Chemical Decomposition of High-Level Nuclear Waste Storage/Disposal Glasses under Irradiation

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Contents

- This poster comprises several modules which may be visited in the same order as they are presented or in some other order. The present **Intro** module credits collaborators and lists the compositions of several sample materials which are mentioned most frequently in the other modules.
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- Module **ESR** is an introduction to the technique of electron spin resonance as applied to single crystals, powdered crystals, and glasses. Here, a careful distinction is made between a powder and a glass.
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- Module **Silicates** details results obtained for some borosilicate high-level waste (HLW) glass simulants and related materials.
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- Module **FeP** outlines some results of a multidisciplinary study of a group of high-iron phosphate glasses which appear highly suitable for immobilization of certain HLW streams.

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Glass Compositions Studied

- Compositions given in weight %

	DWPF*	CSG	PO_4-3*	F43**	GS-78
SiO_2	54.1	55.7	-	-	46.2
Al_2O_3	4.1	11.7	-	-	12.4
B_2O_3	6.8	8.4	-	-	-
P_2O_5	-	-	58.5	57.0	-
Fe_2O_3	12.3	-	27.3	34.8	-
FeO	-	-		8.2	16.5
CaO	1.5	6.0	-	-	10.6
MgO	0.8	-	-	-	10.4
Na_2O	10.3	18.2	-	-	0.4
Li_2O	4.7	-	4.5	-	-
MnO_2	2.9	-	-	-	-
ZrO_2	1.2	-	-	-	-
TiO_2	-	-	-	-	2.5
CeO_2	-	-	9.7	-	-

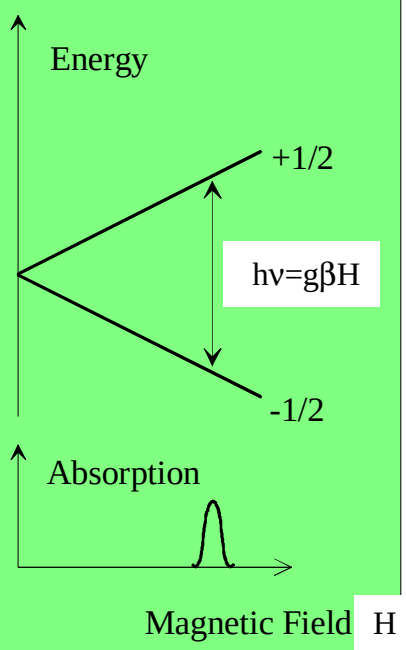
*Defense Waste Processing Facility glass: Iron valence states not determined. Batch compositions shown.
**Iron valence states determined by Mössbauer. Numbers shown pertain only to air melt.

Electron Spin Resonance (ESR)

- ESR is sensitive only to unpaired electrons. Therefore, measurable species include transition-group ions (e.g., Fe^{3+}), certain point defects induced by irradiation, and ferro- or ferri-magnetic materials (e.g., particles of Fe^{0} or magnetite).
- As illustrated on the following slide, resonance absorption of fixed-frequency microwaves (energy=$h\nu$) by unpaired electrons of spin S=1/2 can be achieved by tuning the magnitude H of an externally applied magnetic field (Zeeman Effect). The resonance condition is $h\nu=g\beta H$, where h is Planck's constant and β is the Bohr magneton (a ratio of fundamental constants). The measurable quantity in the experiment is the "g value", which in general is tensor with three principal values. Two other commonly measured effects in ESR are also diagrammed.
- The second slide after this one shows the experimental arrangement.

