INFLUENCE OF RESIDUAL STRESS ON COLOR GENERATION OF GOLD RUBY GLASS

by

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Contents

Introduction

An example of physical colors, original of color is the excitation of surface plasmon modes in metal nanoparticles

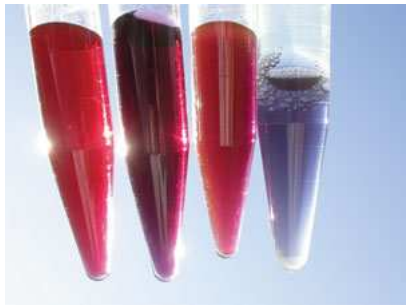
- Gold Ruby Glass

Wine Glass

Brandenburg Cup

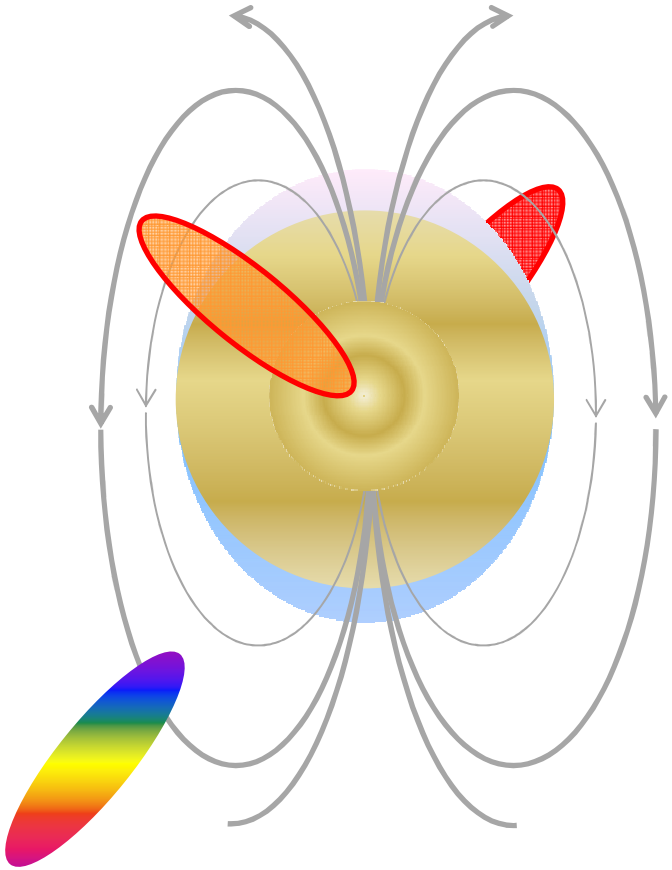
nanoparticle plasmon resonance

reflected light



transmitted light

http://www.primidi.com/2005/03/04.html



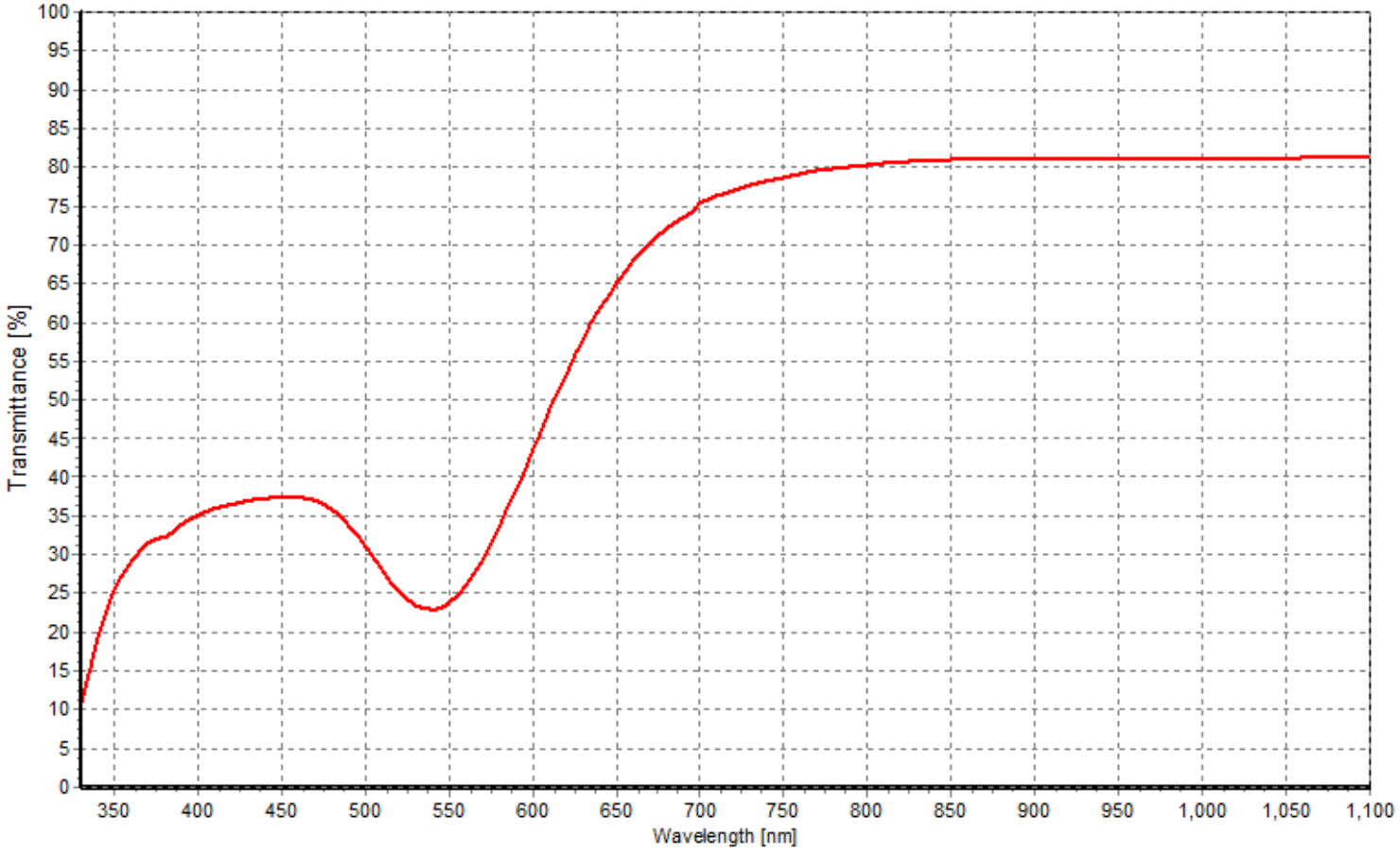
Light incident on a metal sets up a sinusoidally varying electric field

The electron around the metal atoms oscillates with the field

This sets up a polarization field which depends on the frequency of the light

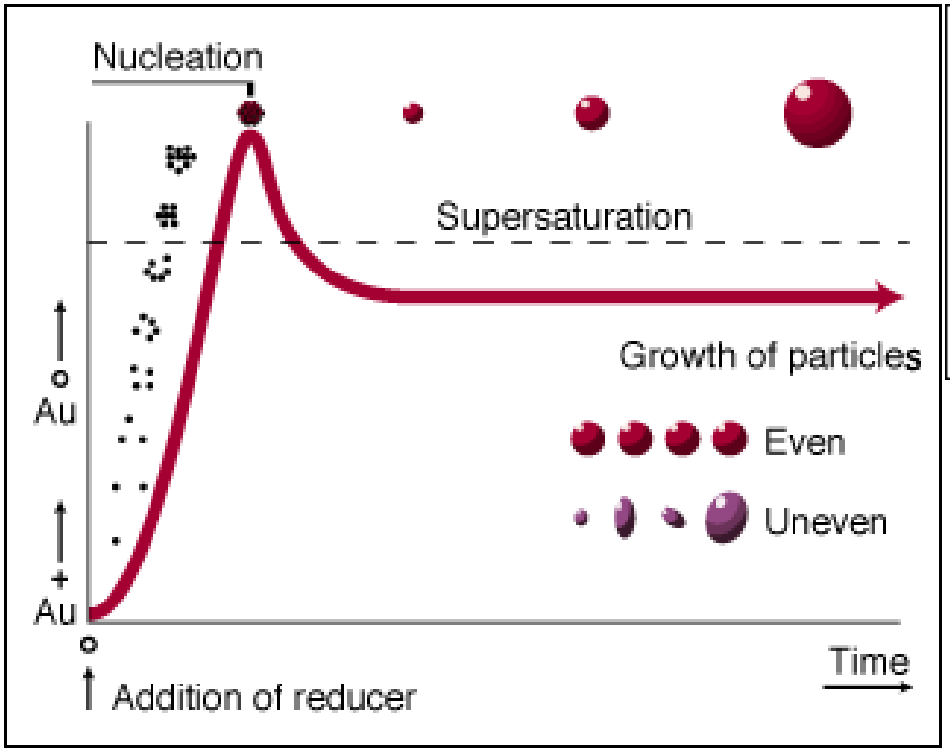
Spherical gold nanoparticles in 10-100 nm

