



## Colored coatings on eye glass lenses by noble metal colloids

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### Abstract

Metal colloids in glass coatings are suitable for preparation of colored transparent coatings with thicknesses of about 0.2 to 1  $\mu\text{m}$  due to their high molar coefficient of absorbance ( $\approx 10^6 \text{ l}/(\text{mol cm})$ ). The absorbance of these metallic particles in a dielectric environment is caused by a surface plasmon resonance effect of the conductive electrons of the colloids. Therefore, it is characteristic for the metal, but can be affected by the dielectric properties of the surrounding matrix. Glass sol–gel coatings have been developed for the preparation of 0.2 to 0.4  $\mu\text{m}$  thick, transparent colored coatings on silicate eye glass lenses by incorporation of Au-, Ag- and Pd-colloids into an 87 mol%  $\text{SiO}_2$ –13 mol%  $\text{PbO}$  glass. A functionalized silane has been used as a complex forming agent for the appropriate noble metal ions to control the nucleation and growth processes of the colloids during the thermal densification of the coatings. By mixing different noble metal salts and addition of  $\text{Co}^{2+}$  ions, pink, brown, green and grey colors with optical densities  $\leq 6$  have been obtained. By variation of the glass composition the refractive index of the coating can be adapted to that of different types of substrate glasses ( $n_D$  from 1.52 to 1.6) to obtain coatings with desirable optical performance. In a similar manner the transformation temperature ( $T_g$ ) of the coatings can be less than the substrate, allowing a complete thermal densification of the coatings at about 500°C. The coatings show glass like chemical durability and mechanical stability. Due to the optical and thermomechanical properties of the colored coatings and due to the thermal and UV-stability of the colloids these coatings were applied to eye glass lenses. © 1997 Elsevier Science B.V.

### 1. Introduction

Yellow and ruby colored glasses have been prepared by using silver and gold colloids [1]. The coloring is due to a surface plasmon resonance of the conductive electrons in the metal particles which leads to an absorbance band at 410 to 430 nm in the case of silver colloids and around 530 nm for gold colloids.

The molar coefficients of absorbance of noble

metal colloids in dielectric media are large ( $10^5$  to  $10^6 \text{ l}/(\text{mol cm})$ ) [2] and therefore they open up a possibility to obtain colored thermally stable glass like coatings even with a thickness of less than 1  $\mu\text{m}$  and a noble metal content of about 3 wt%.

By using functionalized silanes as complexing agents [3–6], noble metals could be dispersed homogeneously in  $\text{SiO}_2$ -xerogels [1,4], in  $\text{B}_2\text{O}_3$ - $\text{SiO}_2$ -xerogels [5] and in organic–inorganic- and  $\text{SiO}_2$ -coatings [6,7]. In these investigations it was proved that the organic groups of the used silanes act as reducing agents for silver and gold. These investigations showed the possibility to control the formation and growth of the colloids and the size of the metal

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particles in a wide range (5 to 30 nm). However, the  $\text{SiO}_2$ -coating matrix is not completely densified at temperatures below the  $T_g$  of an optical glass substrate and moreover, the small refractive index ( $n_D = 1.46$ ) may lead to colored interference effects on optical glass substrates which have larger refractive indices (e.g., 1.55 to 1.6 for optical glasses).

Therefore, the aim of the investigation was to synthesize matrix systems with lower  $T_g$ 's and larger refractive indices to adapt the optical properties and the densification behavior to optical glass substrates and to investigate the incorporation and coloring effects of various metals in these matrices.

