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GROWTH AND DEFORMATION OF GOLD COLLOIDS IN LEAD CRYSTAL GLASS

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INTRODUCTION

Nonspherical silver colloids in glasses with sizes in the nanometer range show interesting optical properties (1-3). Since spherical colloids show a single surface plasmon absorption band, spheroidal colloids are characterized by two bands, according to the extinction of light that is linearly polarized parallel and perpendicular to the axis of symmetry of the ellipsoid. Prolate silver particles have been generated for instance by elongation of flat glass near its softening point that contained spherical colloids (2,3). The optical properties of nonspherical gold colloids have not been reported yet. It may be assumed that the generation of prolate spheroidal gold colloids by tensile deformation of the glass matrix is much less effective than in the case of silver, because the surface energy of gold is higher than for silver (4). For silver colloids it has been shown that for a given degree of glass deformation the colloidal deformation increases with the colloid size. For this reason our approach to obtain ellipsoidal gold colloids in glass by elongation was first to choose a glass with relatively large colloids and second to use a deformation apparatus that already has shown a very efficient colloidal deformation in the case of silver (5). The aim of this paper is to present the first calculated spectra of spheroidal gold colloids of uniform orientation in glass and to show how large gold colloids can be obtained in lead crystal glass and to prove that they can be deformed.

EXPERIMENTS

Samples were prepared by melting colourless pieces of commercial gold ruby lead crystal glass containing about 0.015 wt. % of gold in an alumina crucible at 1350 °C. The melt was cast into a rectangular graphite mould (120 x 40 x 20) mm^3 preheated at 550 °C and then slowly cooled down. For the investigation of the colloidal growth samples of (30 X 10 x 1) mm^3 were cut, grinded and polished. The samples were thermally treated at temperatures between 440 °C and 1050 °C for different times between 1 and 14 h. Absorbance spectra were measured and colloidal size and concentration were determined as function of temperature and time. After it was clear that large colloids can only be obtained at temperatures higher than 1000 °C the whole glass block was tempered in the graphite mould at 1030 °C (heating rate 5 K/min) in N_2-atmosphere for 20 minutes, then rapidly cooled to 550 °C and after 1 h slowly cooled down to room temperature. For the deformation experiments samples of 100 mm x 10 mm and thicknesses between 1.4 mm and 2 mm were cut, grinded and polished. For the deformation experiments an apparatus according to (5) was used, that moves the glass rod through a relatively small heating zone (37 mm in length) under a constant tensile load. By variation of the transport speed, different degrees of deformation can be obtained under constant conditions yielding to samples with a unique degree of deformation in a length of 5 to 20 cm, depending on the degree of deformation. Absorbance spectra were measured with a microscope photometer (MPM 800, Zeiss-Oberkochen) with polarized light parallel and perpendicular to the tensile axis.

RESULTS AND DISCUSSION

Calculation of spectra

The extinction spectra of spherical gold colloids in lead crystal glass (refractive index n_D = 1.59) have been calculated in order to follow the growth of the colloids before deformation. A computer calculation programme (6) was used, that is based on the MIE-theory (7), and which considers the mean free path effect of the conduction electrons in small particles as well as the contribution of the valence electrons to the dielectric function of gold. The peak position and the halfwidth of extinction bands, calculated for different colloid radii were determined graphically and plotted in the diagram shown in fig. 1. This diagram was used for the determination of the colloid size form measured absorbance spectra following the example for silver colloids in glass (8). Fig. 1 shows that the colloidal size has a relatively weak influence on the peak position but a strong influence on the halfwidth. Since the extinction band of gold colloids is asymmetric, caused by interband absorption at wavelengths shorter than the peak position, the halfwidth was determined from the large wavelength part of the absorbance band. The measured spectra were in excellent agreement with the calculated ones even for large colloidal radii. For illustration two pairs of measured peak positions and halfwidths are shown in fig 1 (triangles at about 20 and 30 nm radius). From silver colloids it is known that the area beneath the extinction band is proportional to the volume concentration of the colloidal silver (9) and that the proportionality is nearly independent on the colloid size. With the halfwidth, determined as for fig. 1 and the peak extinction the area (A) beneath the calculated spectra was estimated. In first approximation this value is also independent on the colloid size and therefore can be used to determine the concentration (C) of colloidal gold. For a refractive index of 1.59 the proportionality factor (f = C/A) is 0.18. The general, exact solution for the calculation of extinction spectra of spheroidal metal colloids (10) has not been used. This numerical method is not yet suitable in practice. Therefore the so called dipole approximation of GANS (11) was used, that is valid for small particles only (estimated limit 10 nm radius). The main result of this is given in fig. 2, showing the peak positions of the absorption bands for polarized light parallel (squares) and perpendicular (circles) to the long axis of the spheroid (radius of the sphere with the same volume : 10 nm,

