag{2}$$

being k a constant.[24]

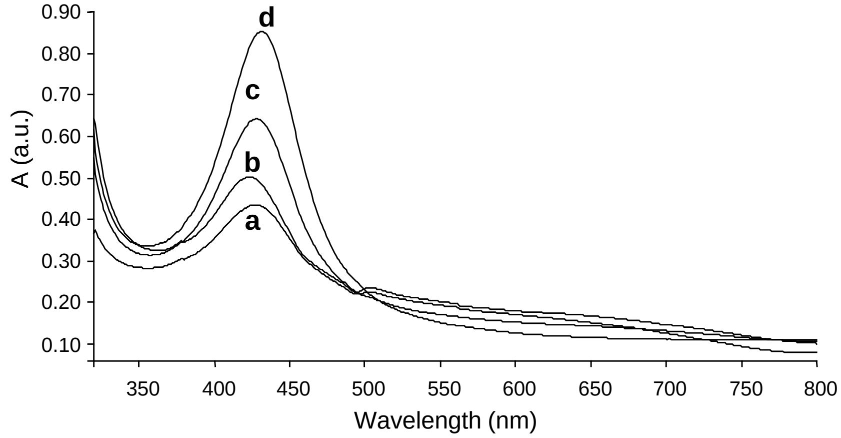

Fig. 9. Visible absorption spectra of lead crystal base glass doped with 5 wt.% As_2O_5, coated at different drawing rates: (a) 0.68 mm s^{-1}, (b) 2.36 mm s^{-1}, (c) 3.35 mm s^{-1} and (d) 5.54 mm s^{-1}. Coatings parameters: composition $3Ag{\cdot}97SiO_2$ (mol%), densification at 500 °C for 45 min.

Those coatings obtained with drawing rates higher than 2.36 mm s^{-1} showed some heterogeneity by the borders and, thus, more possibilities to become cracked. Moreover, the thicker the coatings, the lower the bonding forces and the adherence to the glass substrate. Bearing in mind these limits, a drawing rate at about 2.4 mm s^{-1} was considered as the optimum.

3.2.2. Samples treated under reducing atmosphere

Several coated samples were submitted to thermal treatments under reducing atmosphere with the aim to enhance the silver ions reduction and aggregation to colloids. After such treatments, all the samples obtained were grey-brownish independently of the experimental conditions with which they were obtained (different silver molar percentage in the sol, dopant content in the substrate glass, thermal densification temperature and time; see Table 1). The grey-brownish colouring appeared more intense for the higher treatment temperatures in the entire samples surface, both for the coated and the uncoated area. Such colouring was attributed to the lead reduction in the base glass, due to the strong reducing conditions used. Thus, for this kind of lead crystal glass substrates, the silver containing coatings densification under reducing conditions is not possible, in contrast to the results obtained with soda lime silicate glasses coated with silver containing sol–gel films.[17] Since lead crystal glass is essential as substrate for the present research, the procedure of treatment under reducing atmosphere was discarded to promote and enhance the silver reduction and formation of colloids, responsible for the yellow ruby colouring.

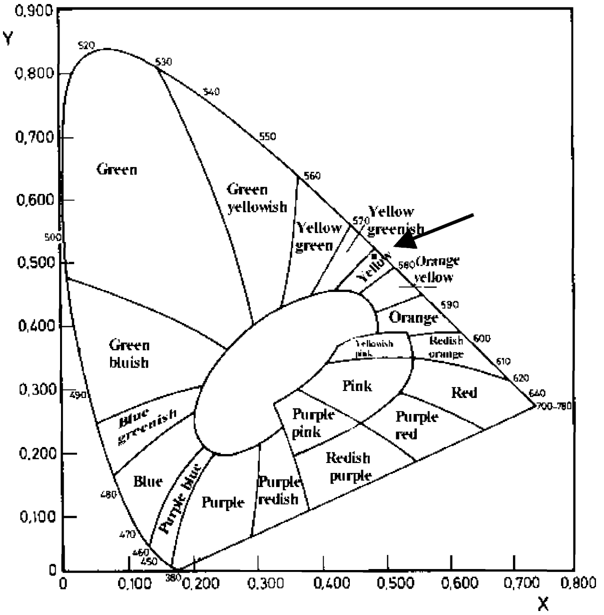

Fig. 10. Chromaticity chart in which the colour co-ordinates of lead crystal base glass doped with 5 wt.% As_2O_5, coated with a $5Ag{\cdot}95SiO_2$ (mol%) sol and densified at 500 °C for 45 min, are shown. Co-ordinates are located in the yellow domain.

3.3. Chromatic co-ordinates

Chromatic co-ordinates *x*, *y* and *z*, corresponding to the sample coated under the best experimental conditions (i.e. 5 wt.% arsenic oxide as a base glass dopant, 5 mol% silver containing sol and thermal densification at 500 °C for 45 min), were calculated according to the standard UNE 40-080-84.[25] The results were plotted in the chromaticity chart of the Fig. 10, where the co-ordinates are located in the yellow domain, with dominant wavelength in the 560–590 nm range. The colour purity percentage is about 96%, which means that the final colouring attained fits well with the requirements stated in the objectives of the present work.

4. Conclusions

The ability of sol–gel silver containing coatings as superficial yellow ruby colouring on lead crystal glass has been demonstrated. This colouring arises as a consequence of the silver ions reduction and aggregation to form nanosized colloids (the well-known surface plasmon resonance band at about 420 nm is the responsible for the yellow ruby colouring attained). To reach such colouring, doping of the lead crystal base glass with a thermoreducing agent (arsenic oxide), is absolutely necessary. Thermal densification of the sol–gel coating under oxidising atmosphere allows the formation of metallic silver colloids, whereas those heat-treatments performed under reducing atmosphere yielded a superficial grey-brownish hue, rather than yellow ruby colouring, due to reduction of lead from the substrate glass. Both thermoreducing dopant content in the lead crystal base glass and silver percentage in the coating precursor sol enhance the superficial yellow ruby colouring.