## 2. Experimental

For the preparation of Ag containing  $\text{SiO}_2$ -PbO-coatings 0.63 g  $\text{AgNO}_3$  was dissolved in a mixture of 20 ml methanol and 0.82 ml *N*-(2-aminoethyl)-3-aminopropyl trimethoxysilane (DIAMO) (molar ratio of Ag:DIAMO = 1:1). 37.2 ml of the  $\text{SiO}_2$  matrix sol, prepared from 160 ml 3-glycidoxypopyl triethoxysilane (GPTS) and 40 ml tetraethyl orthosilicate (TEOS), dissolved in 240 ml ethanol and prehydrolyzed with 28.5 ml of 0.1 M  $\text{HNO}_3$ , was added to the former and stirred for 15 min. The mixture was added to a solution of 4 g  $\text{Pb}(\text{Ac})_2$  and 2.72 ml DIAMO dissolved in 20 ml methanol. For the preparation of Au containing  $\text{SiO}_2$ -PbO-coatings 0.26 g  $\text{H}[\text{AuCl}_4]$  was dissolved in 4 ml methanol and 0.163 ml *N*-(2-aminoethyl)-3-aminopropyl trimethoxysilane (DIAMO) (molar ratio of Au:DIAMO = 1:1) was added to it. 7.4 ml of the  $\text{SiO}_2$  matrix sol prepared as above was added to it and stirred for 15 min. The mixture was added to a solution of 0.8 g  $\text{Pb}(\text{Ac})_2$  and 0.55 ml DIAMO dissolved in 4 ml methanol. For the preparation of Pd containing  $\text{SiO}_2$ -PbO-coatings 0.48 g  $\text{Pd}(\text{Ac})_2$  was dissolved in 5 ml methanol and 0.47 ml *N*-(2-aminoethyl)-3-aminopropyl trimethoxysilane (DIAMO) (molar ratio of Au:DIAMO = 1:1) was added to it. This solution was mixed with 6.6 ml of the  $\text{SiO}_2$  matrix sol and stirred for 15 min. The mixture was added to a solution of 0.89 g  $\text{Pb}(\text{Ac})_2$  and 0.61 ml DIAMO dissolved in 4.5 ml methanol. For the preparation of Co containing  $\text{SiO}_2$ -PbO-coatings 2.13 g  $\text{Co}(\text{Ac})_2$  was dissolved in 18.8 ml methanol and 1.75 ml

*N*-(2-aminoethyl)-3-aminopropyl trimethoxysilane (DIAMO) (molar ratio of Co:DIAMO = 1:1) was added to it. 13.1 ml of the  $\text{SiO}_2$  matrix sol was mixed with it and stirred for 15 min. The mixture was added to a solution of 1.5 g  $\text{Pb}(\text{Ac})_2$  and 1.02 ml DIAMO dissolved in 12.4 ml methanol.

To investigate the mechanical and optical properties of the coatings they were applied to fused silica slides by dip coating with a withdrawal speed of 4 mm/s and dried at 120°C before they were treated in ambient air between 200 and 600°C. Convex eye glass lenses were coated by spin coating and the coating parameters used were: step 1: 3 s at 1000 rpm; step 2: 15 s at 3000 rpm. The coatings were dried at 120°C and densified at 460°C in air.

To get red and brown colored eye glass lenses ( $n_D = 1.55$  and 1.60 respectively,  $T_g$  about 550°C), respectively with transmission values of about 85%, the Au containing sol and the Pd containing sol was diluted with ethanol (1:2). Green colored optical glasses were synthesized by mixing the Ag-sol and the Co-sol in a molar ratio Ag:Co = 1:20. A tint of grey was obtained by mixing the Pd-sol and the Co-sol in a molar ratio Pd:Co = 1:2. The blue colored eye glass lenses were synthesized by coating them with the Co containing sol.

The colloid formation was investigated by UV-VIS-spectroscopy (Bruins instruments, Omega 30). The data were evaluated with regard to colloid size and colloid volume fraction according to Ref. [8] using calculated spectra [9] according to the Mie theory [10] for comparison. The thickness of the coatings was determined by ellipsometric measurements (Sopra, ES4G). The chemical stability of the coatings was measured by changes of transmission (UV-VIS spectroscopy) after dipping the coated substrates in  $\text{H}_2\text{O}$ , organic solvents and weak acids. The adhesion and the mechanical properties of the coatings were tested by cross cut tests (DIN 53151), tape tests (ASTM D 335978) and rubber test (DIN 58196T4).

## 3. Results

Fig. 1 shows the refractive index,  $n_D$ , as function of the PbO content in the two component system PbO- $\text{SiO}_2$  calculated by the formula of Appen [1].

