Oxide Glass Properties by Analogy with Oxide Crystals

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Outline

- Analogies between glass and crystal
- XPS spectra of tellurites and silicates
- A new correlation between glass structure and stress-optic coefficient
- Calculation of NMR observables in ABINIT

Learning about Glass from Crystals

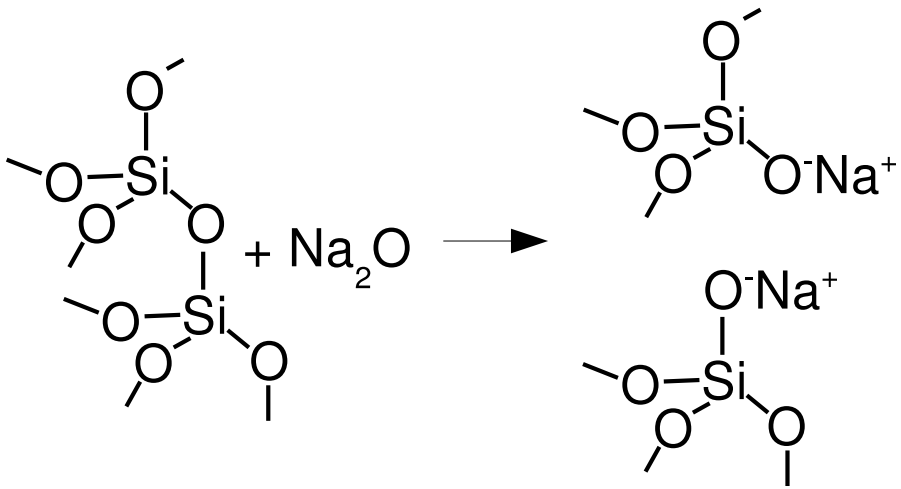
The glassy state of matter is thermodynamically different from the crystalline state, but

- Short range structures are the same
- Therefore bonding is the same
- Therefore electronics are the same
- And properties can be understood by considering crystals!

Therefore glass scientists learn a lot about glasses by using DFT and other computational methods, without simulating full glass structure or “quenching” an MD or Car-Parinello model.

Formation of Nonbridging Oxygen

A very standard concept in glass science is the formation of nonbridging oxygen upon modification:



The nonbridging oxygen bonds are shorter than the original bridging oxygen.

Oxygen 1s X-ray Photoelectron Spectra

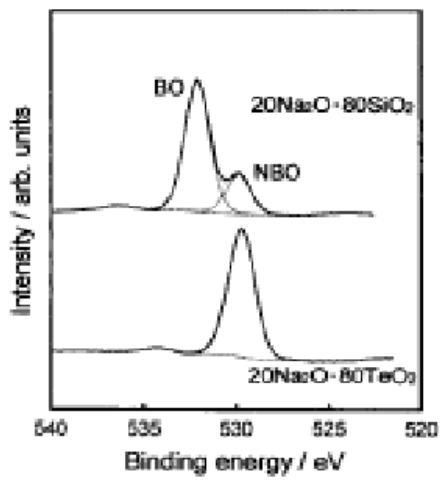


Fig. 7. O 1s photoelectron spectra for $20Na_2O \cdot 80TeO_2$ and $20Na_2O \cdot 80SiO_2$ [21] glass. Solid lines and dotted lines represent the experimental spectra and resolved Gaussian–Lorentzian components, respectively.

