INFLUENCE OF RESIDUAL STRESS
ON
COLOR GENERATION OF GOLD RUBY GLASS

by

Tepiwan Jitwatcharakomol

Dept of Science Service, Min of Science and Technology, THAILAND
Contents

1. Introduction
2. Experimental
3. Results + conclusions
4. Next jobs
Introduction

• Gold Ruby Glass

An example of physical colors, original of color is the excitation of surface plasmon modes in metal nanoparticles
Light incident on a metal sets up a sinusoidally varying electric field. The electron around the metal atoms oscillates with the field. This sets up a polarization field which depends on the frequency of the light.

Spherical gold nanoparticles in 10-100 nm

http://www.primidi.com/2005/03/04.html
Transmission spectra and discussion

Absorption peak at 530 nm
Effect of size and shape

Credit: John Chandler, Tracey Gurmin, and Nicola Robinson, March 2000, IVD Technology Magazine
Self-striking gold ruby glass for food contact
\[4\text{Au}^0 + \text{Se}^{4+} \Leftrightarrow 4\text{Au}^+ + \text{Se}^0\]

\text{Low temp} \quad \text{High temp}

\text{Se}^{2-} \quad \text{Se}_{x}^{2-} \quad \text{Se}^0 \quad \text{Se}^{4+} \quad \text{Se}^{6+}

\text{Colorless} \quad \text{Brown} \quad \text{Pink} \quad \text{Colorless} \quad \text{Colorless}

\text{SeO}_2 \text{ is used as oxidizing agent}
Base glass composition

<table>
<thead>
<tr>
<th>Oxide</th>
<th>weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>71.29</td>
</tr>
<tr>
<td>CaO</td>
<td>10.89</td>
</tr>
<tr>
<td>Na₂O</td>
<td>10.89</td>
</tr>
<tr>
<td>K₂O</td>
<td>5.94</td>
</tr>
</tbody>
</table>

PbO was added 0.99 %

Au (as Au⁰) 200-450 ppm  Se (as SeO₂) 0-250 ppm  C 0-0.3 %
Experiments

Mixing → Melting

High Temperature Chamber Furnace
Carbolite model BLF1700

Alumina crucibles

melting schedule

0 15 30 45 60 75 90 105 120 135 150 165 180 195 210

0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600

temperature (°C)
time (min)
Experiments

Annealing

Gold ruby glass

Development of Gold ruby glass for glassware in contact with food
Experiments

Thermal properties

Dilatometer

Specimen size $0.5 \times 0.5 \times 4 \text{ cm}^3$
Au=250, Se=200 ppm, C=0
<table>
<thead>
<tr>
<th>SeO2 (ppm)</th>
<th>0</th>
<th>0.05</th>
<th>0.1</th>
<th>0.15</th>
<th>0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
</tr>
<tr>
<td>100</td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Au was fixed at 200 ppm
X-ray Absorption Near Edge Structure (XANES), fast scan
### Base glass composition

<table>
<thead>
<tr>
<th>Oxide</th>
<th>weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>71.29</td>
</tr>
<tr>
<td>CaO</td>
<td>10.89</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>10.89</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>5.94</td>
</tr>
</tbody>
</table>

B\(_2\)O\(_3\) LiO\(_2\) BaO in the amount of 0.99 % was replaced PbO

Au (as Au\(^0\)) 250 ppm Se (as SeO\(_2\)) 100 ppm C 0.1 %
Experimental

Viscometer fiber elongation

Size 5 cm
Experimental

Measurement of the stress in glasses

Strainmatic

Specimen size $3 \times 3 \times 1 \text{ cm}^3$
Experimental

- Chemical attack

Titration

H$_2$SO$_4$
0.02 N Methyl red indicator

Auto clave

PbO B$_2$O$_3$ BaCO$_3$ Li$_2$CO$_3$

Standard Test Methods for Resistance of Glass Containers to Chemical Attack

ASTM : C225 - 85
Results

![Graph showing the relationship between temperature (Temp, C) and log viscosity. The graph includes curves for different substances: B2O3 (blue), BaO (purple), Li2O (cyan), and PbO (red). The x-axis represents temperature in Celsius, ranging from 500 to 1500, and the y-axis represents log viscosity, ranging from 0 to 14. The curves show a decreasing trend as temperature increases.]
Results

- Chemical attack
Results

PbO  B\textsubscript{2}O\textsubscript{3}  BaO  Li\textsubscript{2}O
How does red color generation relate to residual mechanical stress
Patterns of stress corresponded with color strip
Good color: good stress
Overcolor was also get along with bad stress
<table>
<thead>
<tr>
<th>C(%wt)</th>
<th>0</th>
<th>0.05</th>
<th>0.1</th>
<th>0.15</th>
<th>0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SeO2 (ppm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
</tr>
<tr>
<td>100</td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C(%wt)</th>
<th>0</th>
<th>0.05</th>
<th>0.1</th>
<th>0.15</th>
<th>0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SeO2 (ppm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
<td><img src="image15.png" alt="Image" /></td>
</tr>
<tr>
<td>100</td>
<td><img src="image16.png" alt="Image" /></td>
<td><img src="image17.png" alt="Image" /></td>
<td><img src="image18.png" alt="Image" /></td>
<td><img src="image19.png" alt="Image" /></td>
<td><img src="image20.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Conclusion

=Self striking gold ruby is possible but for replacing PbO, some work need more to be done

=Mechanical stress is one of the key to generate steady color
Thank you for your attention!