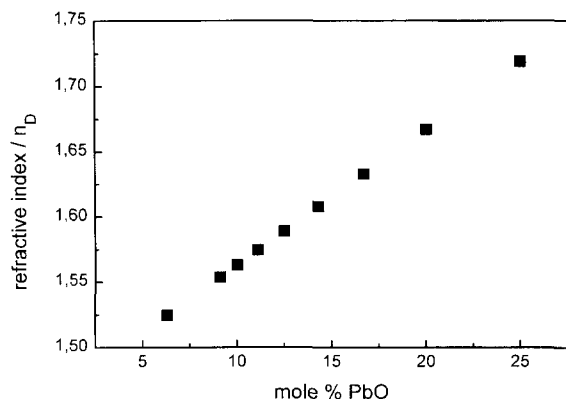


Fig. 1. Main refractive index  $n_D$  as function of the Pb content in the two component system PbO–SiO<sub>2</sub> calculated by the formula of Appen [1].

By increasing the PbO content in that system a linear dependence of  $n_D$  on PbO content can be expected. In order to obtain coatings with a main refractive index in the range of  $n_D$  from 1.55 to 1.6 a two component system SiO<sub>2</sub>–PbO with a content of 13 mol% PbO and 87 mol% SiO<sub>2</sub> was synthesized by using lead acetate as precursor. Lead acetate was chosen due to its ability to form stable amine complexes [11], its good solubility in alcoholic solution and the possibility to prepare a water-free salt easily. Thus the precipitation of basic lead compounds can be avoided and aminosilanes (i.e., DIAMO) can be used as complex forming agents. Without the addition of a complex forming agent a white color was obtained after drying the coatings at 120°C and was attributed to the formation of basic lead compounds. With aminosilanes clear coatings were obtained and the  $n_D$  of this coating densified at 500°C was determined to be 1.57 by ellipsometric measurements. The PbO content was 13 mol% and the resulting refractive index is in good agreement with the calculated value (Fig. 1). As a result, glass substrates with  $n_D = 1.55$  as well as with  $n_D = 1.6$  could be coated with the same sol system without any undesired interference effects caused by the mismatch of the  $n_D$  of the substrate and that of the coating with a thickness of 0.2 to 0.5  $\mu\text{m}$ .

To investigate the dependence of the transformation temperature on the Si:Pb ratio the amount of PbO in the two component system was varied from a Si:Pb ratio of 11:1 up to 6:1 and the  $T_g$  of the

resulting coatings were determined by thermomechanical analysis (TMA). The results of these measurements are shown in Fig. 2.

By variation the Si:Pb ratio from 11:1 to 6:1 in the SiO<sub>2</sub>–PbO matrix the  $T_g$  decreased from 570°C to 490°C as determined by thermal measurements. Coatings made from these sols were heated to temperatures of 500°C and completely densified and clear coatings of 0.4  $\mu\text{m}$  in thickness were measured by ellipsometry. The coatings showed an excellent adhesion to the fused silica substrates and the optical glass (class 0 in cross cut test and tape test), resistance against acids and organic solvents and no abrasion in the rubber test (DIN 58196T4). Therefore this matrix system was considered to be suitable for the investigation for the colloid formation experiments.

Fig. 3 shows the absorbance spectra of Ag containing SiO<sub>2</sub>–PbO-coatings on fused silica with a Si:Pb ratio of 7:1 and a Si:Ag ratio of 22:1 dried at 120°C and after thermal treatments at several temperatures in the range from 200 to 600°C in air (reference air).

The maxima of the absorbance of the Ag containing coatings are detectable in the range of 400 to 450 nm depending on the thermal treatment. In the same way as the position of the absorbance maxima the height of the absorbance bands depended on the firing conditions. After drying at 120°C an absorbance band with a local maximum at 350 nm and a shoulder at 420 nm was obtained. The absorbance at 350 nm is attributed to Ag<sup>0</sup> [12] and the absorbance at 420 nm to small Ag-colloids [10]. Firing

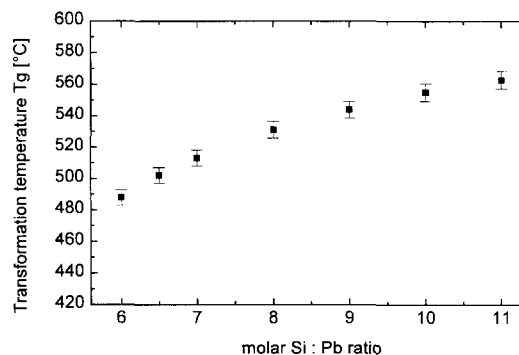


Fig. 2. Dependence of the transformation temperature  $T_g$  on the Si:Pb ratio determined by thermomechanical analysis.