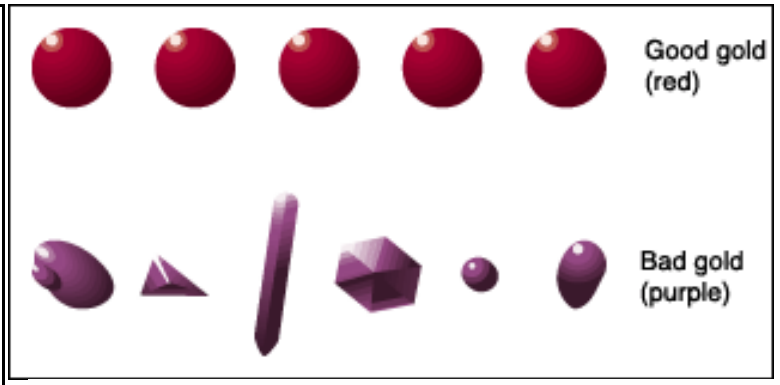
Transmission spectra

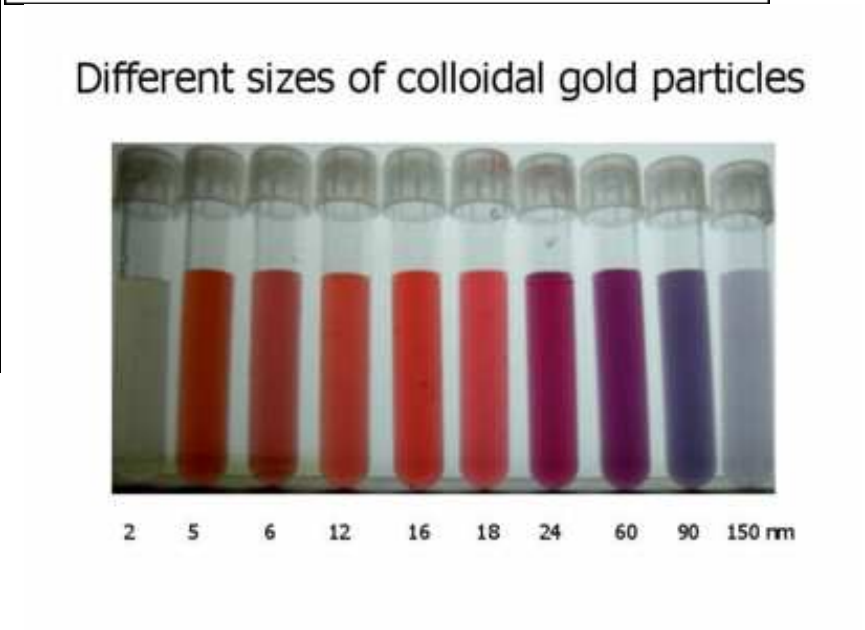


Absorption peak at 530 nm

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

$$4Au^0 + Se^{4+} <=> 4Au^+ + Se^0$$

Low temp High temp

$$Se^{2-} \leftarrow\square\rightarrow \mathbf{Se_x^{2-}} \leftarrow\square\rightarrow Se^0 \leftarrow\square\rightarrow Se^{4+} \leftarrow\square\rightarrow Se^{6+}$$