Measurables in Electron Spin Resonance

Zeeman Interaction

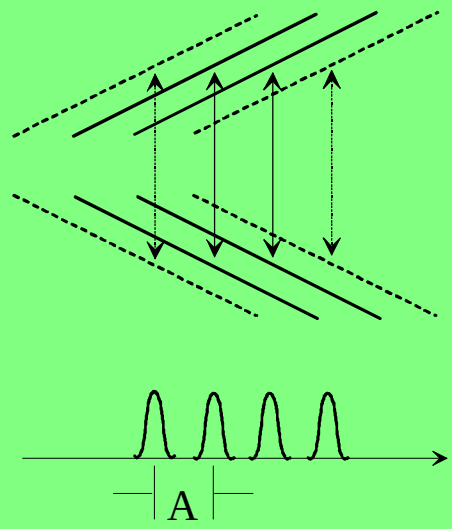


One Electron: S = 1/2

Nuclear Spin: I = 0

Single-line spectrum

Zeeman + Hyperfine

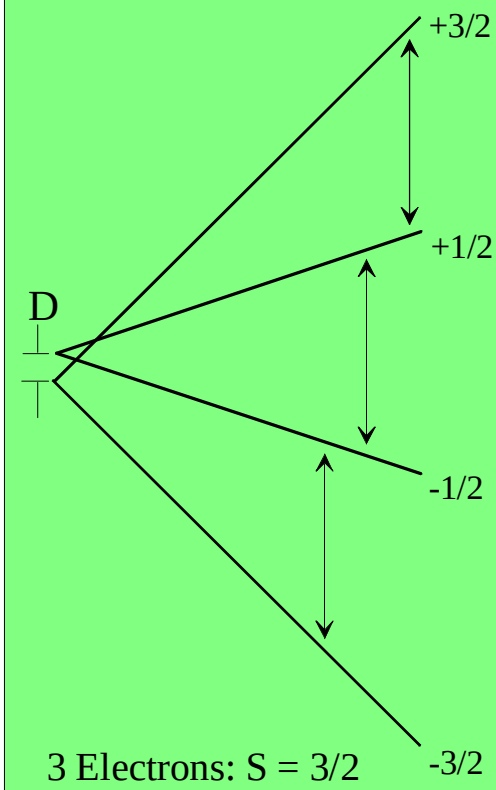


One Electron: S = 1/2

I = 1/2 (or I = 3/2)