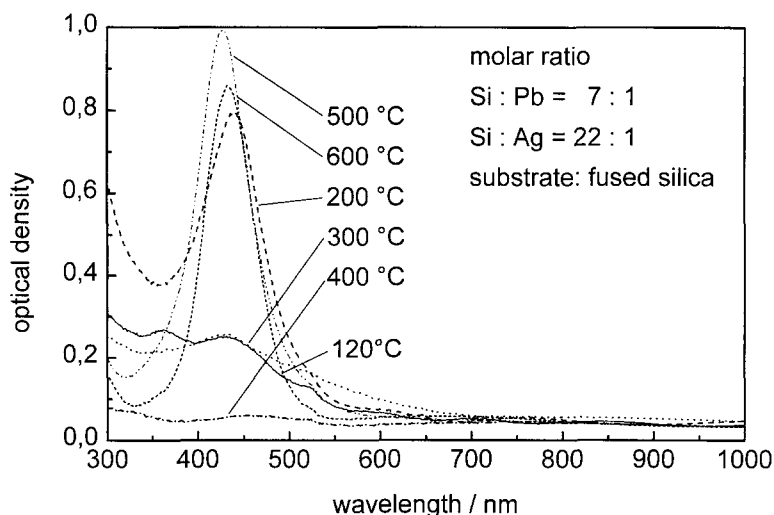


Fig. 3. Absorbance spectra of Ag containing  $\text{SiO}_2$ -PbO-coatings with a Si:Pb ratio of 7:1 and a Si:Ag ratio of 22:1 dried at 120°C and after different thermal treatments in air (reference air).

to 200°C generates an absorbance band at 420 nm and after firing the coating at 300°C the absorbance band at 420 nm decreases. At a densification temperature of 400°C a minimum of absorbance is detected. At a heat treatment of the coating of 500°C and 600°C the absorbance at 420 nm increases and the maximum is shifted to about 410 nm. The amount of

colloidal silver after a densification at 600°C was calculated to about 50% of the total Ag content.

Au colloids in a  $\text{SiO}_2$ /PbO matrix were synthesized using the same synthesis route used for the formation of Ag containing coatings. The change of the optical properties of the coatings during thermal densification between 120°C and 600°C in air was

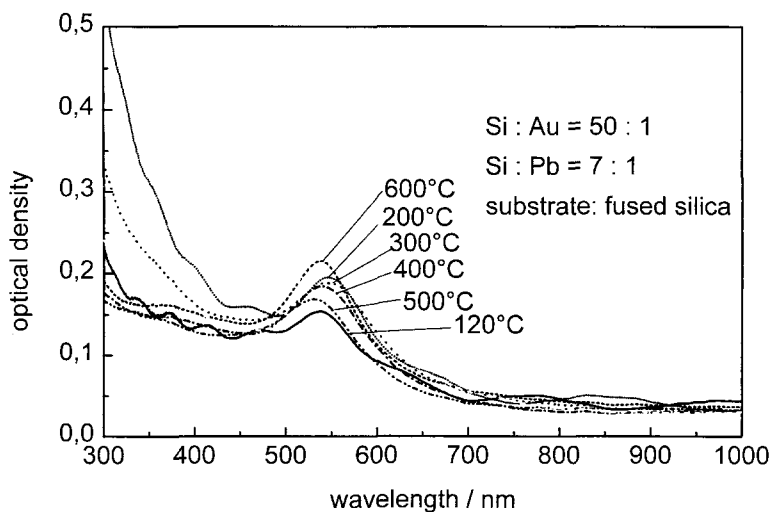


Fig. 4. Absorbance spectra of Au containing  $\text{SiO}_2$ -PbO-coatings with a Si:Pb ratio of 7:1 and a Si:Au ratio of 50:1 dried at 120°C and after different thermal treatments in air (reference air).