Colorless **Brown** **Pink** **Colorless** **Colorless**

SeO_2 is used as oxidizing agent

Base glass composition

Oxide	weight %
SiO_2	71.29
CaO	10.89
Na_2O	10.89
K_2O	5.94

PbO was added 0.99 %

Au (as Au^0) 200-450 ppm Se (as SeO_2) 0-250 ppm C 0-0.3 %

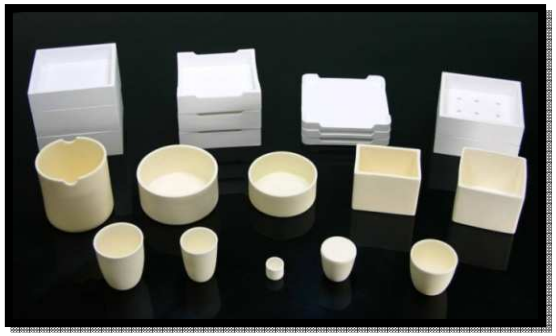
Experiments

High Temperature
Chamber Furnace
Carbolite model BLF1700

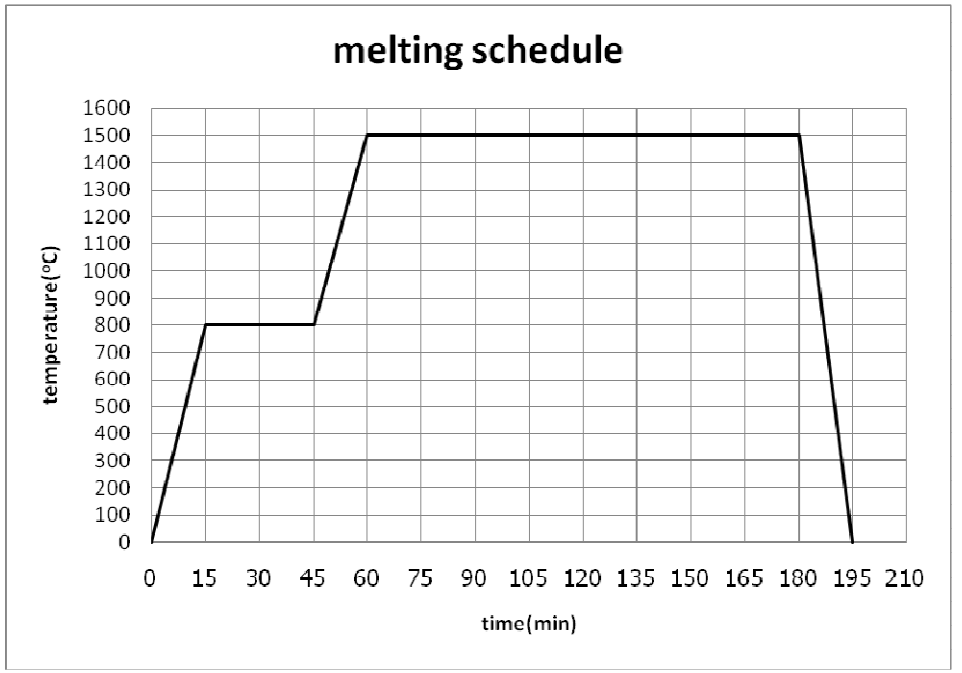
Mixing

↓

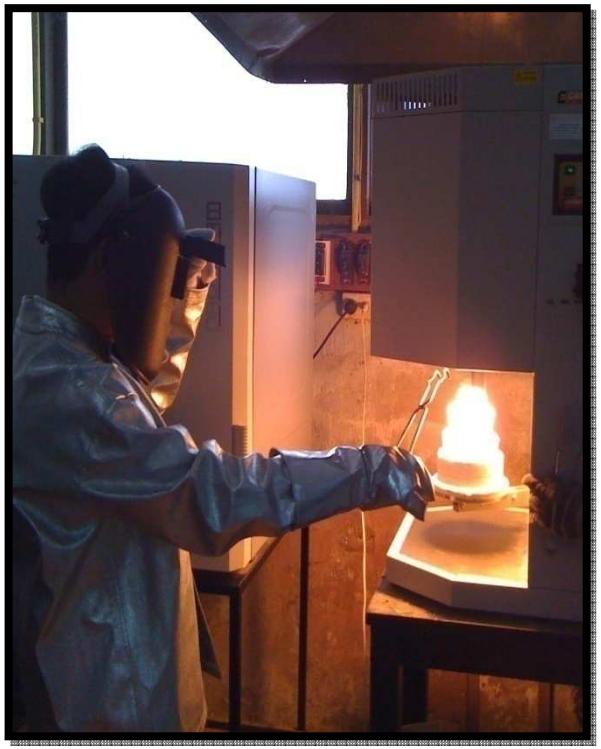
Melting



Alumina crucibles

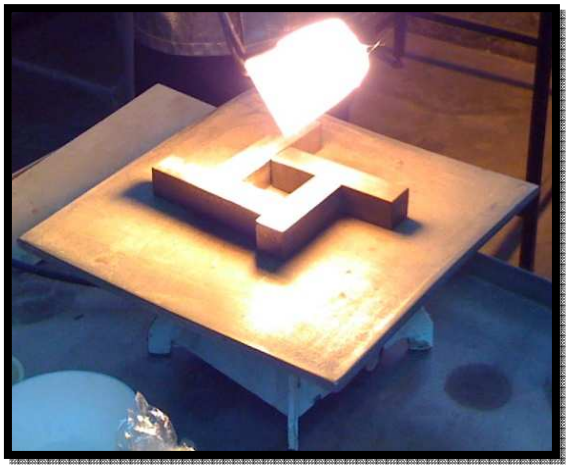


Experiments



Annealing

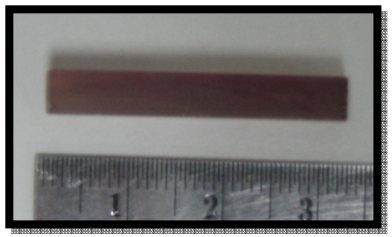
Gold ruby glass

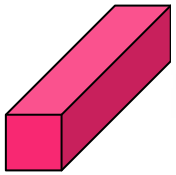


