Controlling Rehydration in Sol-Gel Silicate Glasses

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REs in Sol-Gel Glasses

- Dopant concentrations of ~10% can be included without loss of optical quality
- Fluorescence yield is lower than expected
- Two main causes of fluorescence quenching
  - Excitation of hydroxyl and matrix vibrations
  - Energy transfer within RE clusters

Sol Gel Silicate Glass

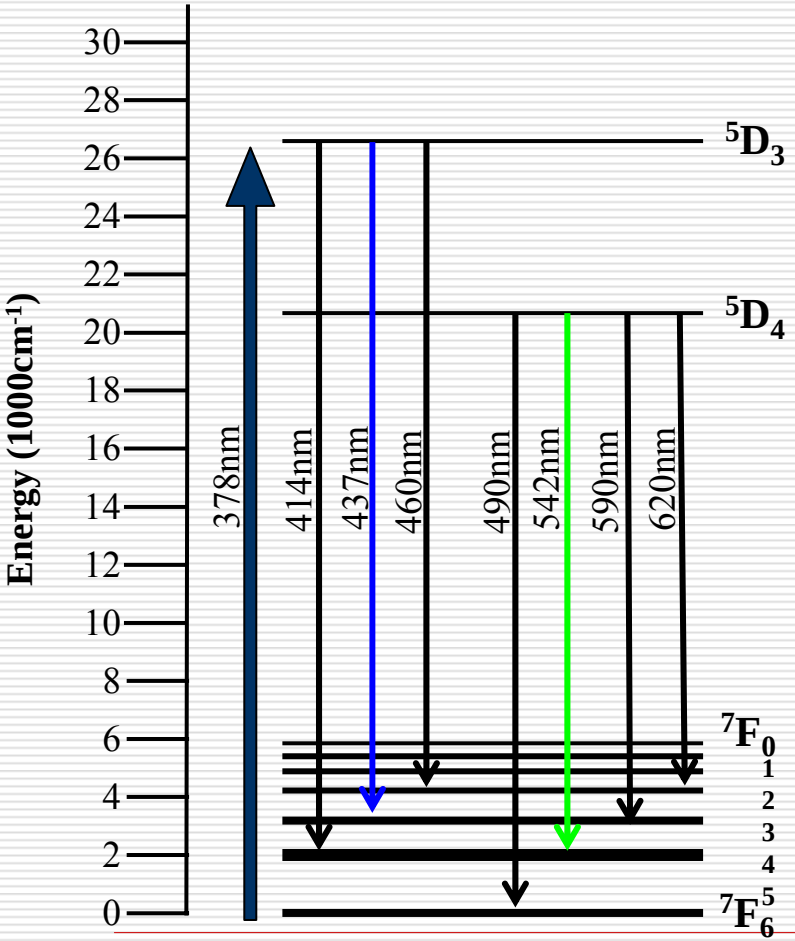
Synthesis

- Sol: TMOS + H_2O (with catalytic acid)
- Gel: Aging at 25°C and 60°C
  Drying at 90°C and 110°C
- Glass: Annealing to ≥850°C

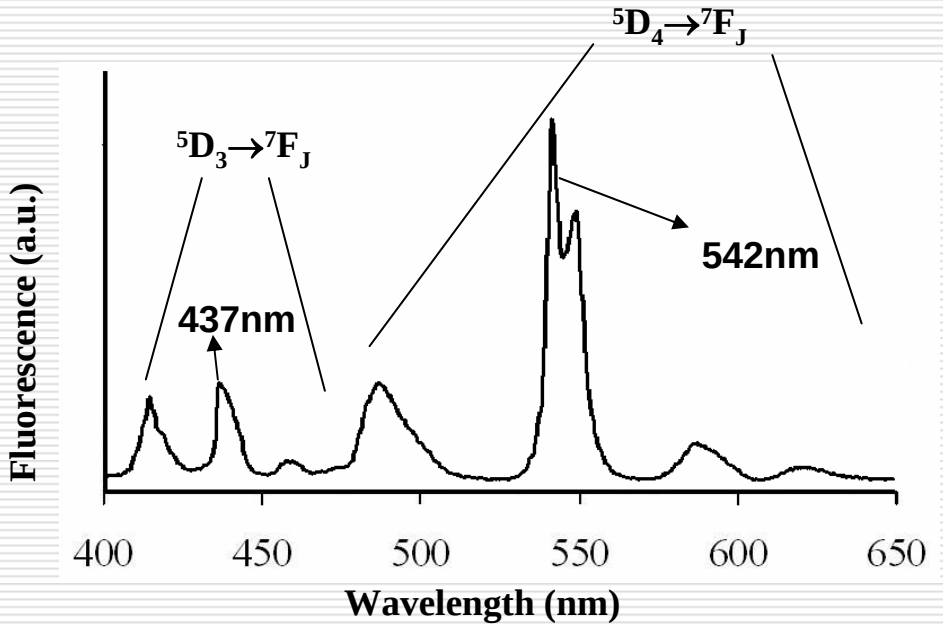
Properties

- Interconnected nano-porous network
  pore size ~ 2nm; pore volume fraction ~30%
- Density
  (1.5gcm^{-3} vs. 2.2gcm^{-3} for vitreous silica)