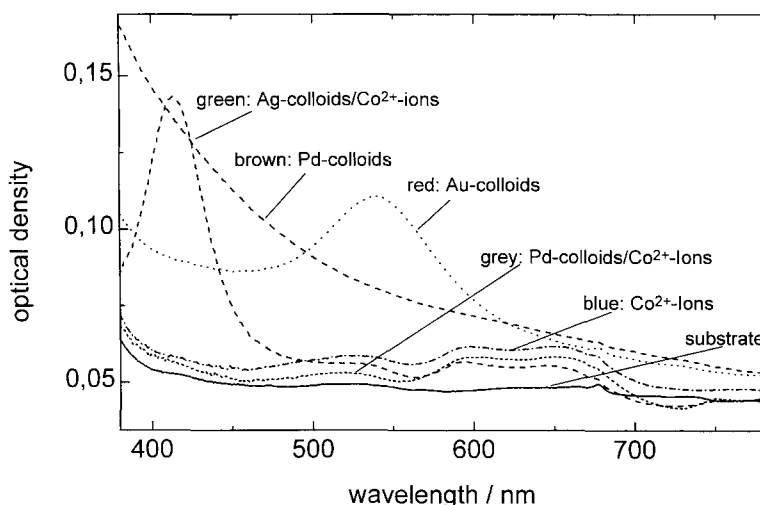


Fig. 5. Absorbance spectra of  $\text{SiO}_2/\text{PbO}$  coatings with Au, Ag and Pd colloids and  $\text{Co}^{2+}$  ions, densified at  $460^\circ\text{C}$  in air (reference air).

followed by UV-VIS-spectroscopy. Fig. 4 shows the absorbance spectra of Au containing  $\text{SiO}_2\text{--PbO}$  coatings ( $\text{Si}:\text{Au} = 50:1$ ,  $\text{Si}:\text{Pb} = 7:1$ ) on fused silica dried at  $120^\circ\text{C}$  before and after further heat treatment between 200 and  $600^\circ\text{C}$ .

After drying at  $120^\circ\text{C}$  an absorbance band with a maximum at 530 nm was observed that is characteristic for the plasmon resonance of gold colloids [1]. After heat treatment in the range of  $200^\circ\text{C}$  to  $600^\circ\text{C}$  this absorbance band is maintained without a significant change of the optical density.

With these procedures yellow (Ag-colloids) and red (Au-colloids) glasslike coatings on glass substrates were produced. The optical and thermomechanical properties of the coatings were congruent with those of the substrates. Pd- and  $\text{Co}^{2+}$ -containing sols were synthesized to produce brown and light blue colored coatings, respectively. In the case of  $\text{Co}^{2+}$  no reduction to colloids takes place. Due to the low coefficient of extinction of the  $\text{Co}^{2+}$  ions a molar ratio of  $\text{Si}:\text{Co} = 3:1$  was used. To get brown colors with transmission values of about 85% the  $\text{Si}:\text{Pd}$  ratio was set to 16:1. The formation of the Pd-colloids which show the plasmon resonance band in the UV-region in a  $\text{SiO}_2\text{--PbO}$  matrix densified at different temperatures in ambient air produced grayish colors in the VIS. The mechanism of the colloid formation has not been investigated by us.

The absorbance spectra of the Au-, Ag-, Pd-col-

loids and  $\text{Co}^{2+}$ -ions containing coatings on eye glass lenses are shown in Fig. 5.

The coatings were thermal treated at  $460^\circ\text{C}$  in air and thickness of the coatings were 0.2 to 0.4  $\mu\text{m}$  as measured by ellipsometry. The spectrum of the Au containing coating has a maximum at 530 nm. The absorbance spectrum of the Pd-containing sol shows a decreasing absorbance in the range of 380 to 780 nm and the  $\text{Co}^{2+}$  containing coating leads to an absorbance in the range of 560 to 680 nm. A mixture of an Ag-sol and a Co-containing sol in a molar ratio of  $\text{Ag}:\text{Co} = 1:20$  leads to an absorbance at 410 nm and at 560 to 680 nm and by mixing Pd- and Co-sols in a molar ratio of  $\text{Pd}:\text{Co} = 1:5$  an absorbance with a low optical density was obtained. The coatings show an excellent adhesion to the substrates (cross cut test and tape test class 0), are stable against organic solvents and weak acids and show no abrasion after the rubber test according to DIN 58196T4.

## 4. Discussion

### 4.1. Development of $\text{PbO}\text{--SiO}_2$ coatings

The thermomechanical and optical properties such as transformation temperature and refractive indices of glasses and glass like coatings can be affected by the incorporation of different network formers or

modifiers into a  $\text{SiO}_2$  matrix [1]. By addition of PbO to  $\text{SiO}_2$  the  $\text{Pb}^{2+}$  can act as network modifier reducing  $T_g$  of the resulting glass and to increasing the refractive index. These glasses can be prepared either by melting [1] or by the sol–gel route [11,13].