Experiments

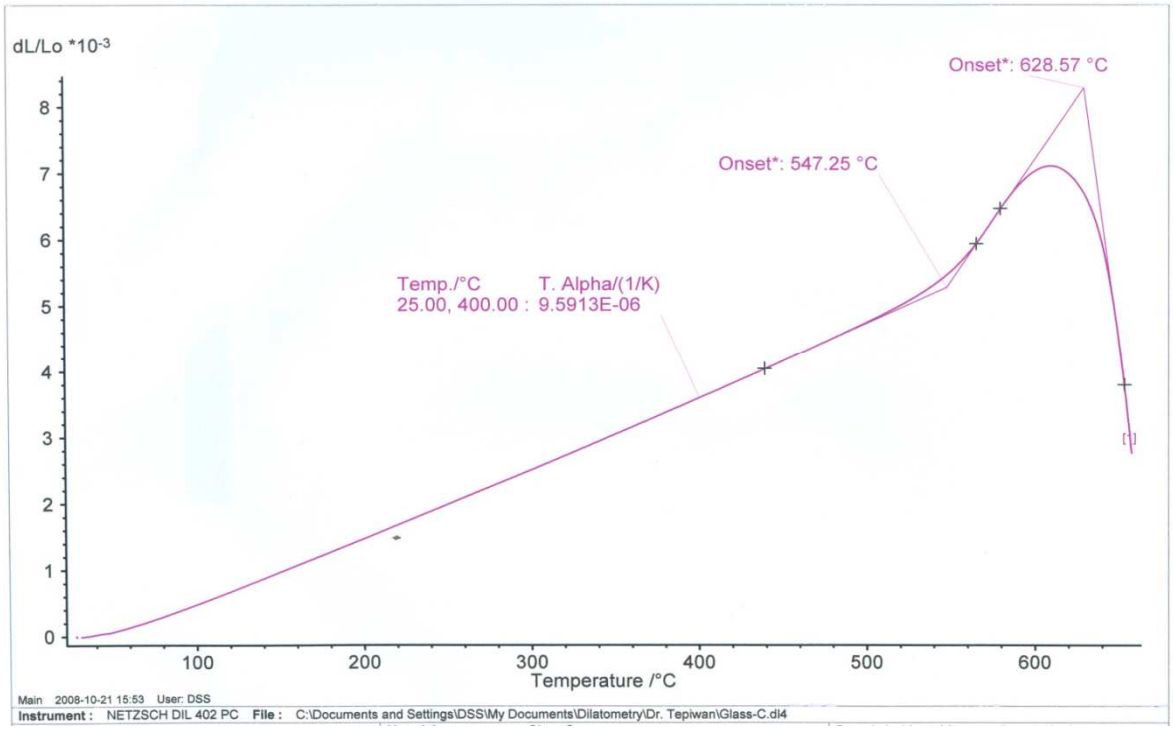
Thermal properties

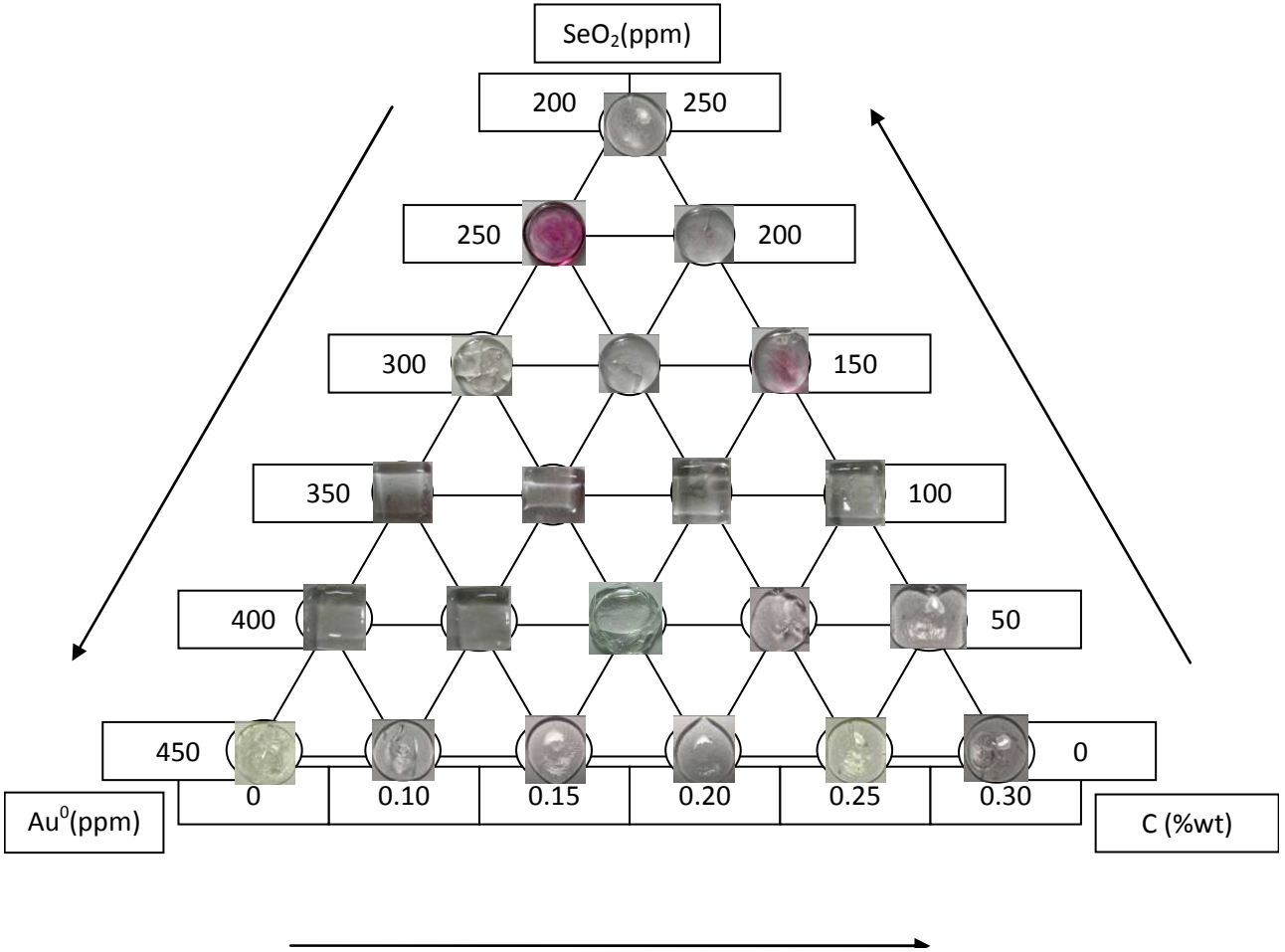
Dilatometer





Specimen size 0.5 × 0.5 × 4 cm^3

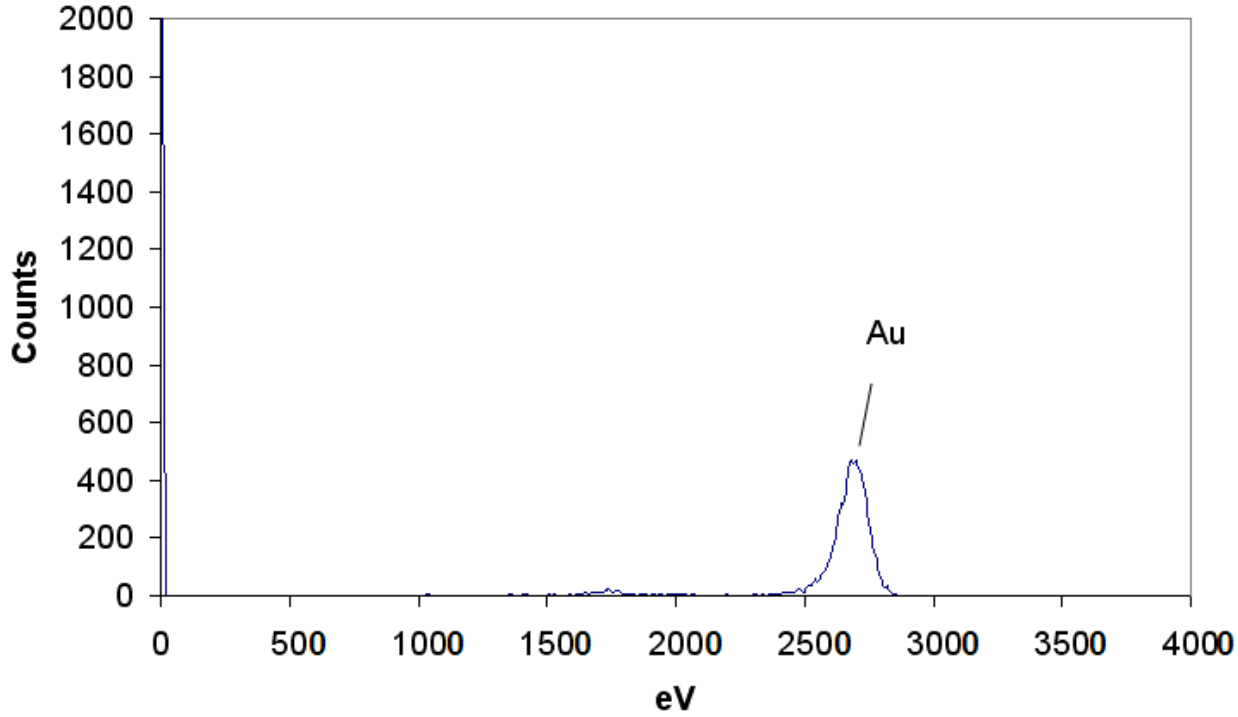




Au=250, Se=200 ppm, C=0

C(%wt) / SeO2 (ppm)	0	0.05	0.1	0.15	0.2
0					
50					
100					

Au was fixed at 200 ppm



X-ray Absorption Near Edge Structure(XANES), fast scan

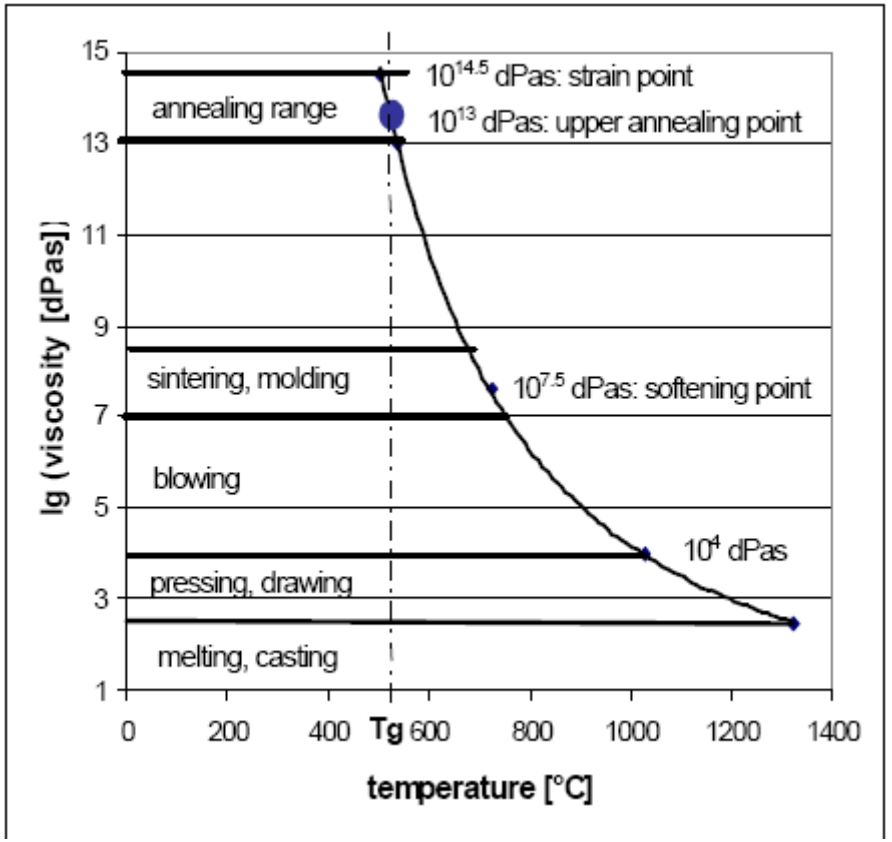
Base glass composition

Oxide	weight %
SiO_2	71.29
CaO	10.89
Na_2O	10.89
K_2O	5.94

B_2O_3 LiO_2 BaO in the amount of 0.99 % was replaced PbO

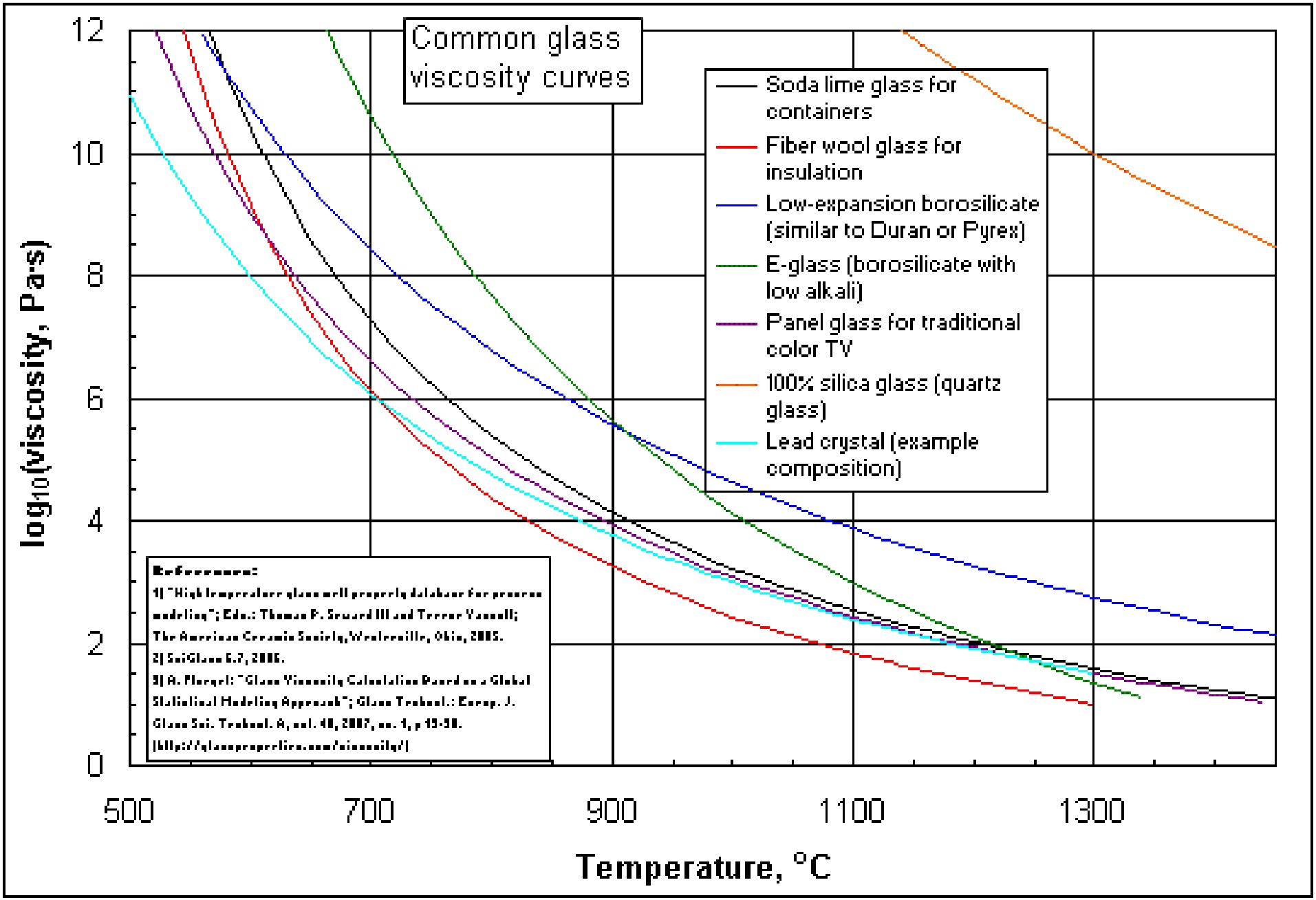
Au (as Au^0) 250 ppm Se (as SeO_2) 100 ppm C 0.1 %

