

Formation of Gold Nanoparticles in Gold Ruby Glass: The influence of Tin

S. Haslbeck¹, K.-P. Martinek², L. Stievano³ and F. E. Wagner¹.

¹Physik-Department, Technische Universität München, D-85748 Garching, Germany

²F. X. Nachtmann Bleikristallwerke GmbH, 94566 Riedlhütte, Germany

³Laboratoire de Réactivité de Surface, Université Paris VI, 4 Place Jussieu, 75252 Paris, France

Gold ruby glass is a silicate glass containing well-dispersed nanometre size gold metal particles imparting the glass its distinctive red colour. Gold ruby glass is mainly used for making household glassware but recently glass of this type has also been suggested for technical applications [1]. Gold ruby glass is usually prepared by adding several hundred ppm of a gold precursor to the melt of a silicate glass. At the usual melting temperatures around 1500°C the gold dissolves in the melt as individual Au(I) ions and remains in this state on quenching to ambient temperature [2]. Only when the quenched glass is annealed again at about 500°C for times of the order of minutes or hours does it strike red owing to the formation of metallic gold nanoparticles with sizes between a few and about 50 nm. The typical ruby colour of the glass arises from a strong light absorption of the gold particles in the green region of the visible spectrum caused by surface plasmon excitation and from the interband absorption of metallic gold in the blue. The hue of the colour strongly depends on the size distribution of the gold particles.

This size distribution depends not only on the duration and the temperature of the annealing step, but also on the composition of the base glass and particularly on the presence of characteristic elements acting as nucleating agents or other wise influencing the precipitation of the gold nanoparticles. Tin is well known to increase the speed with which the glass strikes red, but the mechanism by which it acts has been an matter of discussion. In order to elucidate the role of tin in the formation of gold ruby glass, we have undertaken Mössbauer experiments with both ¹⁹⁷Au and ¹¹⁹Sn.

All measurements were performed at 4.2 K in a helium bath cryostat. Two different base glasses were used: a sodium silicate glass containing 26 wt.% of Na₂O and a soda lime glass (22 wt.% Na₂O, 8 wt.% CaO, 70 wt.% SiO₂). All glasses contained between 200 and 300 ppm of gold, and varying tin loadings going from 20 ppm to about 2 wt.% SnO₂.

Three spectral components can be distinguished in the ¹⁹⁷Au Mössbauer spectra:

- The single line of metallic gold at an isomer shift of -1.23 mm/s with respect to a source of metallic Pt.
- A quadrupole doublet with an isomer shift of 1.0 mm/s and a splitting of 6.2 mm/s attributable to Au(I) dissolved in the glass matrix [2].
- In some cases, a broad peak with no visible quadrupole splitting and a mean isomer shift of about -0.3 mm/s. Because of its resemblance to the one previously observed for gold nanoparticles in a mylar matrix [3], this component has been attributed to gold atoms on the surface of the gold particles.

The particle size of the gold metal particles can be estimated from the intensity ratio of the surface to the core component in the Mössbauer spectra. In fully annealed glasses with 0.2 wt.% or more Sn, the particles sizes were found to be 2 to 3 nm only. In annealed glasses containing 200 ppm or less tin, the particles are much larger, as can be concluded from the near absence of the surface component.

The UV-visible spectra of the studied samples confirmed these conclusions. In fact, the absorption maximum in the green region, typical for gold ruby glass, shifts to smaller wavelength when the tin content increases, as expected when the size of the gold particles decreases.

The kinetics of gold nanoparticle formation has been studied by isothermal annealing experiments of a sample of tin-free glass and one that contained 2.4 wt.% of SnO₂. These experiments show in a rather direct manner that the addition of tin to the gold ruby glass increases the speed of gold particle formation.

In the tin-rich annealed glasses, the ¹⁹⁷Au Mössbauer isomer shift of the spectral component attributed to core atoms in the gold nanoparticles shifts from -1.23 mm/s for tin-free glasses to slightly larger velocities, indicating that some tin is incorporated into the metallic particles.

This conclusion is supported by ¹¹⁹Sn Mössbauer measurements on the tin-containing glasses, in which a weak component with an isomer shift expected for a dilute alloy of tin in gold is seen in the annealed glasses in addition to the main component of tetravalent tin.

The experiments thus show that the presence of tin in gold ruby glasses increases the number of gold nanoparticles and decreases their size. A simple explanation of this effect is that tin might act as condensation nuclei for the gold particles. In such an hypothesis, when nucleation begins at more spots in the glass matrix, more particles are formed, but the overall content of gold then is insufficient to form particles larger than a few nm. The tin of the condensation nuclei remains incorporated into the metallic matrix of the gold nanoparticles in concentrations up to about 15 at.%. Alternative mechanisms may, however, also be considered and will be discussed in the light of the Mössbauer results.

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[2] Wagner, F.E., Haslbeck, S., Stievano, L., Calogero, S., Pankhurst, Q.A., and Martinek, K.-P., Nature 407 (2000) 691.

[3] Stievano, L., Santucci, S., Lozzi, L., Calogero, S. and Wagner, F.E., J. Non-Cryst. Solids 232-234 (1998) 644.