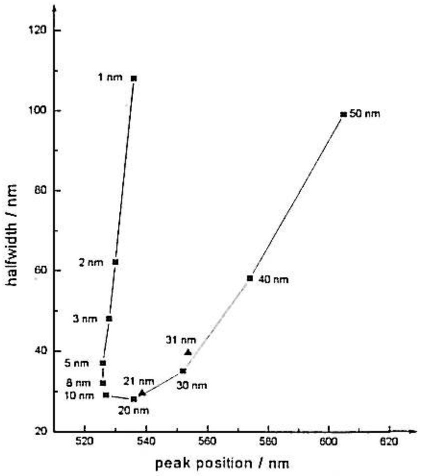

Fig. 1: Peak position and halfwidth of calculated spectra for different radii of gold colloids in glass (n_D = 1.59)
- ● calculated values
- ▲ measured values

n_D = 1.59). It is clear to be seen, that the axis ratio of spheroidal gold colloids has an extreme influence on the optical properties. The band caused by absorption of light polarized parallel to the long axis strongly shifts to larger wavelengths and reaches the NIR region at an axis ratio of about 1 : 3. The influence of the colloid geometry on the absorption of polarized light perpendicular to the long axis of the spheroid is much less, because this band is shifted only very slightly to shorter wavelengths. Qualitatively this is the same behaviour as found for silver colloids (2,3). Since the calculation is an approximation for small colloids, fig. 2 will be only used for a qualitative discussion of measured spectra and other spectral characteristics as halfwidths and peak extinction will not be discussed.

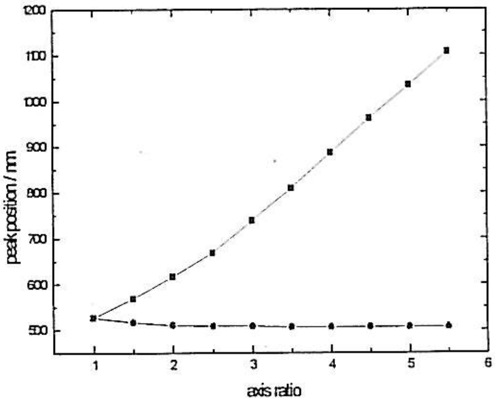

Fig. 2: Calculated peak positions of calculated absorption bands of spheroidal gold colloids in glass

Experimental results

The glass remained colourless after melting the pieces at 1350 °C and rapid quenching. This gave us the opportunity to follow the colloidal growth at different temperatures as a function of time by spectroscopy. Fig. 3 shows the radius of gold colloids as a function of time for three selected temperatures. It is to be seen, that the colloid size reaches a saturation level within the first few hours. Although the height of this level depends on the temperature, the difference in the colloid radii that can be obtained are relatively small. On the other hand we found that the concentration of colloidal gold in the glass was independent of the temperature. In all cases we detected a saturation volume concentration of about 25 · 10^{-6}. This is about the total amount of gold in the glass as analyzed by ICP-AES. One may conclude that the amount of reducing agents is high enough in order to reduce all of the gold ions. At 480 °C this level was reached after 25 h, at temperatures higher than 600 °C within the first hour. For a more