Experimental



Size 5 cm

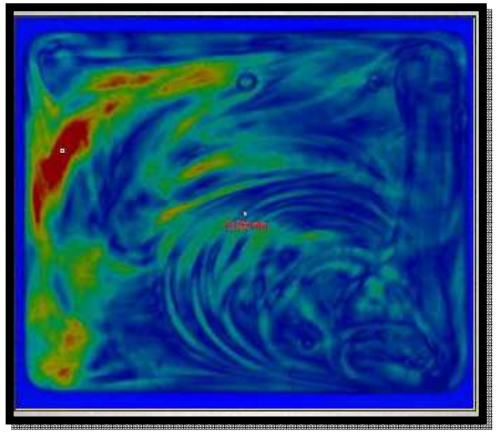
Viscometer fiber elongation

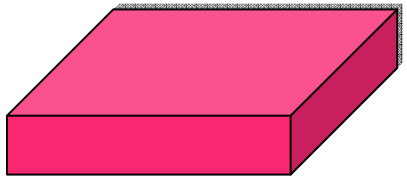

Common glass viscosity curves
Soda lime glass for containers
Fiber wool glass for insulation
Low-expansion borosilicate (similar to Duran or Pyrex)
E-glass (borosilicate with low alkali)
Panel glass for traditional color TV
100% silica glass (quartz glass)
Lead crystal (example composition)
log10(viscosity, Pa·s)
Temperature, °C
0
2
4
6
8
10
12
500
700
900
1100
1300