The optimum sol–gel based yellow ruby coatings were obtained with lead crystal base glass doped with 5 wt.% arsenic oxide, 5 mol% silver containing sol and heat-treatments at 500 °C for 45–60 min. The experimental method here investigated for obtaining superficial yellow ruby sol–gel coatings on doped lead crystal glass, appears as a suitable process from the industrial point of view (good reproducibility and low-cost investment processing).

References

1. *Five Thousand Years of Glass*. British Museum Press, London, 1995, pp. 246–247.
2. Gil, C., *Superficial Colouring of Glasses by Ion-exchange and by Application of Thin Coats*. Ph.D. thesis dissertation, Faculty of Geology, Universidad Complutense, Madrid, June 2002.
3. Lee, D. I., Lee, Y. K. and Lee, H. S., Effects of silver and potassium ions on ion-exchange in float glass. *J. Mater. Sci.* 1992, **27**, 2908–2913.
4. Matsuoka, J., Mizutani, R., Kaneko, S., Nasu, H., Kamiya, K., Kadono, K. *et al.*, Sol–gel processing and optical non-linearity of

gold colloid-doped silica glass. *J. Ceram. Soc. Jpn. Int. Ed.* 1993, **101**, 51–55.

5. Lakshmi, B. B., Dorhout, P. K. and Martin, C. R., Sol–gel template synthesis of semiconductor nanostructures. *Chem. Mater.* 1997, **9**, 857–862.
6. Di Maggio, R., Fedrizzi, L., Rossi, S. and Scardi, P., Dry and wet corrosion behaviour of AISI 304 stainless steel coated by sol–gel ZrO_2-CeO_2 films. *Thin Solid Films* 1996, **286**, 127–135.
7. Lechna, M., Holowacz, I., Ulatowska, A. and Podbielska, H., Optical properties of sol–gel coatings for fibre optic sensor. *Surf. Coat. Technol.* 2002, **151/152**, 299–302.
8. Sakka, S., Sol–gel processing. *Ceram. Transact.* 1995, **56**, 325–336.
9. Villegas, M. A., Chemical and microstructural characterization of sol–gel coatings in the ZrO_2–SiO_2 system. *Thin Solid Films* 2001, **382**, 124–132.
10. Kozuka, H., Zhao, G. and Sakka, S., Control of optical properties of gel-derived oxide coatings films containing fine metal particles. *J. Sol–Gel Sci. Technol.* 1994, **2**, 741–744.
11. Stepanov, A. L., Abdullin, S. N. and Khaibullin, I. B., Optical properties of polymer layers with silver particles. *J. Non-Cryst. Solids* 1998, **223**, 250–253.
12. Ritzer, B., Villegas, M. A. and Fernández Navarro, J.M., Incorporation of silver in silica glasses prepared by sol–gel. *Glastech. Ber. Glass Sci. Technol.* 1995, **68C1**, 417–424.
13. Fernández Navarro, J.M. and Villegas, M. A., Preparation of gold ruby glasses by the sol–gel method. *Glastech. Ber.* 1992, **65**, 32–40.
14. Mennig, M., Endres, K., Schmitt, M. and Schmidt, H., Colored coatings on eye glass lenses by noble metal colloids. *J. Non-Cryst. Solids* 1997, **218**, 373–379.
15. Villegas, M. A., García, M.A., Llopis, J. and Fernández Navarro, J.M., Optical spectroscopy of hybrid sol–gel coatings doped with noble metals. *J. Sol–Gel Sci. Technol.* 1998, **11**, 251–265.
16. Nagase, N., Izaki, S., Shimizu, J., Miura, N. and Yamazoe, N., Preparation of gold-dispersed vanadium oxide thin films by an alternative spin-coating method for electrochromic applications. *J. Mater. Chem.* 1994, **4**, 1581–1584.
17. García, M.A., Paje, S. E., Llopis, J., Villegas, M. A. and Fernández Navarro, J.M., Optical spectroscopy of arsenic- and silver-containing sol–gel coatings. *J. Phys. D: Appl. Phys.* 1999, **32**, 975–980.
18. De, G., Licciulli, A., Massaro, C., Tapfer, L., Catalano, M., Battaglin, G. *et al.*, Silver nanocrystals in silica by sol–gel processing. *J. Non-Cryst. Solids* 1996, **194**, 225–234.
19. Standard UNE 43-603-79. Vidrio. Nomenclatura y terminología. *Cristal. Vidrio sonoro.*
20. Standard UNE 43-703-78. Ensayos de vidrio. *Determinación dilatométrica de la temperatura de transformación*.
21. García, M.A., Paje, S. E., Llopis, J. and Villegas, M. A., Influencia de las condiciones de preparación en la luminiscencia de recubrimientos de sílice pura. *Bol. Soc. Esp. Ceram. Vidr.* 2000, **39**, 641–646.
22. Gago García, R. and Joglar Tamargo, A., *El color en el vidrio: una propiedad científicamente medible y calculable*. University of Sevilla, 1978, pp. 115–146.
23. Villegas, M. A., Fernández Navarro, J. M., Paje, S. E. and Llopis, J., Optical spectroscopy of a soda lime glass exchanged with silver. *J. Phys. Chem. Glasses* 1996, **37**, 248–253.
24. Pulker, H. K., *Coatings on Glass. Thin Films Science and Technology, Vol 6.* Elsevier, Amsterdam, 1984, pp. 109–115.
25. Standard UNE 40-080-84. *Determinación de coordenadas cromáticas*.