2I+1 lines in spectrum

Zeeman + Crystal Field



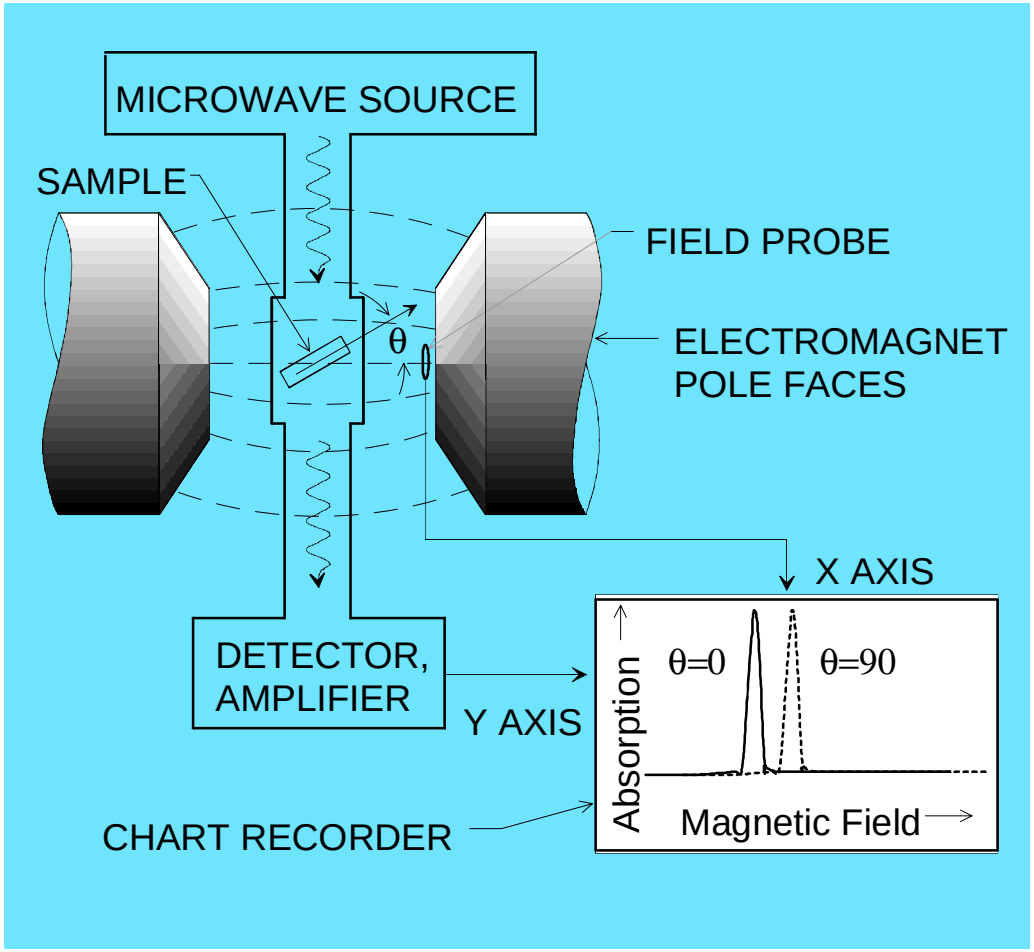
3 Electrons: S = 3/2

I = 0

2S Lines in spectrum

Electron Spin Resonance Spectrometry

- Source of microwaves of fixed frequency ν.
- Sample is held in resonant cavity located between the pole faces of an electromagnet.
- Microwave power absorption detected as functions of the magnitude of the applied field and the angle ν between the field and the crystallographic axes of the sample.



ESR Spectra of Crystals … and Glasses

- Crystals have symmetries which can be exploited in studies of their physicochemical properties. For example, the angular relationship of the ESR "g tensor" to the crystallographic axes can conclusively identify a paramagnetic defect site within a crystal.
- Polycrystalline or powdered crystals still reveal a great deal of information when studied by ESR, but the precise relationship of the measured parameters to the crystallography cannot be ascertained without a single crystal.
- Glasses are isotropic media, *but they differ from powders in a profound way*. Specifically, real glasses are characterized by molecular-scale density fluctuations. Thus, it can be helpful to imagine a glass as a powder composed of crystallites of identical structures but exhibiting random variations in density from grain to grain.
- The following two slides guide the reader through the ESR spectra (Zeeman effect only) of a powdered crystal and an analogous glass. It can be seen that a bell-shaped statistical distribution of density fluctuations is implied (and in principle can be determined) from an analysis of the glass spectrum.