Experimental

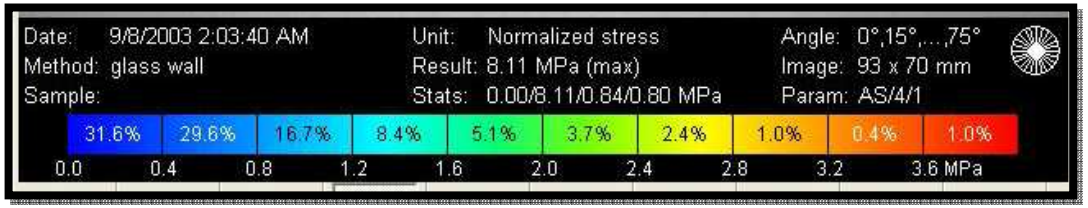
Measurement of the stress in glasses

Strainmatic





Specimen size 3 × 3 × 1 cm^3

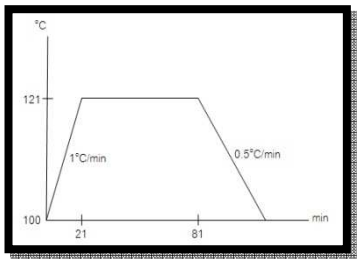


Experimental

- Chemical attack

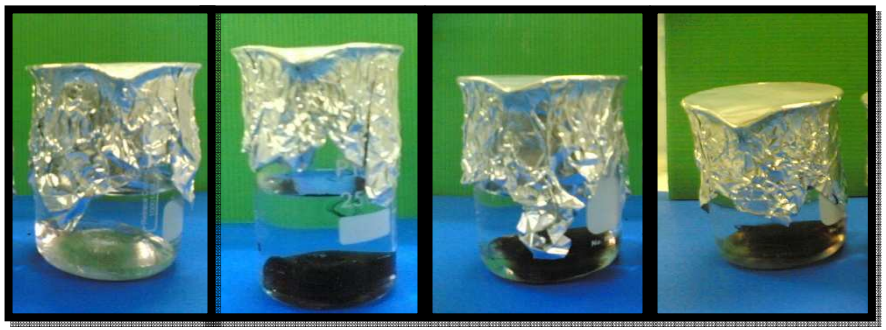
Titration

Auto clave



H_2SO_4 0.02 N

Methyl red indicator

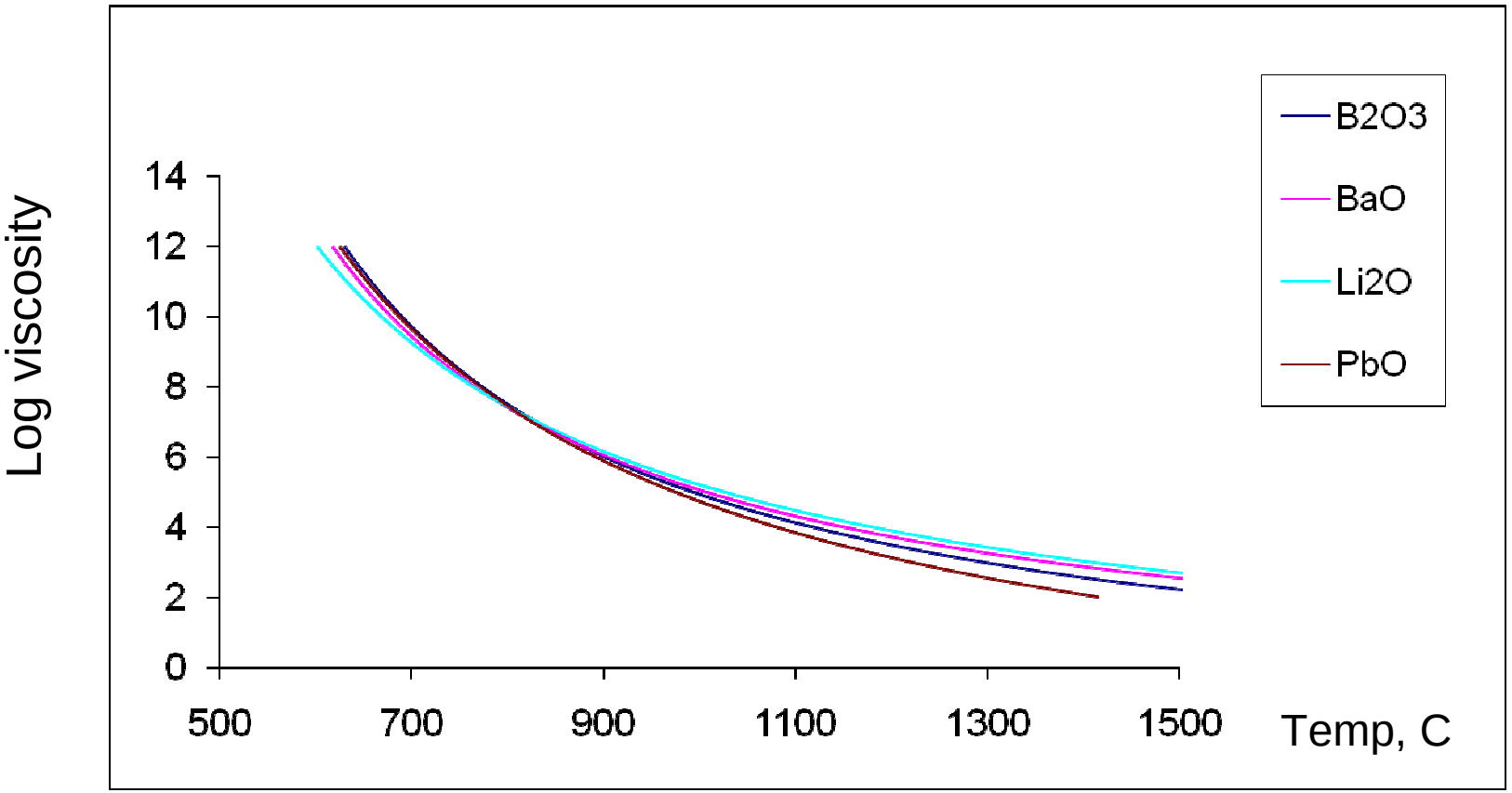


PbO B_2O_3 $BaCO_3$ Li_2CO_3

Standard Test Methods for Resistance of Glass Containers to Chemical Attack

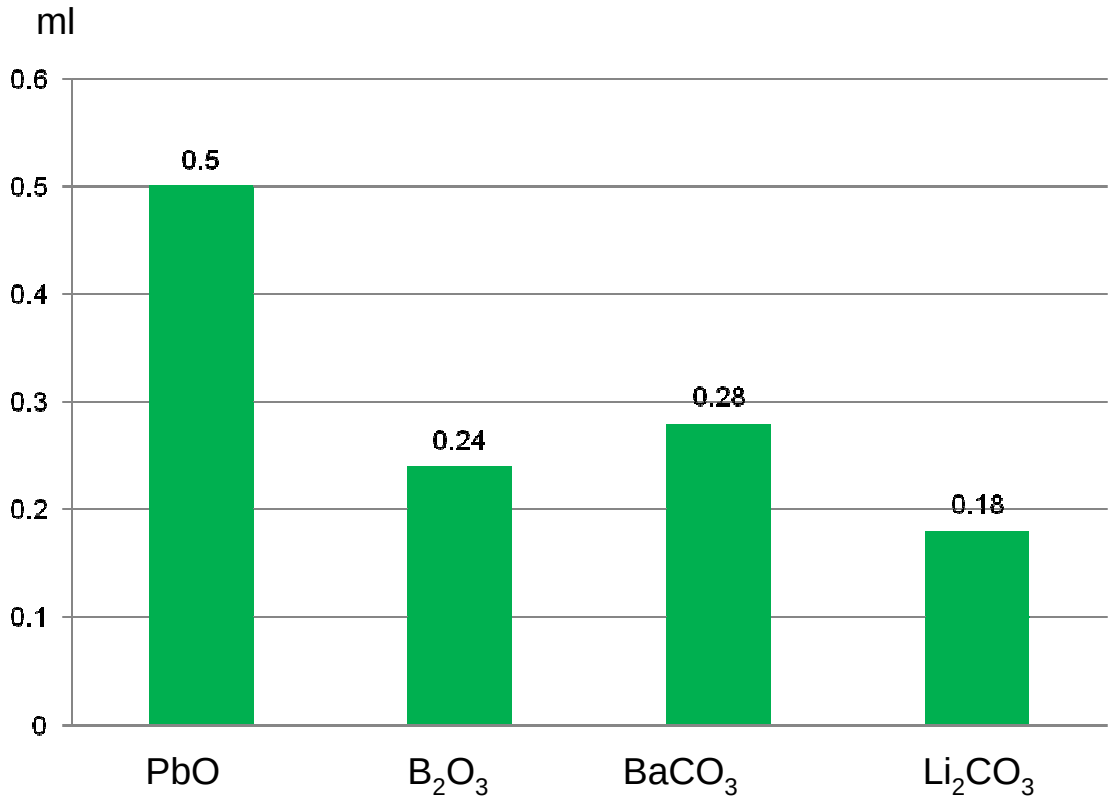
ASTM : C225 - 85

Results


Log viscosity
14
12
10
8
6
4
2
0
500
700
900
1100
1300
1500
Temp, C
B2O3
BaO
Li2O
PbO