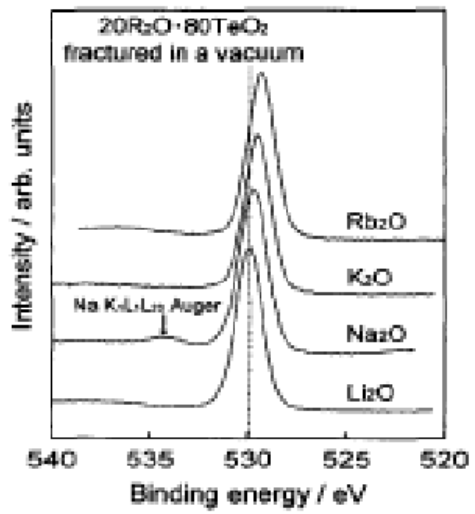
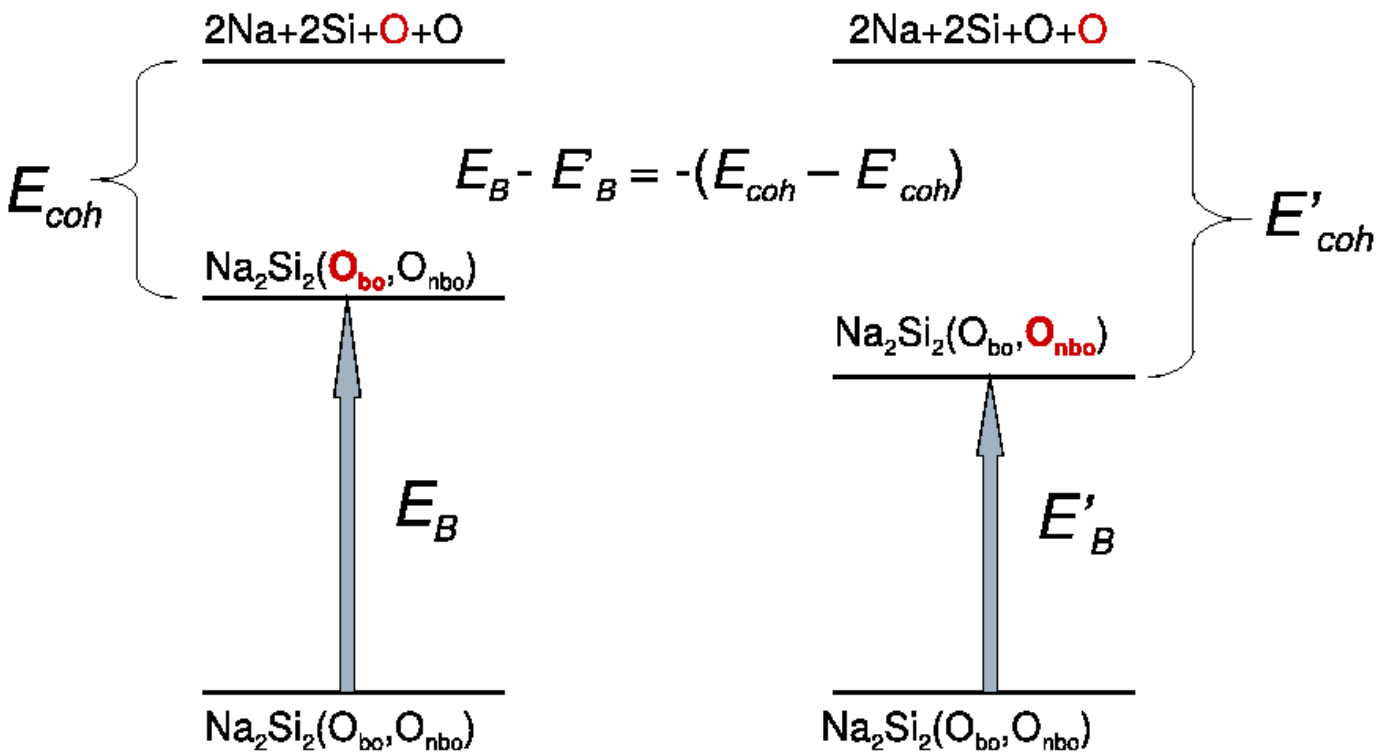


Fig. 3. O 1s photoelectron spectra for $20R_2O \cdot 80TeO_2$ (R: Li, Na, K and Rb) glasses.

Himei et al. *JNCS* **211**, 64 (1997)

XPS is a standard method to observe nonbridging oxygen in silicates, but fails in tellurites. Why?