ESR Spectra of Crystals … and Glasses

- Angular dependence of single-crystal ESR spectra.
-
-
-
- The "Powder Pattern": average of single-crystal absorption spectra over solid-angle sphere.
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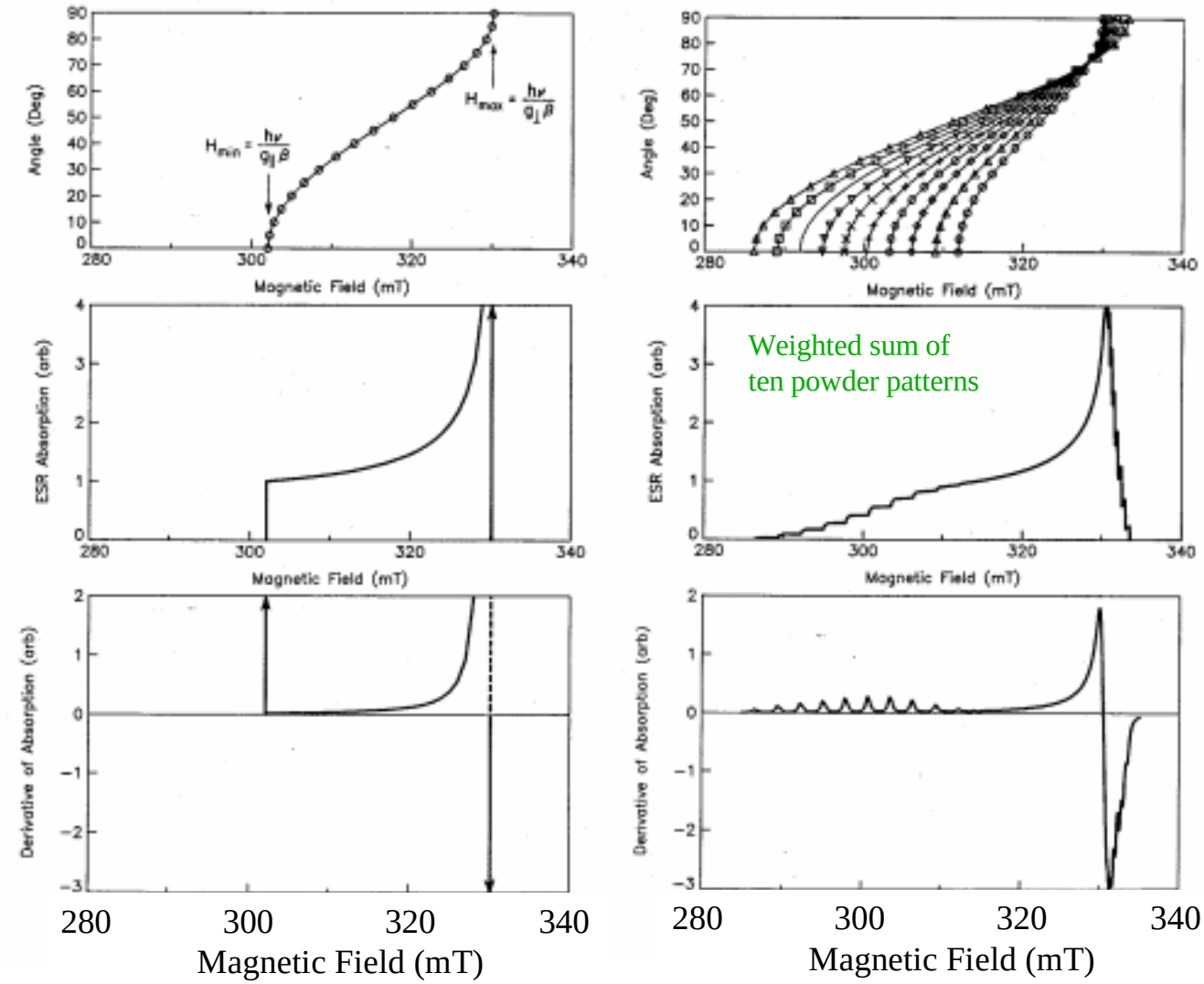
-
- First derivative of the powder pattern.

N.B. These theoretical spectra assume *zero* single-crystal linewidth.

Uncompressed crystal

Ten crystals in differing states of compression

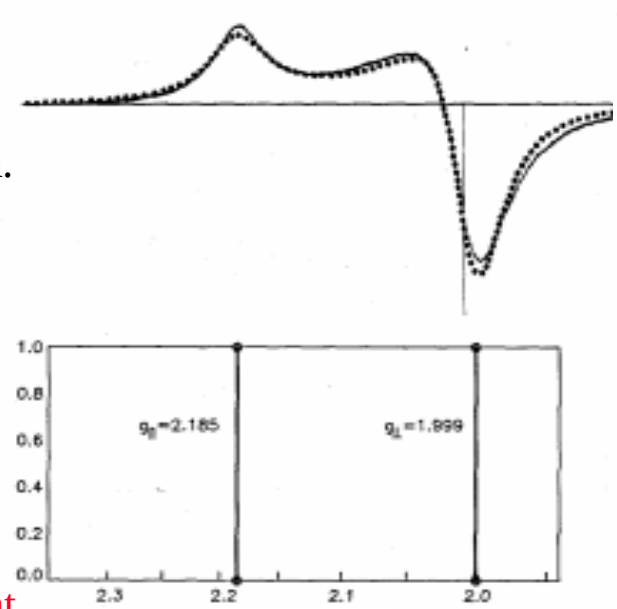


ESR Spectra of Crystals … and Glasses

- Experimental (curves) and computer-simulated (dots) first-derivative "powder pattern" spectra.