Results

- Chemical attack



Results

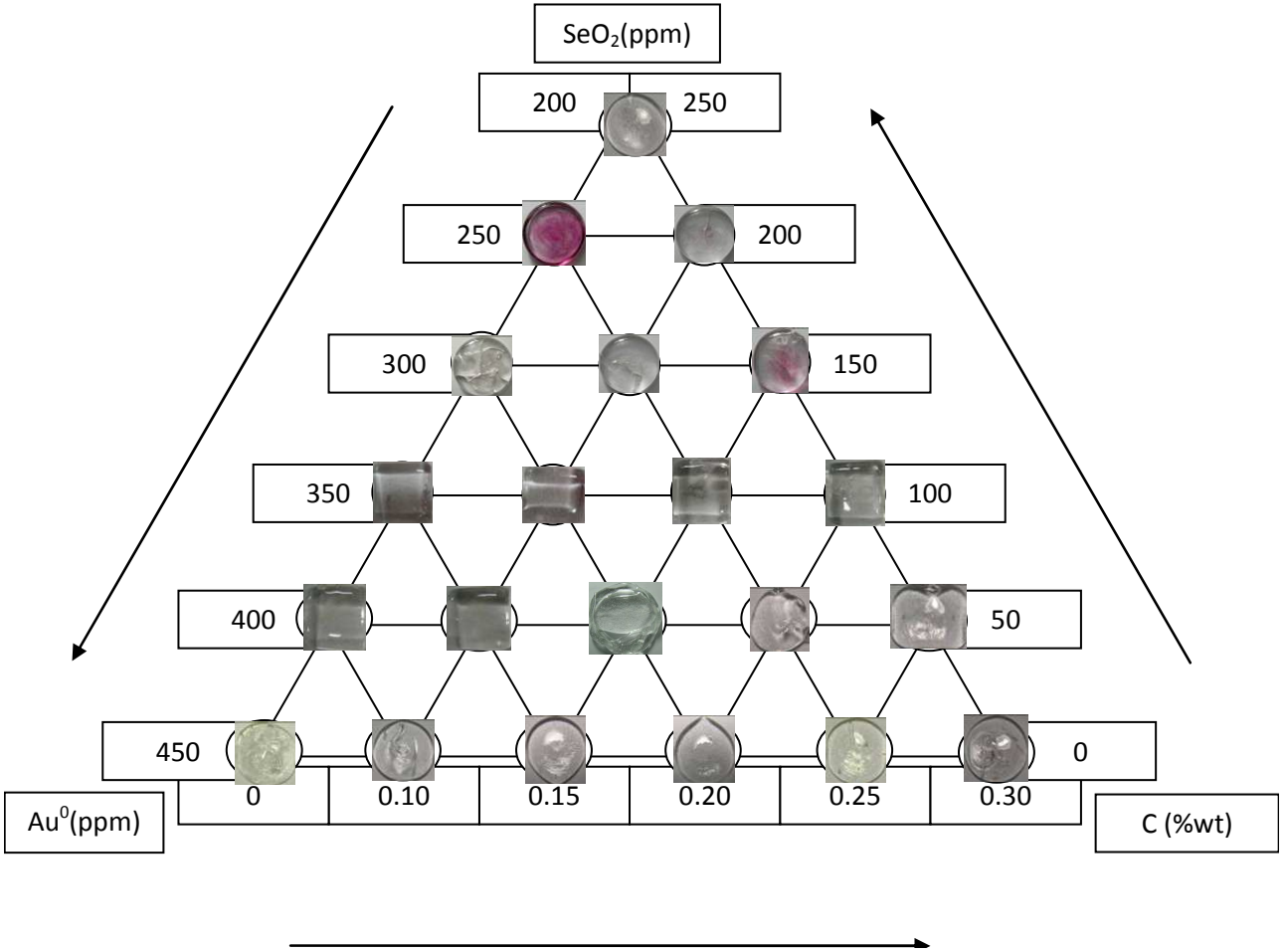
PbO

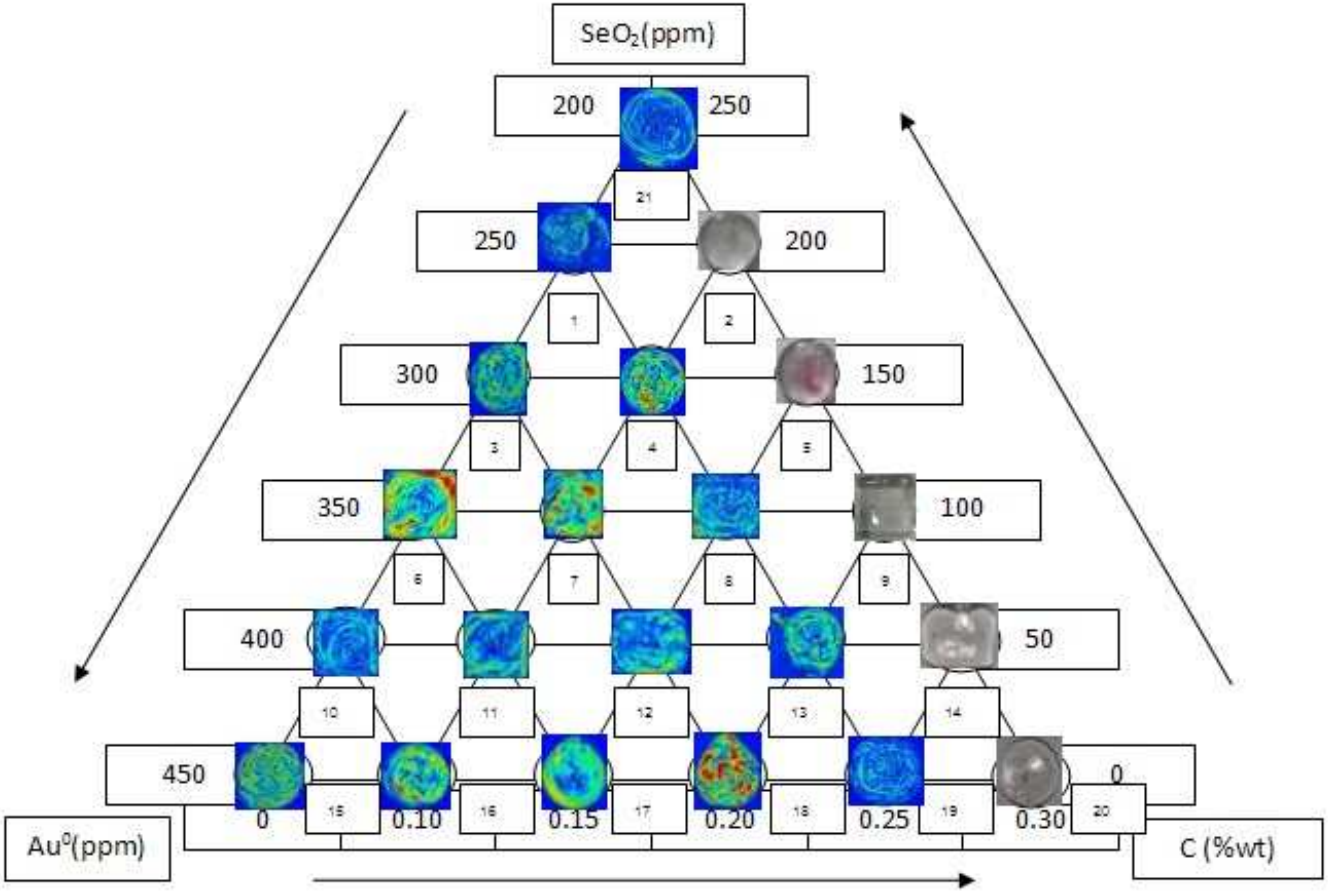
B_2O_3

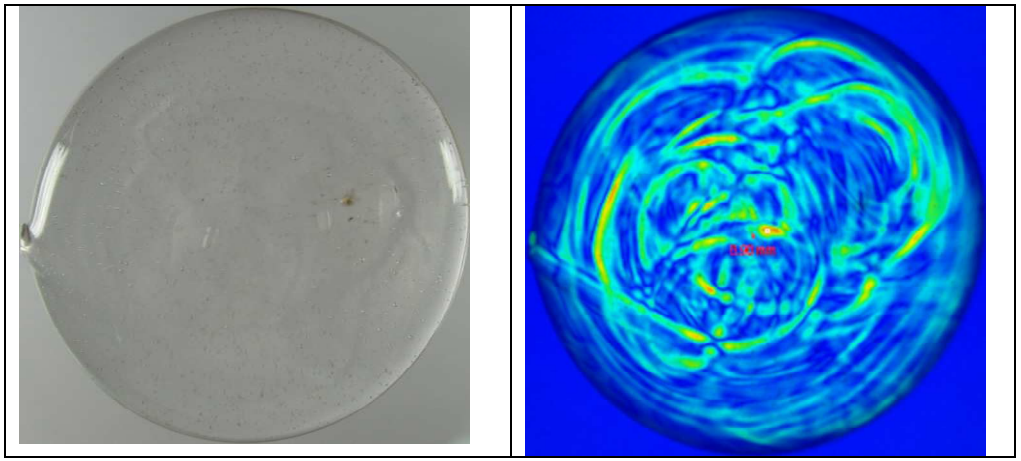
BaO

Li_2O

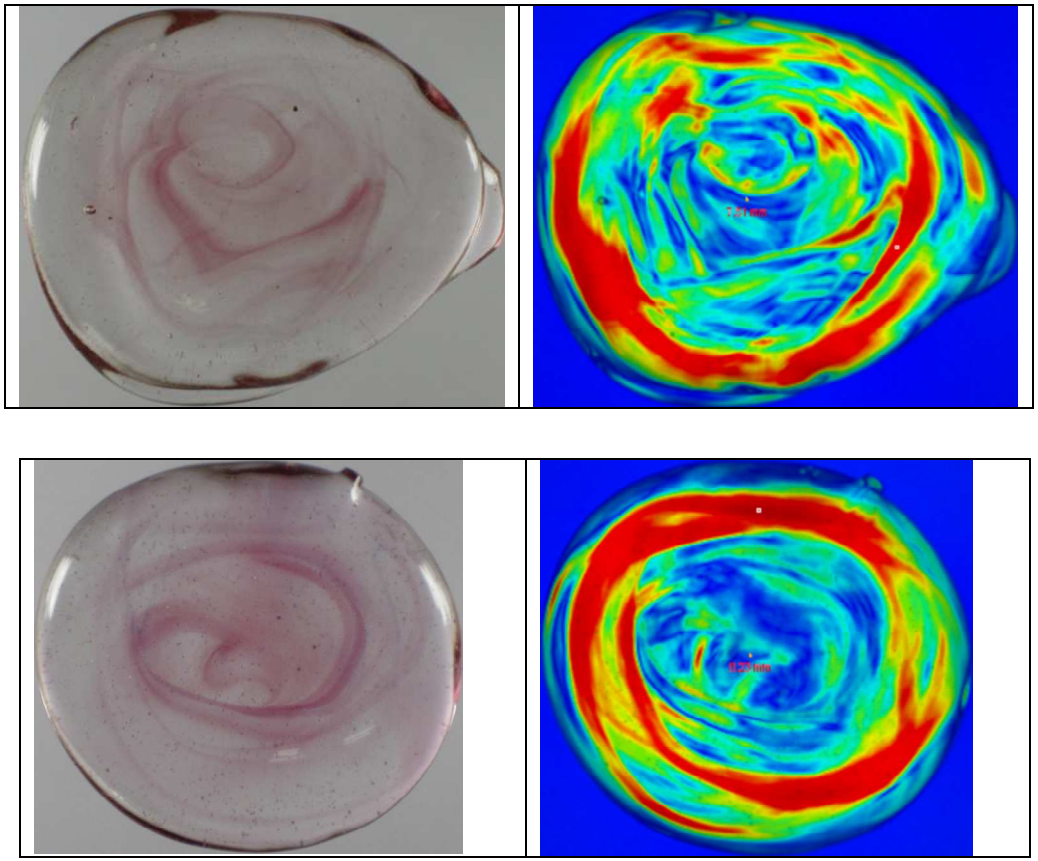
How does red color generation relate to residual mechanical stress


SeO2(ppm)
200
250
250
200
300
150
350
100
400
50
450
0
0
0.10
0.15
0.20
0.25
0.30
Au0(ppm)
C (%wt)