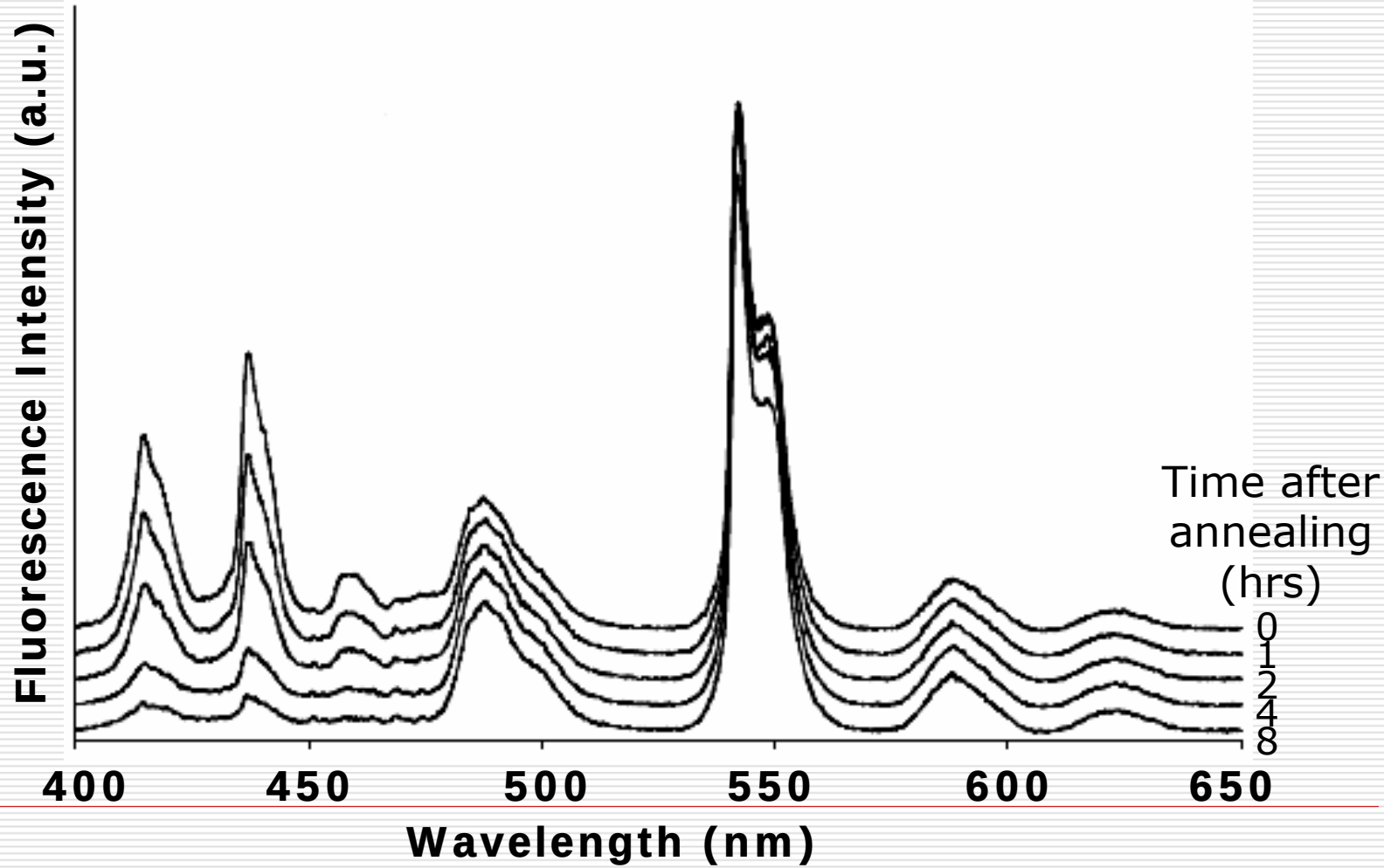
Energy Levels of Tb^{3+}



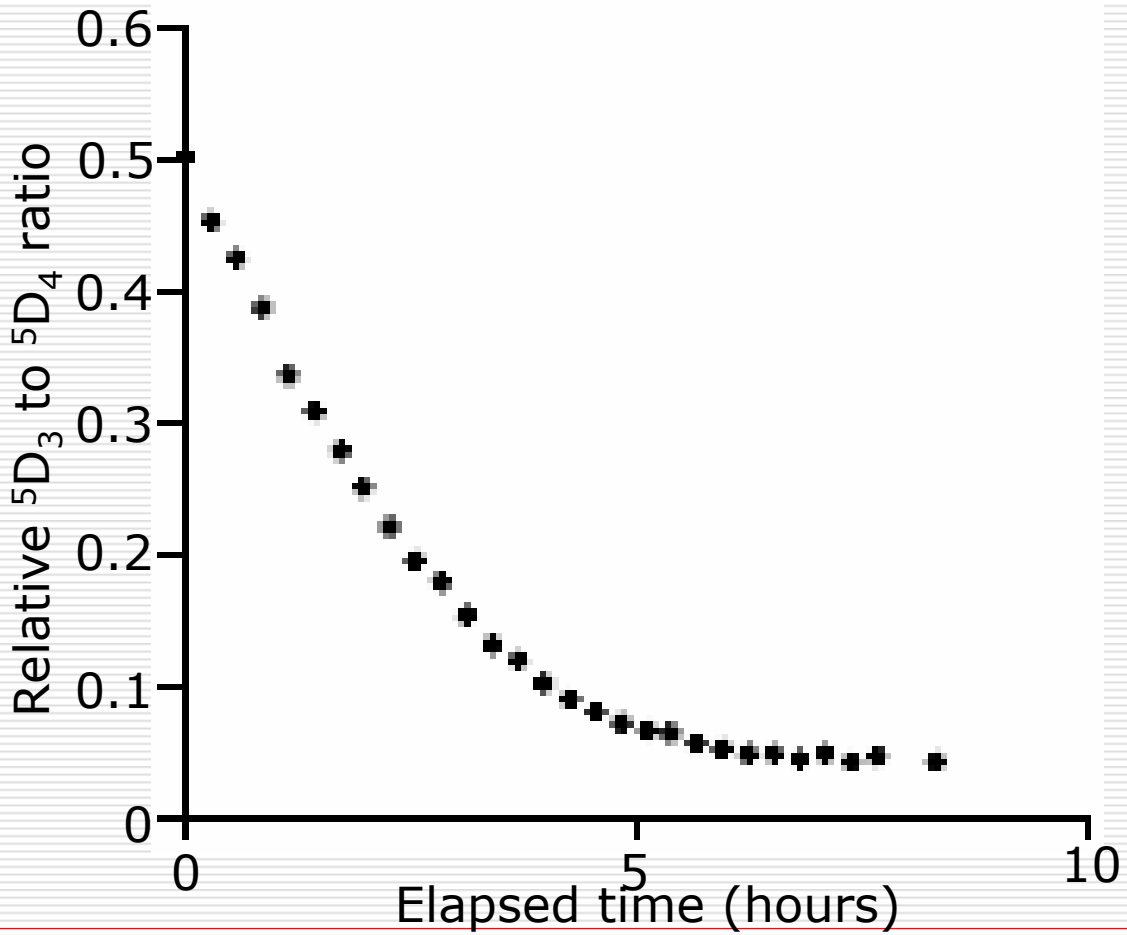