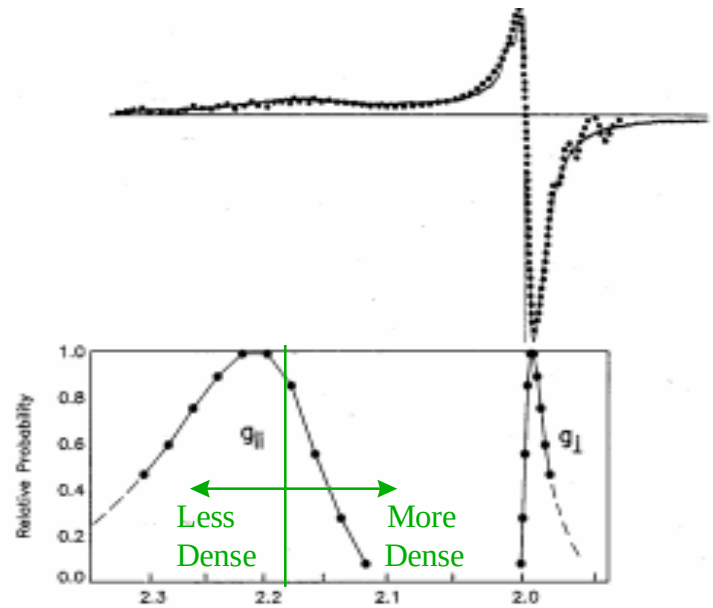
- g values determined from line-shape simulations (a) allow identification of paramagnetic species and (b) provide important insights into the structures of amorphous materials.

O_2^- Ions in Polycrystalline Na_2O_2



g values

O_2^- Ions in Amorphous $NaBO_3 \cdot H_2O$



g values

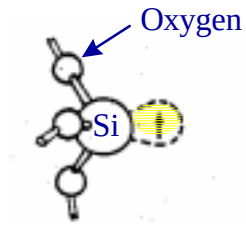
N.B. The empirically-determined distribution in $g_{\parallel}$ values is rigorously linked to the distribution in $g_{\perp}$ values (used in the fit) by the theory of Känzig and Cohen for O_2^- molecular ions.

Structures of Some Point Defects in Pure and Boron-Doped Amorphous SiO_2

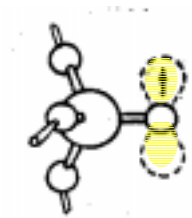
ESR

NRL

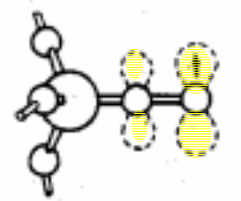
- The E´ Center



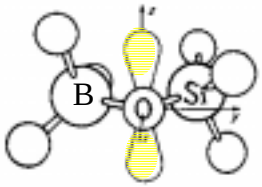
- The Nonbridging-Oxygen Hole Center



- The Peroxy Radical



- The Boron-Oxygen Hole Center



The structures of these (and other) defects in glassy silica have been determined in considerable detail by means of ESR experiments performed over the past 40 years.

Measurements of hyperfine interactions of the unpaired electron spin with the nuclear magnetic moments of ^{17}O, ^{29}Si, ^{11}B, and ^{10}B were crucial to determination of the ground-state wavefunctions of the unpaired spins (yellow-tinted ‘balloons’).