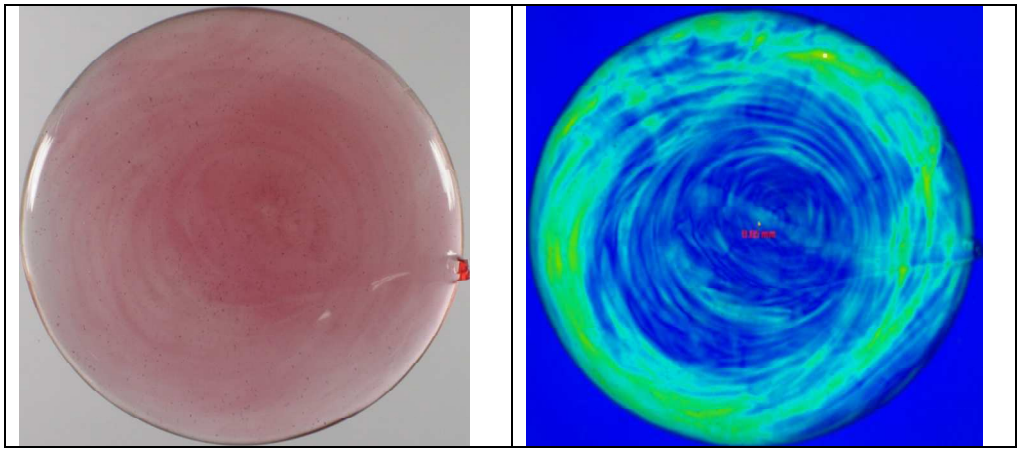

SeO2(ppm)
200
250
21
250
200
1
2
300
150
3
4
5
350
100
6
7
8
9
400
50
10
11
12
13
14
450
0
15
0.10
16
0.15
17
0.20
18
0.25
19
0.30
20
Au0(ppm)
C (%wt)

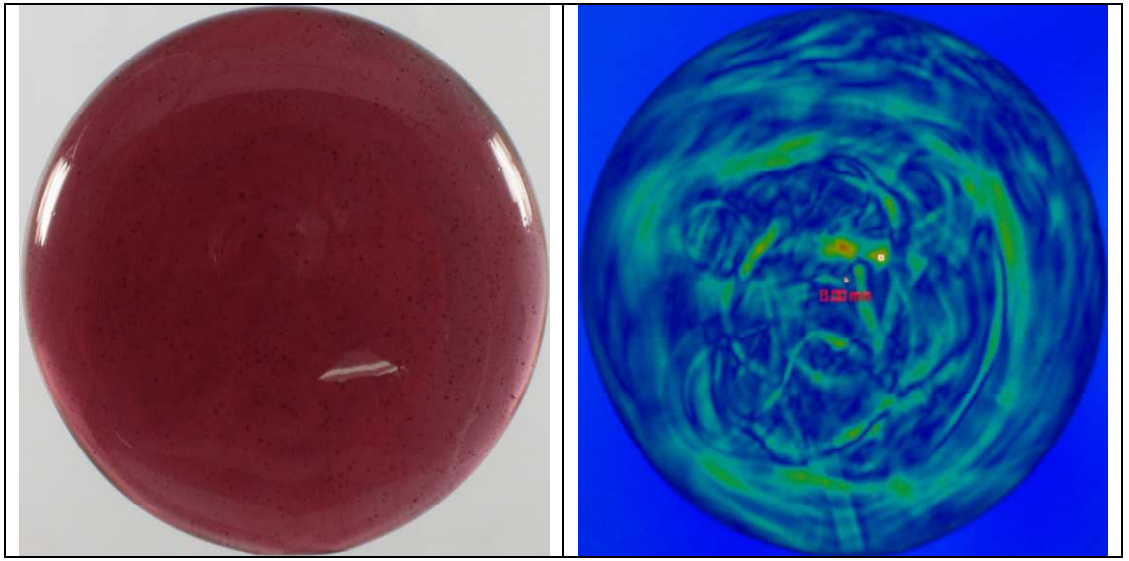


No gold dispersed

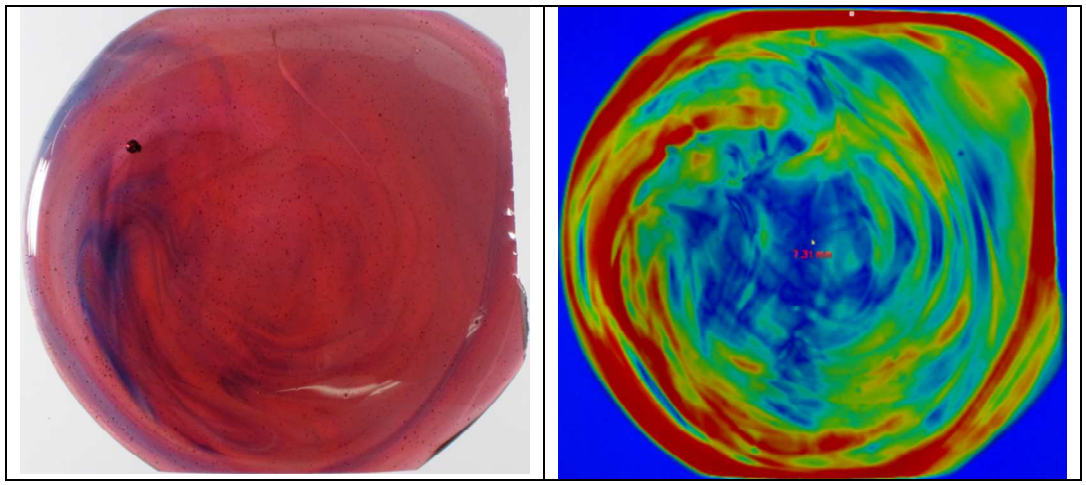


Patterns of stress corresponded with color strip



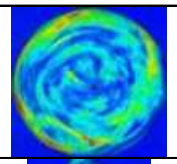
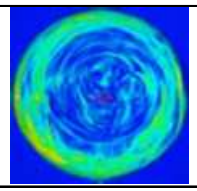
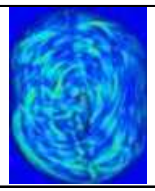
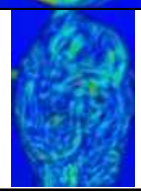
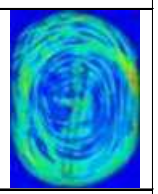
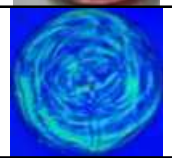


Good color: good stress



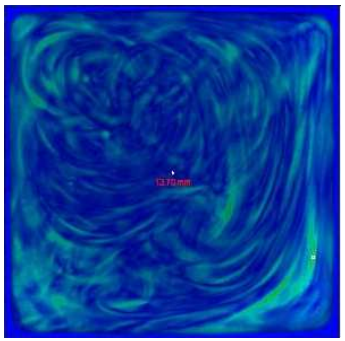
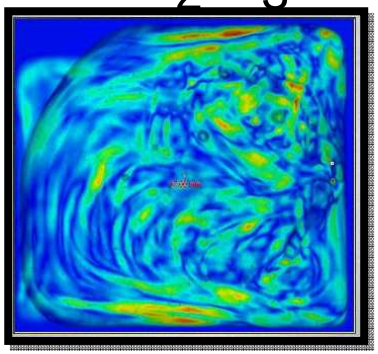
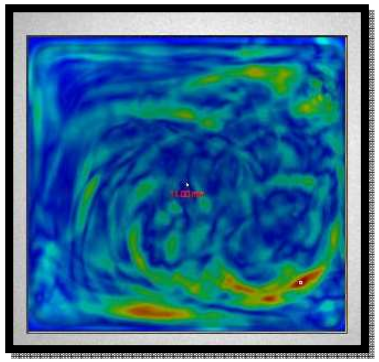
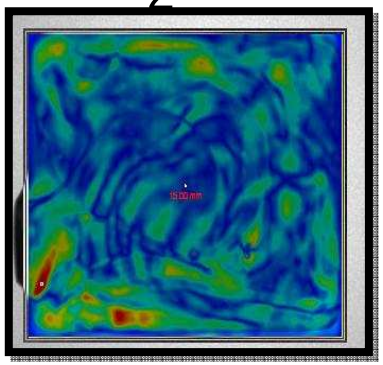
Overcolor was also get along with bad stress

C(%wt) / SeO2 (ppm)	0	0.05	0.1	0.15	0.2
0					
50					
100					

C(%wt) / SeO2 (ppm)	0	0.05	0.1	0.15	0.2
0					
50					
100					




PbO B_2O_3 BaO Li_2O

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 !