Emission Spectrum (λ_{exc}=240nm)



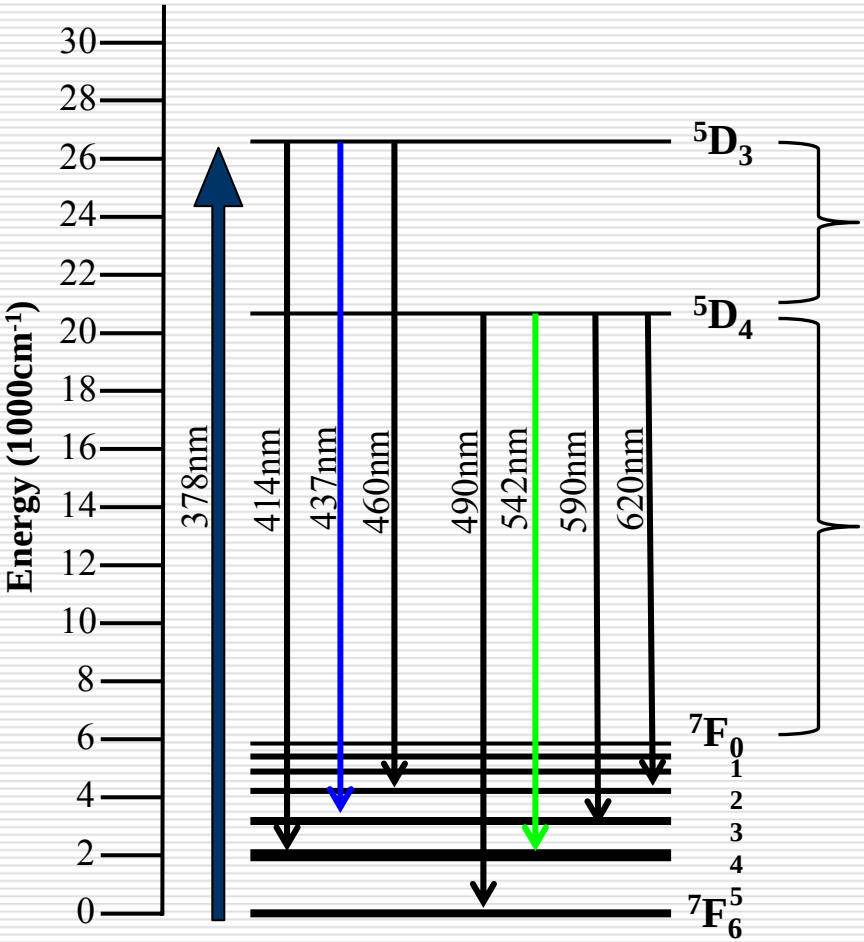
Rehydration in sol-gel glasses: Standard Recipe