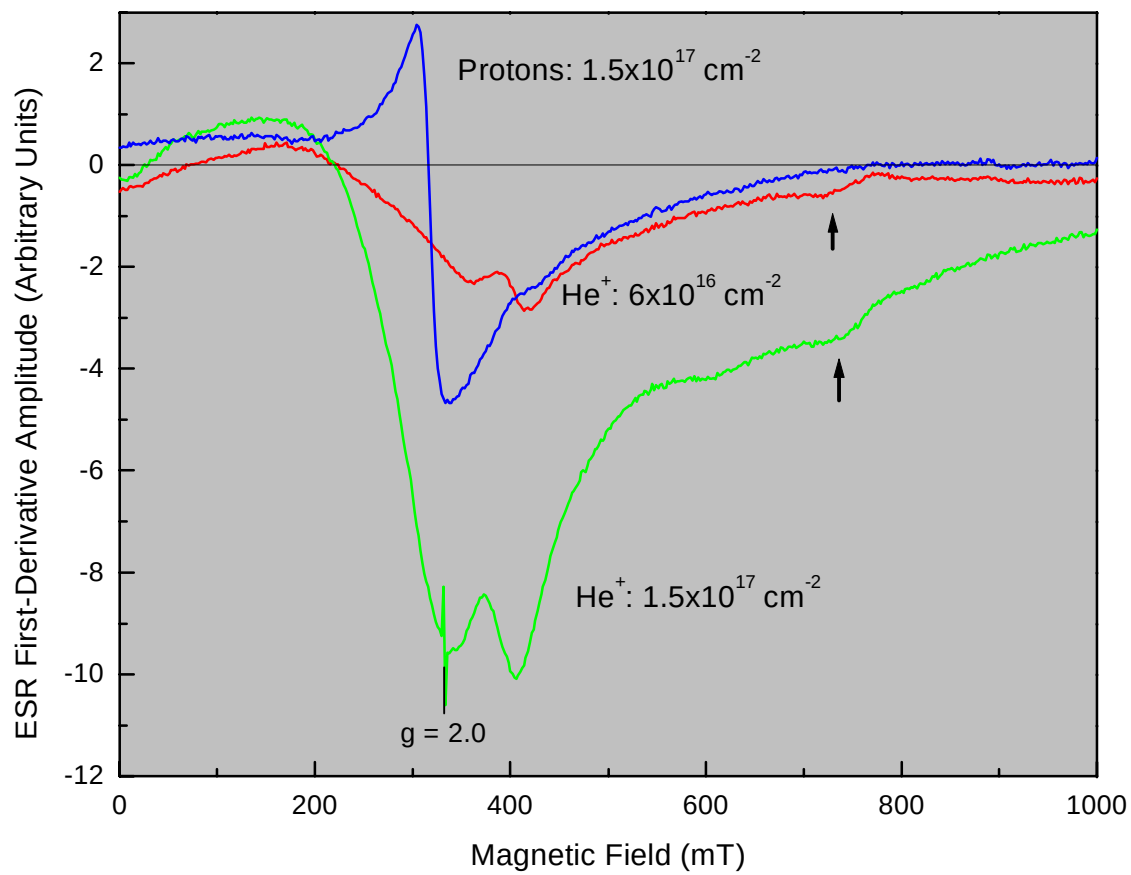
Knowledge of the ESR signatures of these fundamental defects is an important reference point for interpreting the spectra of irradiated borosilicate HLW glass simulants.

Radiation Effects in HLW Simulants and Related Glasses

- Non-radioactive Savannah River (DWPF) HLW glass simulants exhibited strong ESR spectra due to Fe^{3+} ions in possible combination with ferrimagnetic precipitates (see spectra in slide 2 of Module **FeP**). Within the accuracy of the experiment, ± 1%, a γ irradiation dose of 30 MGy(Si) did not affect the shape or intensity of this spectrum.
- An aluminosilicate glass (GS-78) containing 16 wt% iron oxide as Fe^{2+} was also little affected by γ rays, but was profoundly influenced by He^{+} and H^{+} ion implantations (see next slide).
- Much of the remainder of the present module reports the results of γ irradiations and ion implantations of an *iron-free* HLW glass simulant (CSG) and γ irradiations of a still simpler binary potassium silicate glass. In the former case the γ irradiation had larger initial effects than the implantations (see second slide following this one where a probable explanation is given).