The calculation of the dependence of the main refractive index  $n_D$  as function of the Pb content in the two component system ( $\text{PbO-SiO}_2$ ) according to the formula of Appen [1] shows, that the increase of the PbO content from 7 to 25 mol% increases  $n_D$  of a  $\text{SiO}_2$ –PbO-coating from 1.52 to 1.72 (Fig. 1).

It was expected that the  $\text{PbO:SiO}_2$  ratio would also determine the transformation temperature of the coating material. From Fig. 2 it is evident, that with an increase of the Pb content the  $T_g$  decreases from 570°C ( $\text{Si:Pb} = 11:1$ ) to 490°C ( $\text{Si:Pb} = 6:1$ ). The transformation temperature of the coating received by the matrix composition with the required refractive index of 1.57 ( $\text{Si:Pb} = 7:1$ ) was determined to be 510°C (Fig. 2). The results show that the matrix composition with a  $\text{Si:Pb}$  ratio of 7:1 allows the densification of the coating at a temperature below the  $T_g$  of the substrate glasses (550°C).

#### 4.2. Colloid formation

The synthesis of Au-, Pd- and Ag-colloids in sol–gel derived  $\text{SiO}_2$  coatings on soda–lime and silica glass are already described [4,6,7,14]. The formation and the growth of the noble metal colloids has been controlled by using silanes with functional amino, thio or thiocyanato groups. The organically modified silanes act as complexing and reducing agents for the noble metal ions. To transfer these results to the  $\text{SiO}_2$ –PbO two component system, the noble metal salts ( $\text{AgNO}_3$ ,  $\text{Pd}(\text{CH}_3\text{COO})_2$  or  $\text{H}[\text{AuCl}_4]$ ) were incorporated into the sol according to the synthesis described in the experimental part with a metal:DIAMO ratio = 1:1. Coatings have been prepared by a one step procedure by either dip or spin coating with thicknesses to 0.5  $\mu\text{m}$  measured after thermal densification in air at 500°C. For determining the optical properties fused silica substrates were used due to their high transmission in the UV-VIS region.

To initiate the colloid formation the samples were dried for 1 h at 120°C in air before any further heat treatment. The colloid formation in Au- and Ag-con-

taining coatings between 120°C and 600°C was measured by UV-VIS-spectroscopy. The resulting absorbance spectra were evaluated with regard to the colloid radii and the colloid formation according to the Mie theory [10] by means of numeric calculations [9] as described in Ref. [6].

Fig. 3 shows the absorbance spectra of Ag containing  $\text{SiO}_2$ –PbO-coatings with a  $\text{Si:Pb}$  ratio of 7:1 and a  $\text{Si:Ag}$  ratio of 22:1 dried at 120°C and after different thermal treatments. It is assumed that the decrease of colloidal Ag after the heat treatment at 400°C was either due to a conversion of small Ag-colloids (4 nm) to  $\text{Ag}_x\text{O}_y$ -particles which could be found in high resolution transmission microscopy investigations (HRTEM) [6,14] or due to a dissolution of formed colloids. Probably both mechanisms take place simultaneously. Further it is assumed that the Ag-colloid formation above 400°C in the coatings takes place by the decomposition of the  $\text{Ag}_x\text{O}_y$ -particles. At lower temperatures the oxidation of Ag should be prevented by the reducing effect of the organic components. After the combustion of the organics, the oxidation of Ag takes place between 300 and 400°C in the still porous matrix, and the plasmon bands disappear. The color of the coating is yellow to brown depending on the firing temperature. The Ag content is about 1.3 at.%.