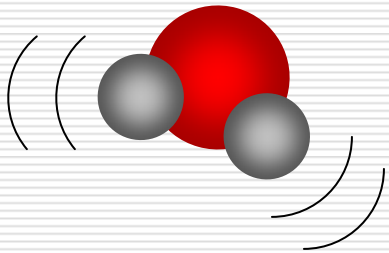
Rehydration Quenches Terbium Emission



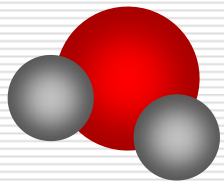
Selectivity in Rehydration Effect for Terbium Emission



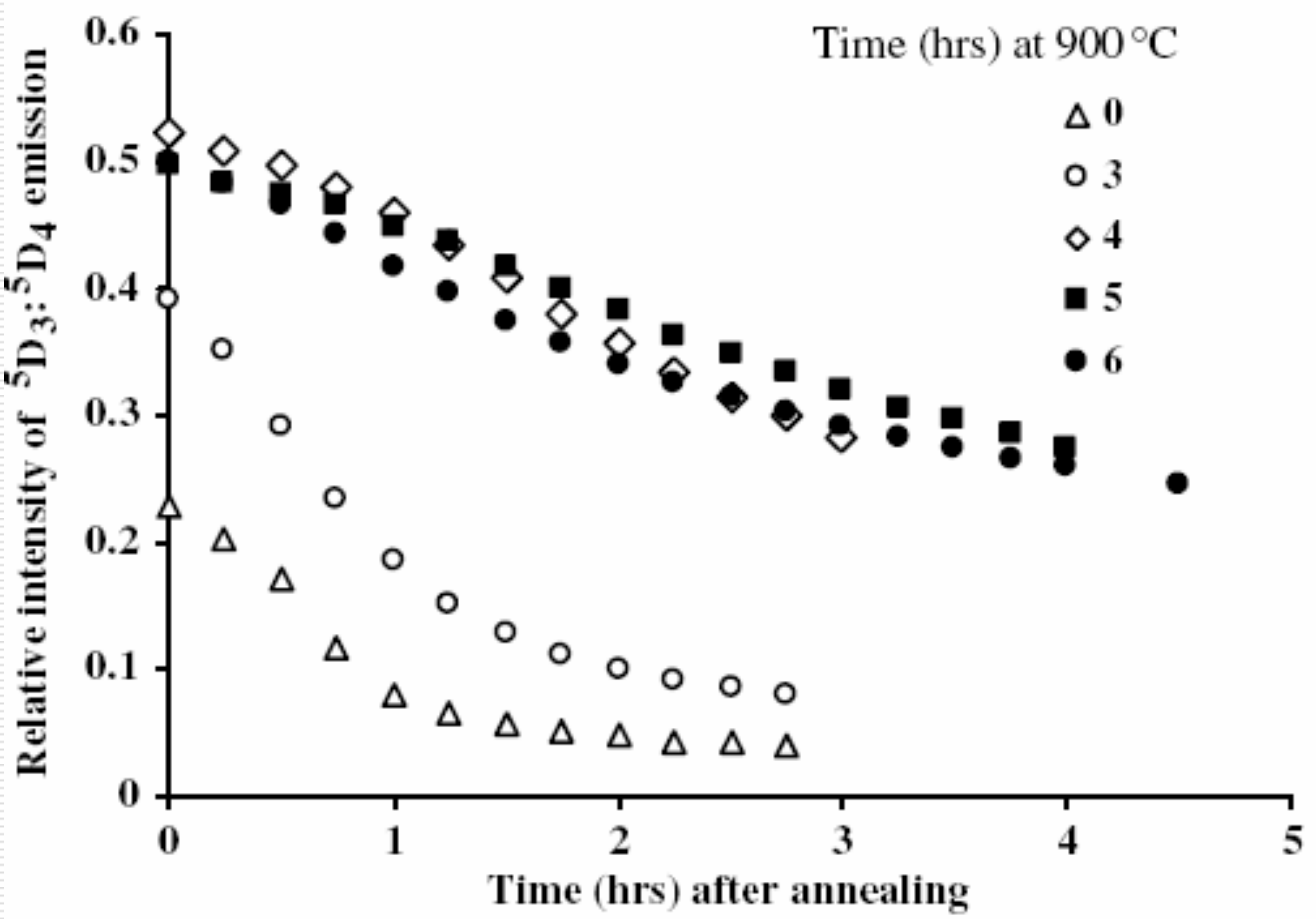
ΔE can be bridged by H_20 and matrix vibrations