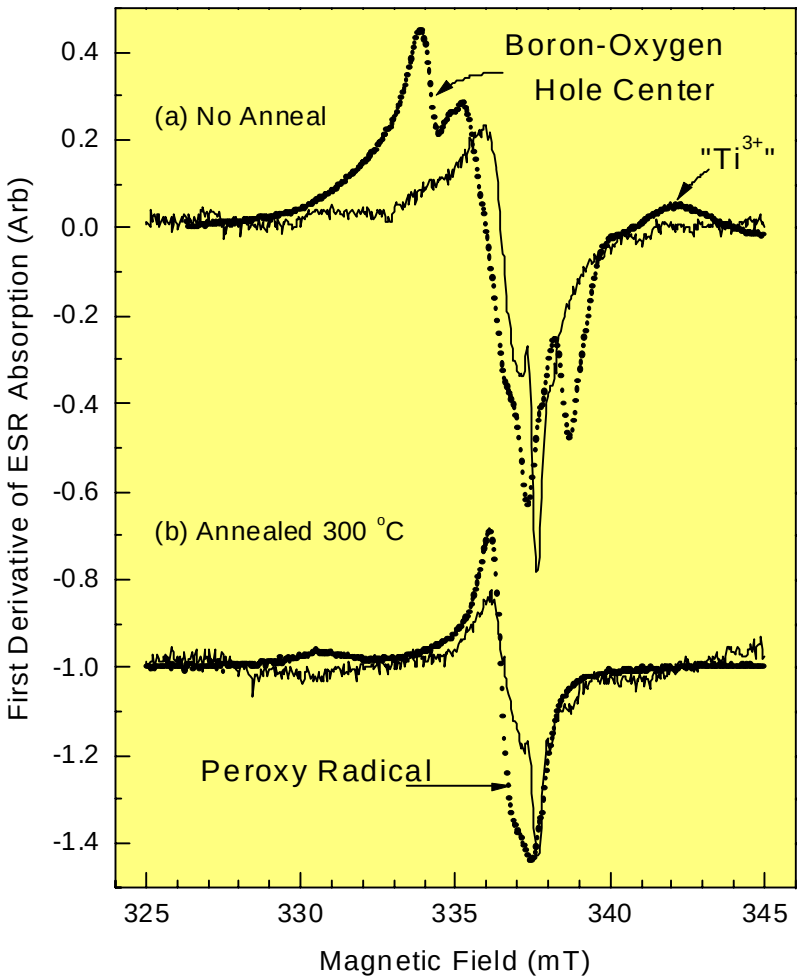
ESR Evidence of Radiation-Induced Disproportionation in a Glass Containing 16 wt% FeO

- Simulated lunar glass (GS-78).
- The illustrated *ferromagnetic resonance* signals were induced by 160-keV ion implantation.
- The relatively smaller effects of proton implantation point to the importance of nuclear collisions.
- Vertical arrows mark positions of features arising from multidomain particles of metallic iron. Other features are due to single- and multi-domain Fe^0 and magnetite (Fe_3O_4).
- The disproportionation reaction, $4FeO \rightarrow Fe^0 + Fe_3O_4$, is thermodynamically favored below 560 °C.

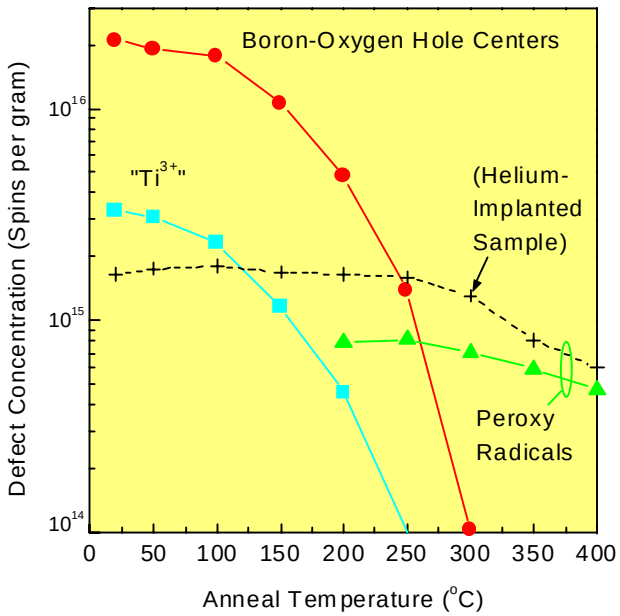


Ionization Effects vs. Knock-on Damage in HLW Glasses

Induced ESR Spectra (dots = g-induced)