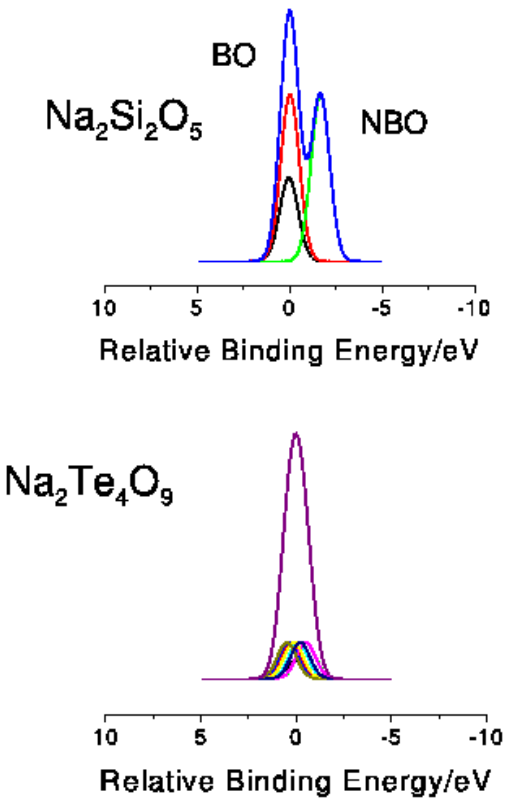
ABINIT Simulation of XPS Spectra

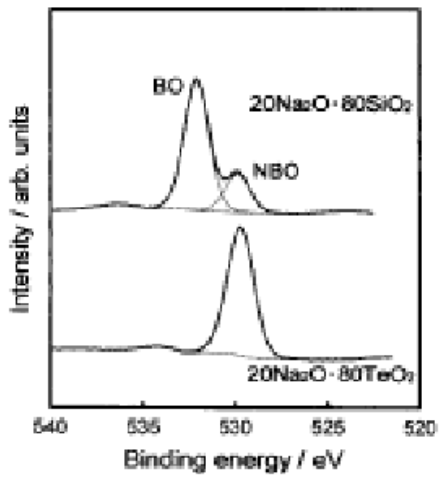


Mäder, Baroni, *Phys. Rev. B* **55**, 9649 (1997).

An oxygen pseudopotential with a core hole, $1s2s^22p^5$, was made with the FHI package and used in the following cycle to simulate XPS spectra.

Comparison with Data





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Simulations showed details of XPS in tellurites, and led to conclusion that tellurites, symmetry breaking *has already occurred* in un-modified TeO_2.[1]

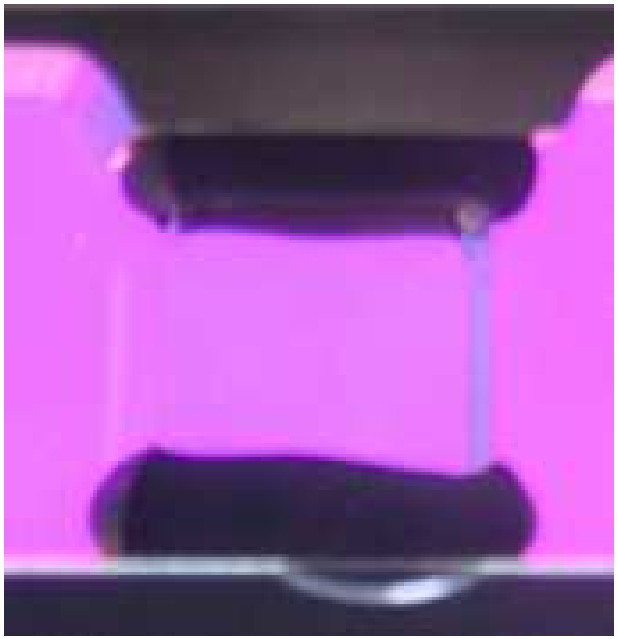
[1] Hart, Zwanziger, Werner-Zwanziger, and Yates, *J. Phys. Chem. A* **109**, 7636–7641 (2005)