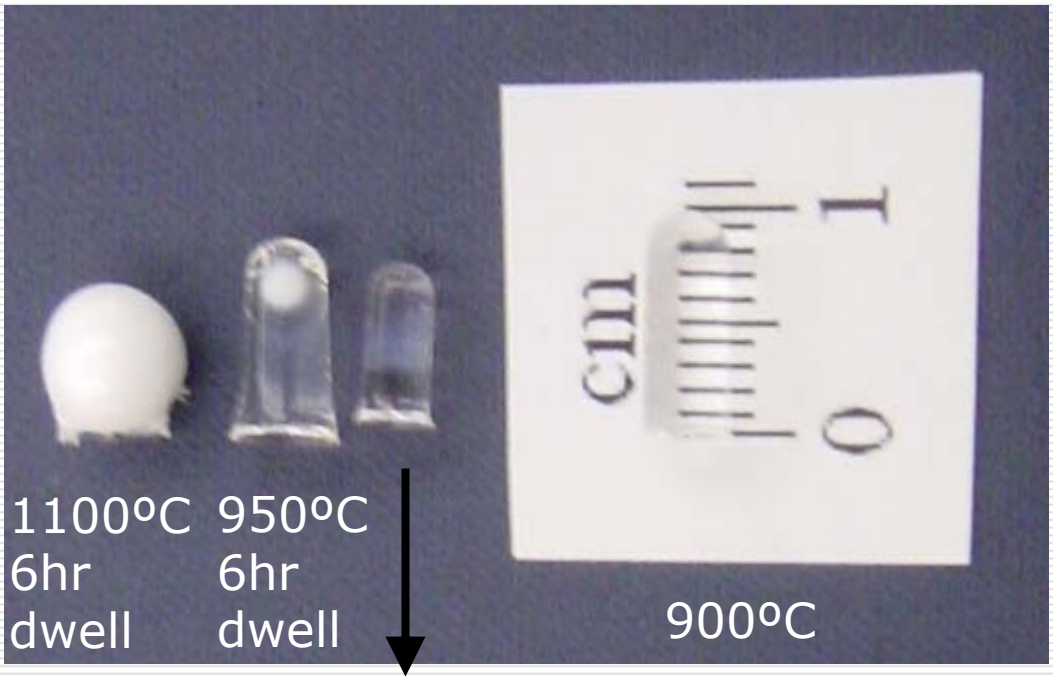
ΔE large, thus much less suited for vibrational quenching



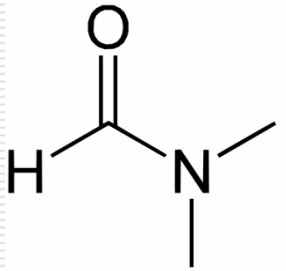
Effect of Annealing on Rehydration



Viscous Flow with Annealing



Adding DMF

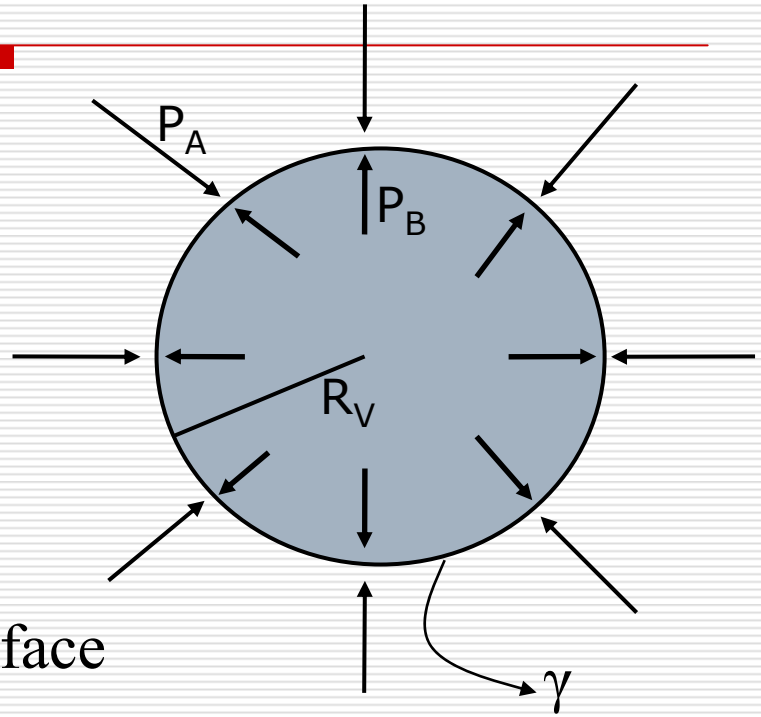


- DMF = N,N-dimethylformamide
- DMF is mixed with precursor solution
- DMF acts as a DCCA—Drying Control Chemical Additive.

Fluid	Boiling Point (˚C)	Surface Tension (dynes/cm)	Density (g/cm³)
Water	100	72.9	1.00
Methanol	64.7	22.7	0.79
DMF	153	36.8	0.94