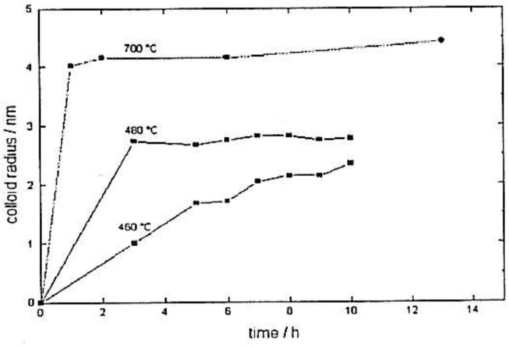

Fig. 3: Growth of gold colloids in lead crystal glass at different temperatures

detailed discussion the processes of nucleation and growth have to be investigated seperately. There are two principle ways to obtain large gold colloids. The first is to choose a low nucleation and a high growth rate. The second is Oswald ripening of small colloids. From fig. 3 one can conclude, that at temperatures below 700 °C the nucleation rate is very high compared with the growth and Oswald ripening does not occur or occurs extremely slow (low diffusion rates). So we decided to apply much higher temperatures in order to generate large colloids. Fig 4 shows the result of the high temperature treatment of colloid containing glass.

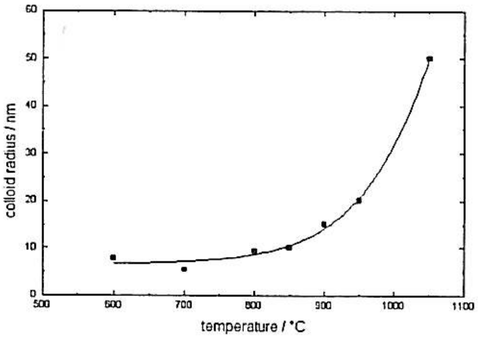

Fig 4: Size of gold colloids as function of temperature in lead crystal glass after 1 h

As one can see the colloid radii increase strongly with temperature. For temperatures below 800 °C the samples were ruby coloured and transparent. At higher temperatures the colour seen in transmission became violet to blue and the samples looked livery in reflected light. Since the measured spectra were in excellent agreement with the calculated ones (see fig. 1), we conclude that the violet colour and the livery appearance of gold ruby glass is caused by gold colloids with radii larger than 10 to 20 nm. The violet colour is due to the shift of the peak position to larger wavelengths (see fig. 1) and the livery look is due to scattering. An alternative explanation for the livery appearance might be that other inhomogenities (immiscibilities, crystallisation of the glass matrix) to be responsible for the scattering, and the gold colloids could act as nuclei and therefore the scattering is not observed in gold free lead crystal. But in this case the optical spectra measured in livery gold ruby glass should differ from the calculated one. The heating rate for the high temperature treatment was 5 K/min. So it took 1 h for heating the sample from 500 to 800 °C. From the time dependent heat treatments at constant temperatures below 700 °C (see fig. 3) it could be concluded that at temperatures higher than 600 °C the formation of relatively small colloids ends up in saturation within the first hour. So one can suggest that at temperatures higher than 900 °C large colloids are formed by Oswald ripening. In order to prove this hypothesis further investigations are required.

Glass samples containing colloids of about 50 nm in radius were used for deformation experiments. It has been proved (5) that during deformation by the applied apparatus the width to thickness ratio of the glass sample remains unchanged. Therefore an uniaxial deformation is assumed that leads to spheroidal colloids, and the degree of glass deformation S_G can be simply described by eq. [1] from the ratio of deformation before (W_0) and after deformation (W).

$$Sg = (Wo / W)^2 - 1 \qquad [1]$$

Fig 5 shows absorbance spectra measured with polarized light for a sample with a deformation degree of about 117 and the undeformed glass. The splitting of the absorbance band can be seen clearly. One band is shifted to shorter wavelengths for about 40 nm since the other band is shifted to larger wavelengths for