Introduction to the Photoelastic Response

20 mol-% PbO

$\sigma = 50$ bar

$C = 2.65$ B



40 mol-% PbO

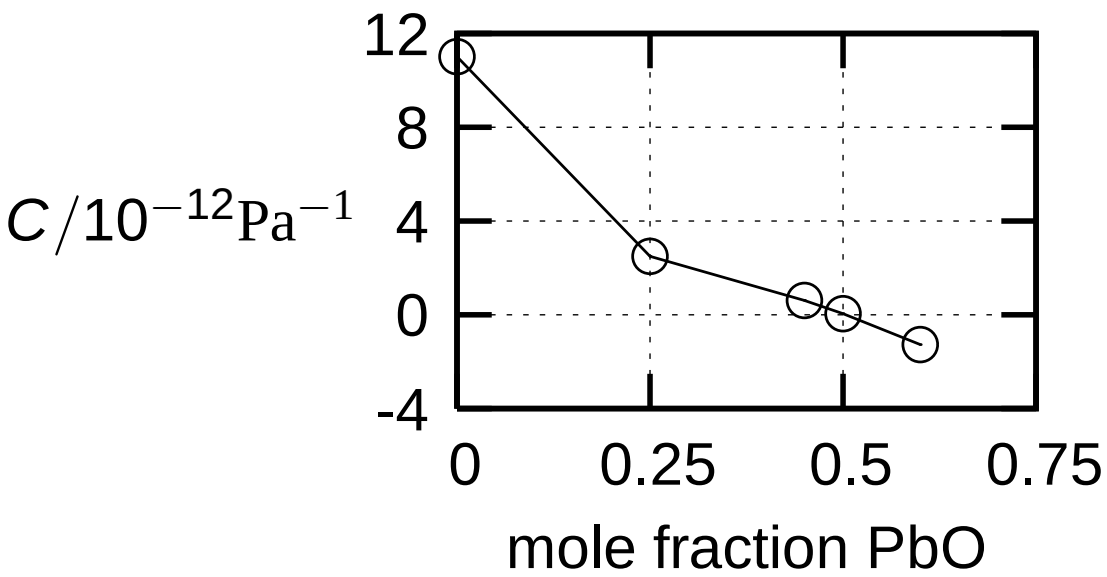
$\sigma = 50$ bar

$C = 0.02$ B

$$\delta = CL\sigma$$

Compositional Dependence

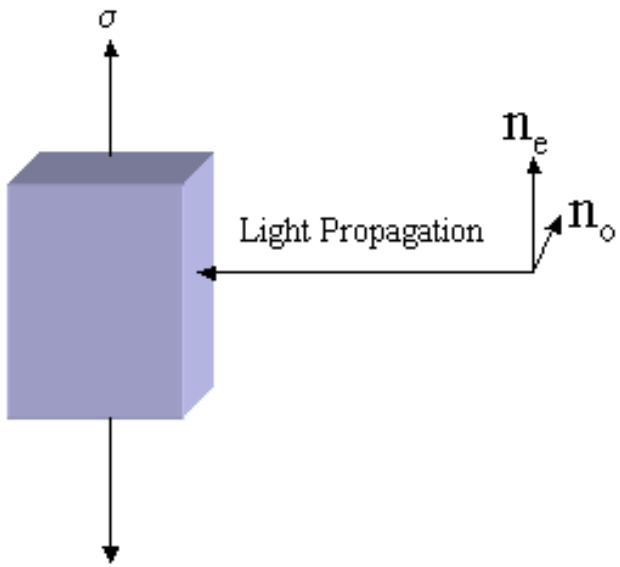
C is positive in glass formers, and is lowered by modifiers; but the effect of Pb is dramatic!



Near-zero response is appealing–but lead has drawbacks: heavy, expensive, hard to recycle (forbidden by EU in 2006!) Can it be understood and replaced?

Photoelastic Response

- $n_e - n_o > 0$ is positive birefringence
- $n_e - n_o < 0$ is negative birefringence
- Tensile stress typically generates positive birefringence
- $\delta = CL\sigma$



Some Definitions

The stress-optic coefficient is related to materials response and the photoelastic tensors as follows:

- $D_i = \epsilon_{ij} E_j$: ϵ_{ij} is the permittivity tensor
- $B = \epsilon^{-1}$: the inverse of ϵ
- $\Delta B_{ij} = \pi_{ijkl}\sigma_{kl} = p_{ijkl}\epsilon_{kl}$: π and p are the photoelastic tensors for stress and strain.
- $C = -\frac{n^3}{2}(\pi_{11} - \pi_{12})$ relates π to C
- $\langle \pi_{ijkl} \rangle = \frac{1}{8\pi^2} \int d\Omega \pi_{mnpq} a_{im} a_{jn} a_{kp} a_{lq}$

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Survey of Additives By Stress-Optic Response

Cmpnd	$\mathrm{sgn}\langle C \rangle$	Meth.
PbO	$-$	expt, *ab initio*
Tl_2O	$-$	expt
Bi_2O_3	$-$	expt
HgO	$-$	*ab initio*
SnO	$-$	expt, *ab initio*
Sb_2O_3	$-$	expt

Cmpnd	$\mathrm{sgn}\langle C \rangle$	Meth.
SiO_2	$+$	expt
B_2O_3	$+$	expt
P_2O_5	$+$	expt
TeO_2	$+$	*ab initio*
BaO	$+$	expt, *ab initio*
MgO	$+$	expt, *ab initio*
SnO_2	$+$	*ab initio*
PbS	$+$	*ab initio*

cf. Donadio, Bernasconi, and Tassone, *PRB* **68** 134202 (2003) and *PRB* **70**, 214205 (2004).