Laplace-Young Equation: Capillary Pressure

$$\Delta P = \frac{2\gamma}{R_V}$$



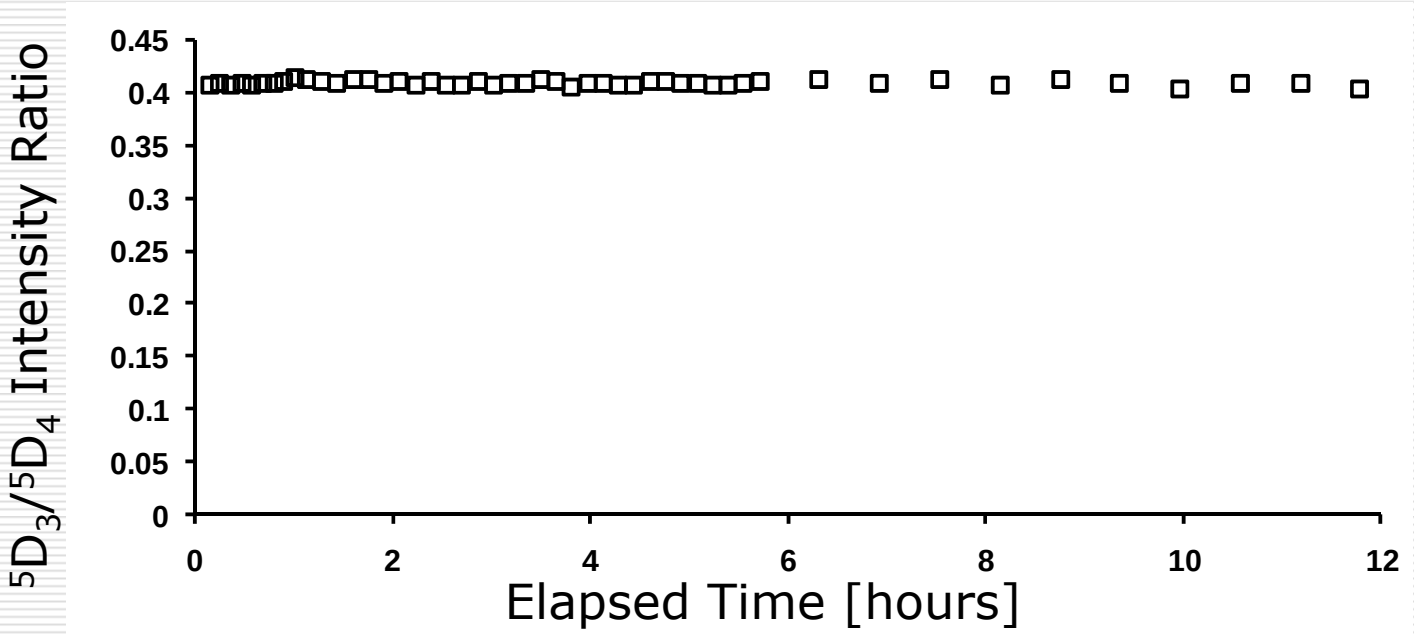
ΔP = pressure difference at interface

R_V = average pore radius

γ = surface tension at the pore interface

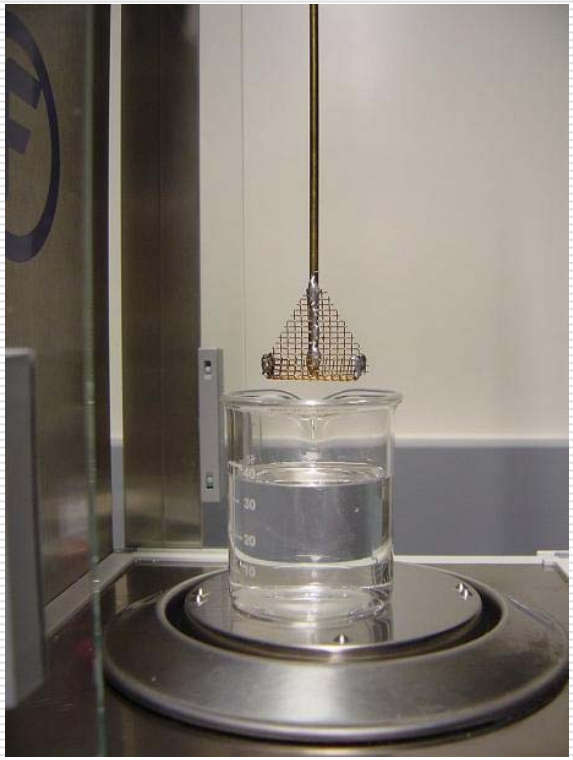
Rehydration in DMF sol-gel glasses

DMF-sol gel glass. 0.02%Tb, 1050C and 6h dwell.