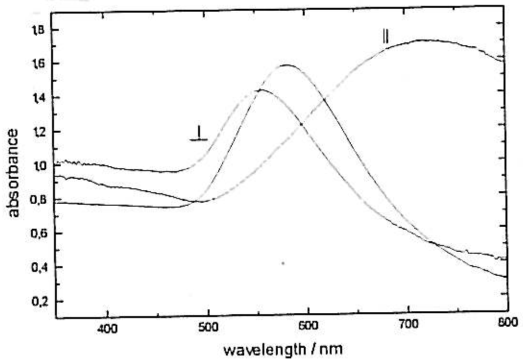

Fig 5: Extinction spectra of gold colloids (sphere radius in undeformed sample: 50 nm) measured with polarized light perpendicular (⊥) and parallel (II) to the tensile axis (absorbance normalized on unique sample thickness)

about 100 nm. It is obvious that the areas of the two bands are quite different, especially since the band shifted to longer wavelengths is very broad and even higher than the other one. These results are qualitatively in good agreemet to the results of the calculation of the spectra (fig. 2). A quantitative discussion of peak positions, halfwidths and areas of the absorbance bands and axis ratios of spheroidal colloids is not possible, because the calculations could only be carried out for small colloids. But with respect to the good qualitative agreement one may conclude that the deformation experiment leads to spheroidal gold colloids.

In order to get a first impression of the dependence of the colloid deformation on the deformation of the glass, the peak positions of the extinction bands for light polarized parallel to the long axis of the speroids (shifted to large wavelengths) have been plotted versus the glass deformation (calculated with eq. [1]) as shown in fig. 6. As expected the colloidal deformation increases with the deformation of the glass. From fig. 2 one may conclude that the peak position of the band shifted to larger wavelengths is a fairly linear function of the axis ratio of the spheroids. Fig. 6 shows the same functional dependence of the peak position on the deformation degree of the glass. Therefore the conclusion can be drawn, that the axis ratio of spheroidal gold colloids in glass is a linear function of the deformation degree of the glass matrix in a semi-quantitative sense. For silver colloids the same qualitative result was obtained (2, 3).

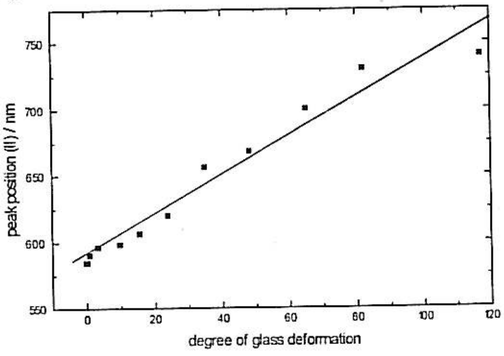

Fig. 6: Peak position of the extinction band as a function of deformation of the glass (S_G, calculated with eq. [1])

The only known model for the deformation of a deformable sphere in a viscous matrix under uniaxial tension (12) describes the sphere deformation under steady state conditions. From this model a functional dependence of the colloid deformation on the matrix deformation was calculated (12), that does not lead to a linear dependence. From this discrepancy the conclusion is drawn that the steady state model is not suiteable for the description of our deformation experiment. This hypothesis has to be proved by further investigations with different colloid sizes and different deformation process parameters.

CONCLUSION

It has been shown, that measured spectra of gold colloids in lead crystal glass are in very good agreement with calculated spectra. So it could be proved that the violet colour of gold containing lead crystal in transmitted light and its livery appearance in reflected light is due to gold colloids with radii larger than 10 nm. Such large colloids cannot be obtained at temperatures below 700 °C. At temperatures higher than 800 °C colloids with radii of 10 nm and more grow within 1 hour. In order to prevent the livery of gold ruby lead crystal during glass manufacturing temperatures higher than 800 °C should be passed as fast as possible. The experiments have shown that gold colloids of about 100 nm in diameter in glass can be deformed to prolate spheroids by uniaxial glass deformation although their interfacial energy in glass should be remarkably higher than for silver colloids. First investigations of silver colloid deformations in the same glass show much larger anisotropic effects (14). It is assumed that this is due to different interfacial energies of the gold and silver colloids, since the interfacial energy causes the reestablishing force of the colloid deformation and the yield strength of bulk gold and silver are nearly identical even at elevated temperatures (15). Interfacial energy data of metal colloids in glasses are not known. In order to investigate this influence it would be very interesting to use glass samples containing silver as well as gold colloids for deformation experiments. Such samples could be obtained in the manner described here by mixing and melting pieces of gold and silver containing lead crystal glass.

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