The different behavior of Au colloids (see Fig. 4) compared to Ag (see Fig. 3) is explained by the fact that Au cannot be oxidized at the investigated temperatures. Once formed, the Au colloids cannot be destroyed, they can only increase in size or concentration due to further diffusion from the molecular precursors used to introduce them into the sol. The calculation of the size of the colloids according to Ref. [14] shows that after densification at 500°C, Au colloids with around 2 nm radius were formed. After further heat treatment at 600°C, the sizes of the colloids were estimated to range from 4 to 10 nm. The amount of Au colloids is dependent on the thermal treatment. After drying at 120°C in air 50% of the ionic Au was converted to Au colloids. With increasing temperature to 500°C additional 10% of colloid formation was obtained. At 600°C an increase of the amount of colloidal Au takes place which was calculated to be 80%. The slight increase of colloid formation between 120°C and 500°C suggests that at 120°C almost all of the Au was con-

verted to Au colloids. Further colloid formation only can be caused by diffusion of ionic Au in the matrix. Due to the small particle size of 4 to 10 nm the color of the coatings heat treated between 400°C to 600°C is shiny ruby red and no scattering is observed which leads to livery gold ruby glasses.

## 5. Application

Due to the optical and thermomechanical properties of the colored coatings and due to the thermal and UV-stability of the colloids these coatings were applied to eye glass lenses.

The advantages of staining eye glass lenses by the coating technology are the low costs as compared to the use of bulk colored glasses and the possibility to react rapidly to a customers demand. Before coating the colloid containing sols were dissolved in alcohol to produce red, blue, grey, green and brown colors with transmissions of about 85%. The convex eye glass lenses were coated by spin coating to prepare films with homogeneous coating thickness which was 0.2 to 0.5  $\mu\text{m}$  as measured by ellipsometry and the films were densified in ambient air at 460°C. The diluted Au containing sol produced a red colored coating with a maximum absorbance at 530 nm (see Fig. 5) which is typical for the plasmon resonance peak of the Au colloids. Brown colored eye glass lenses were obtained by coating them with the Pd-containing sol and blue colored coatings were synthesized by a Co-containing sol which show the absorbance in the range of 560 to 680 nm that is typical for  $\text{Co}^{2+}$  ions. Green coatings were obtained by mixing an Ag-sol and a Co-containing sol in a molar ratio of  $\text{Ag}:\text{Co} = 1:20$ . The maxima of absorbance of this coating at 410 nm and 560 to 680 nm (see Fig. 5) were attributed to the Ag-colloids

and the  $\text{Co}^{2+}$  ions respectively. By coating the eye glass lenses with Pd- and Co-sols in a molar ratio of  $\text{Pd}:\text{Co} = 1:5$  tints of grey were obtained.

## 6. Conclusions

A new method to produce thermally and mechanically stable colored coatings on a wide range of glass substrate compositions has been developed in the present work by the adaptation of the refractive index and the transformation temperature of the coating to that of the substrates. This method provides the flexibility to be integrated with different types of production processes and products.

## References

- [1] H. Vogel, *Glaschemie* (Springer, Berlin, 1992).
- [2] W.A. Weyl, *Coloured Glasses* (Dawson's of Pall Mall, London, 1959).
- [3] M. Mennig, M. Schmitt, U. Becker, G. Jung, H. Schmidt, *Sol-Gel-Opt. III SPIE 2288* (1994) 130.
- [4] U. Schubert, S. Amberg-Schwag, B. Breitscheider, H. Schmidt, *US patent 07/482.860* (1990).
- [5] M. Mennig, L. Spanhel, S. Betzholz, H. Schmidt, *J. Non-Cryst. Solids 147&148* (1992) 326.
- [6] M. Mennig, M. Schmitt, H. Schmidt, *J. Sol-Gel Sci. Technol.* 8 (1997) 1035.
- [7] T. Burkhart, M. Mennig, H. Schmidt, A. Licciulli, in: *Better Ceramics Through Chemistry, VI-MRS Symp. Proc.* 346 (1994) 779.
- [8] K.J. Berg, A. Berger, H. Hofmeister, *Z. Phys.* 20 (1991) 313.
- [9] B. Dusemund, *MSc thesis, Saarbrücken* (1991).
- [10] G. Mie, *Ann. Phys.* 25 (1908) 377.
- [11] Hollemann-Wiberg, *Lehrbuch der Anorganischen Chemie* 91-100. Auflage (Walter de Gruyter, Berlin, 1985).
- [12] E. Klein, *PhD thesis, Halle* (1986).
- [13] M. Mennig, A. Kalleder, H. Schmidt, *Glastech. Ber. Glass Sci.* 68 (C1) (1995) 401.
- [14] M. Schmitt, *PhD thesis, Saarbrücken, submitted*.