$^5D_3/^5D_4$ Intensity Ratio = constant= 0.409±0.001

Density Measurement: Archimedes Principle



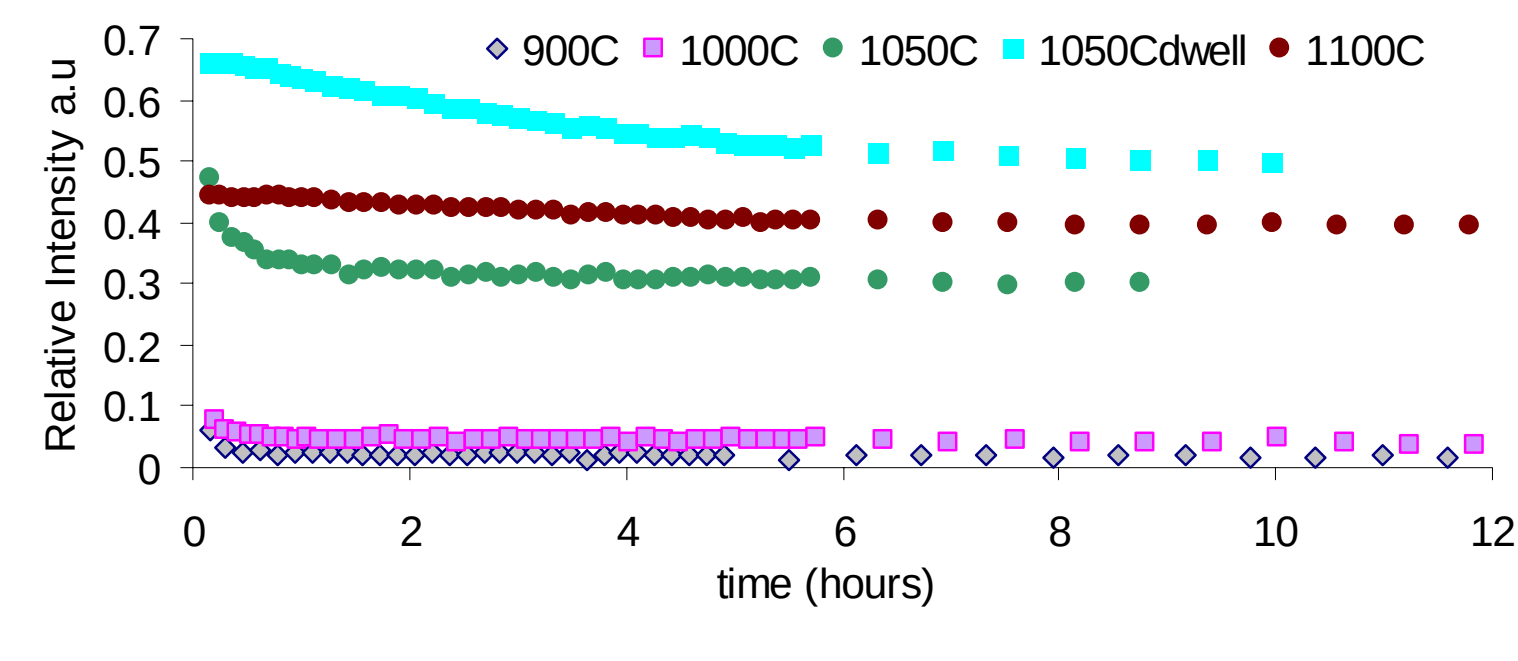
Metal "boat" suspended above fluid on scale.

- Buoyant force determined from relative weight in fluid.
- Time dependent buoyancy capability.