Chemical View of Photoelasticity

We look for a correlation based on:

- Differences in the cation-oxygen bonds;
- Deformability (metallicity) of cation-oxygen bonds[2]
- Anisotropic deformability of structure
- What works: d/N_C

[2] Wemple, *J. Chem. Phys.* **67**, 2151 (1977)

Compound Summary

Compound	d/N_C
HgO	
Tl_2O	
Sb_2O_3	
As_2O_3	
PbO	
SnO	
Bi_2O_3	
TeO_2	
ZnO	
PbS	
BaO	
B_2O_3	
GeO_2	
SiO_2	
P_2O_5	
CdO	
In_2O_3	
PbO_2	
MgO	
SnO_2	

Compound Summary

	Compound	d/N_C
Negative C	HgO	
	Tl_2O	
	Sb_2O_3	
	As_2O_3	
	PbO	
	SnO	
	Bi_2O_3	
Positive C	TeO_2	
	ZnO	
	PbS	
	BaO	
	B_2O_3	
	GeO_2	
	SiO_2	
	P_2O_5	
	CdO	
	In_2O_3	
	PbO_2	
	MgO	
	SnO_2	

Model Predictions

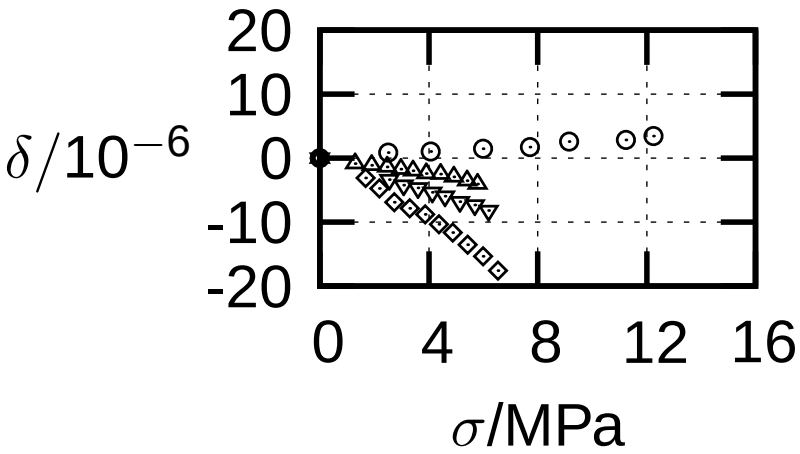
This simple model makes the following predictions:

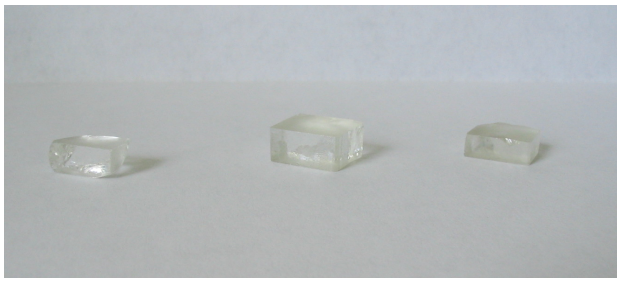
- Standard glass formers are positive stress optic materials
- BaO, ZnO should decrease C but not go negative
- PbO, Tl_2O, Bi_2O_3 should confer negative response
- By averaging d/N_C values, recipes for $C = 0$ are predicted:

$$\sum x_i (d/N_C)_i = 0.5 \Rightarrow C = 0$$

- SnO, Sb_2O_3, HgO, As_2O_3 should also give $C = 0$ and $C < 0$ glasses when added to standard glass formers

Tin Phosphate Glasses





- $(SnO)_{55}(P_2O_5)_{45}$: $C = 0.3$ B
- $(SnO)_{60}(P_2O_5)_{40}$: $C = -0.6$ B
- $(SnO)_{66}(P_2O_5)_{34}$: $C = -1.3$ B
- $(SnO)_{75}(P_2O_5)_{25}$: $C = -2.3$ B

Photoelastic Materials Summary

1. Metal oxide compounds with high metallicity in the bonding and low coordination number confer negative stress optic response
2. $d/N_C > 0.5$ predicts negative stress optic response
3. Lead-free zero stress-optic glasses are predicted for SnO, Sb_2O_3, HgO, As_2O_3
4. Positive and negative stress-optic coefficients have been realized in tin phosphates, tin silicates, antimony borates, barium tellurites[3]
   - 4.1 $C \approx 0$ for $(SnO)_{0.563}(P_2O_5)_{0.436}$
   - 4.2 $C \approx 0$ for $(SnO)_{0.463}(SiO_2)_{0.537}$
   - 4.3 $C \approx 0$ for $(Sb_2O_3)_{0.428}(B_2O_3)_{0.572}$
   - 4.4 $C \approx 0$ for $(BaO)_{0.12}(TeO_2)_{0.88}$