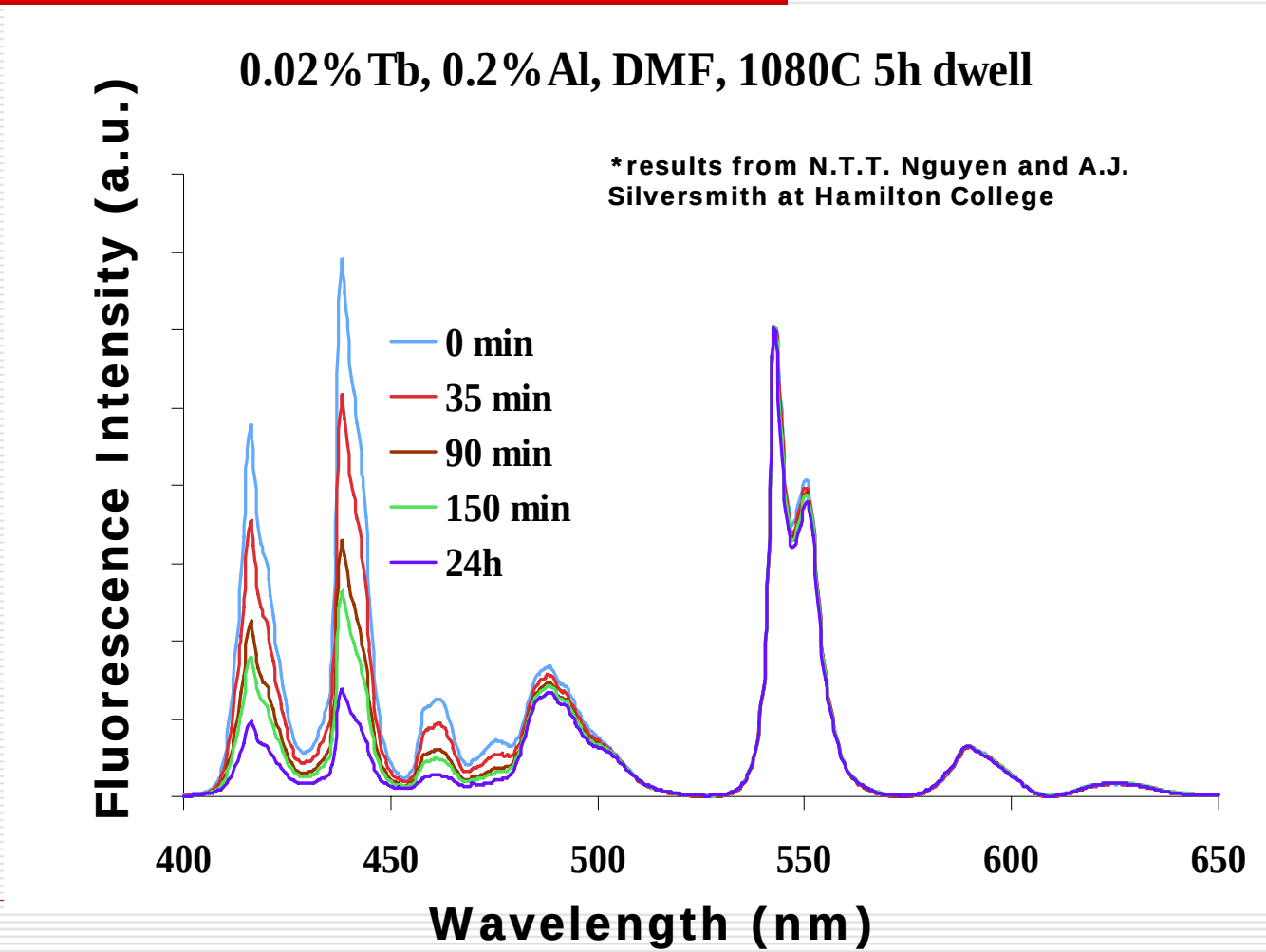
Result

$2.1 \pm 0.1 g cm^{-3}$ compared to $2.2 g cm^{-3}$ for vitreous silica

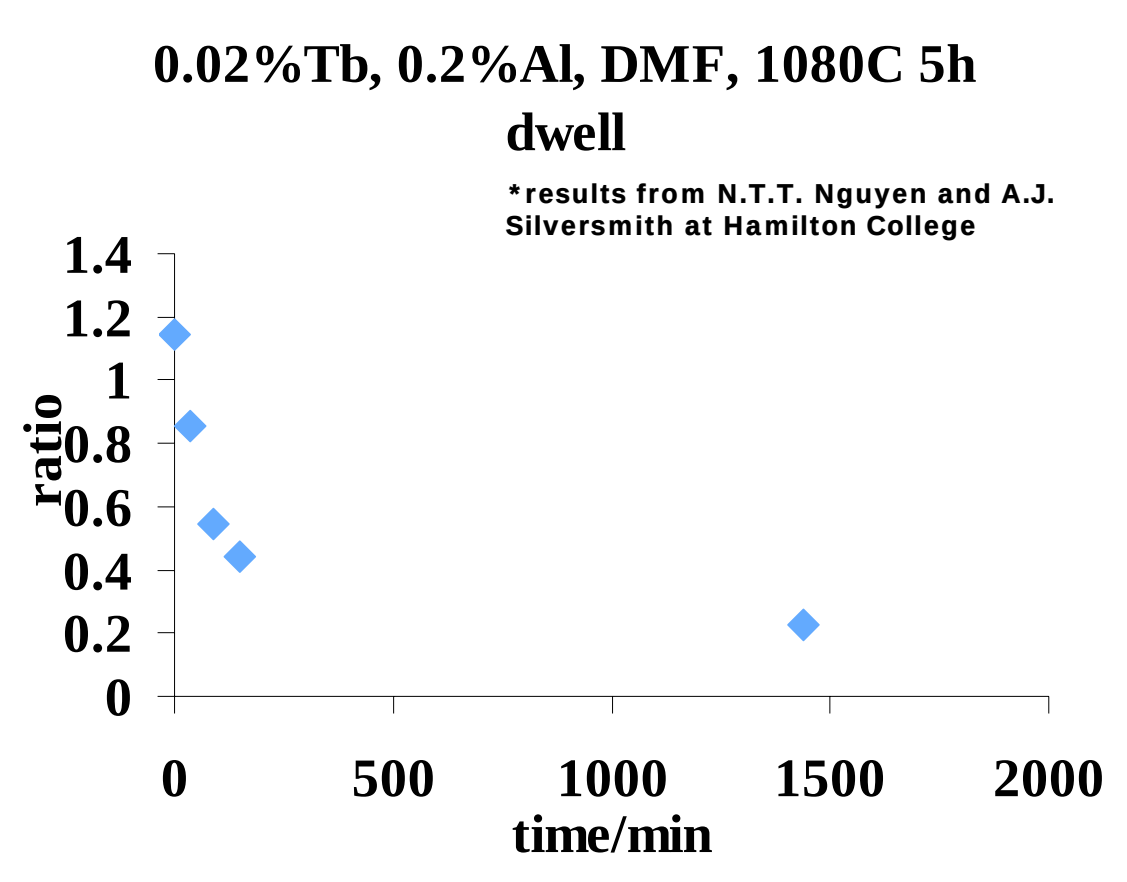
DMF: Varying Annealing Temp



DMF and Al


0.02% Tb, 0.2% Al, DMF, 1080C 5h dwell
*results from N.T.T. Nguyen and A.J. Silversmith at Hamilton College
Fluorescence Intensity (a.u.)
0 min
35 min
90 min
150 min
24h
400
450
500
550
600
650
Wavelength (nm)

Rehydration with Al co-doping



Conclusion and Future Work

- DMF successfully functions as a DCCA
- Capillary stressed reduced and higher annealing possible
- Small pore volume fraction, i.e. samples almost fully densified.
- Future work will focus on the effects of DMF and Al on fluorescence yield