[3] Patent pending; M. Guignard, L. Albrecht, and J. W. Zwanziger, Chemistry of Materials **19**, 286–290 (2007)

NMR Observables

Two most important for solids are

- Chemical shielding: $B_{\text{int}} = (1 - \sigma)B_{\text{ext}}$
- Electric Field Gradient $-\frac{\partial^2 V(\mathbf{R})}{\partial x_\alpha \partial x_\beta}$
- PAW formalisms available for both[4]
- Both available within CASTEP, EFG in PWSCF.
- So why bother?
- Cost, quality, and understanding.

[4] Petrilli, Blöchl, Blaha, Schwarz, *PRB* **57** 14690 (1998); Profeta, Mauri, and Pickard, *J Am Chem Soc* **125** 241 (2003); Pickard and Mauri, *PRB* **63** 245101 (2001)

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EFG Implementation So Far

Three parts to the calculation:

1. Valence electrons on grid:

$$4\pi^2 \sum (G_\alpha G_\beta - \delta_{\alpha,\beta} G^2/3) v(\mathbf{G}) e^{2\pi i \mathbf{G}\cdot\mathbf{R}}$$

2. Ions:

$$\sum q_k \left(\frac{3 r_{k,\alpha} r_{k,\beta}}{r^2} - \delta_{\alpha,\beta} \right) \frac{1}{r^3}$$

3. PAW cores:

$$\sum \rho_{ij} \left(\langle R_i | \frac{1}{r^3} | R_j \rangle - \langle \tilde{R}_i | \frac{1}{r^3} | \tilde{R}_j \rangle \right) \sum_m c^m_{\alpha,\beta} \langle Y_i | Y_{2m} | Y_j \rangle$$

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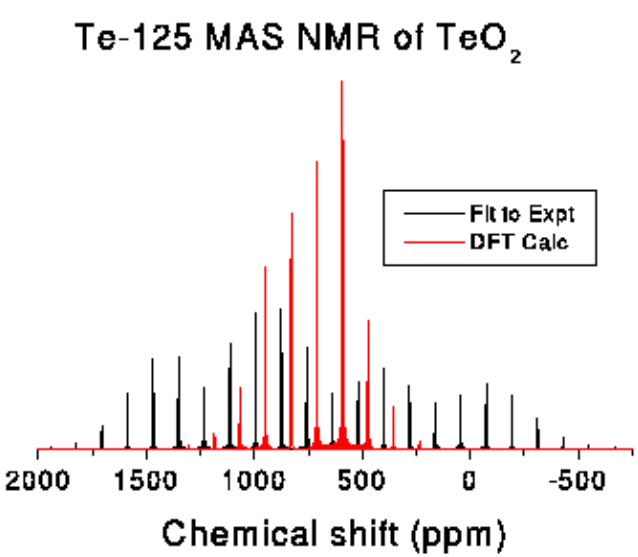
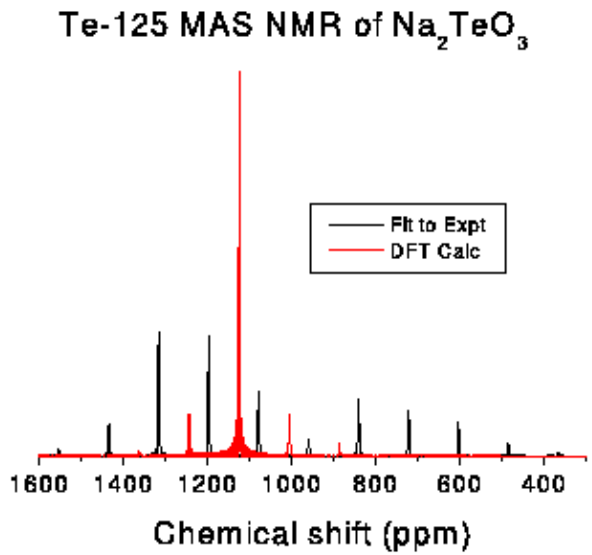
Best Result So Far

Oxygen-17 quadrupole interaction in quartz.

Method	e^2qQ/h/MHz	η
Expt.	5.19	0.19
CASTEP-NMR	5.19	0.20
PWSCF	6.06	0.21
ABINIT/EFG	5.2	0.46

Chemical Shielding: A Serious Challenge?





Te-125 gives trouble with CSA

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