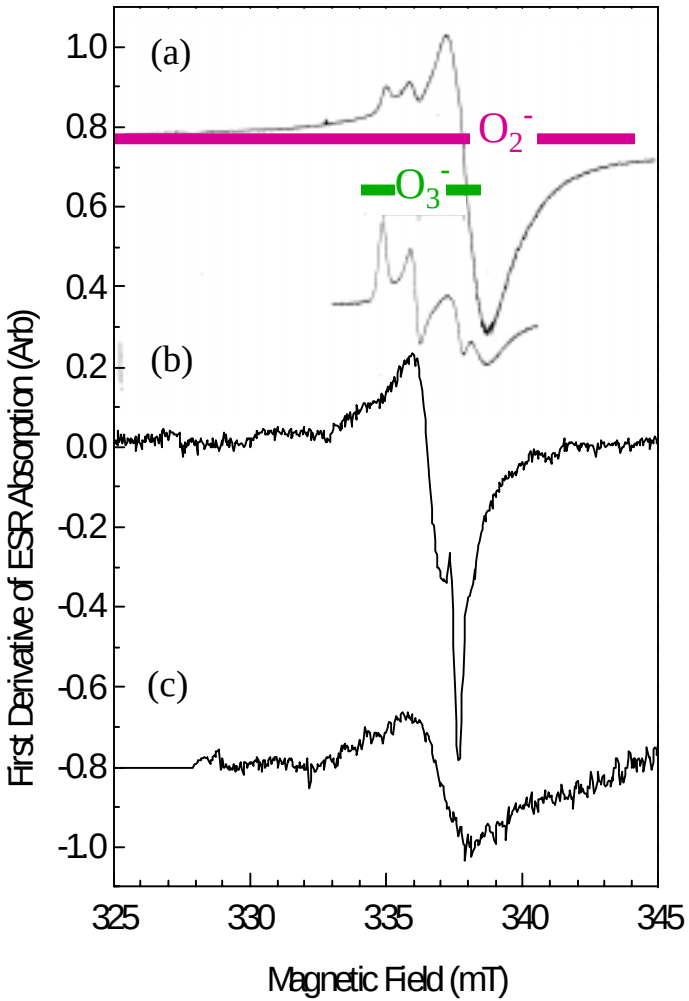
- Iron-free borosilicate HLW glass simulant (CSG).
- Boron-oxygen hole centers (BOHCs) result from γ-irradiation but not 160-keV He^+ implantation.
- It is proposed that local heating associated with nuclear collisions anneals any implantation-induced BOHCs and "Ti^{3+}" centers, leaving only high-temperature-stable peroxy radicals.



10-minute Isochronal Anneals

ESR Evidence for Decomposition of HLW Glasses and Related Materials under Irradiation

- Electron spin resonance (ESR) has been used to investigate radiation-induced decomposition in glasses, including (a) a $44K_2O{\cdot}66SiO_2$ glass, (b) an iron-free borosilicate HLW glass simulant, and (c) a 65-Myear-old tektite glass.
-
- The two γ-ray-induced spectra of (a) are unambiguously identified as arising from superoxide (O_2^-) and ozonide (O_3^-) molecular ions. The He^+-implantation-induced spectrum of (b) is tentatively ascribed to O_2^- ions bonded to the silicate network. The spectrum of (c), presumably induced by α decays of naturally occurring ^{238}U and ^{232}Th, may be the ESR envelope of similar O_2^- and O_3^- species.
-
- The appearance of ozonide and/or superoxide ions in silicate or borosilicate glasses under irradiation implies emergent chemical decomposition into reduced phases (e.g., elemental silicon or alkali metals) and oxidizers, analogous to the case of rock salt (NaCl), which decomposes into sodium colloids and Cl_2. The reported spontaneous detonation of heavily irradiated NaCl crystals under gentle heating near 200 ^oC (H. den Hartog and D. Vainshtein, Mater. Sci. Forum **239-241**, 611, 1997) may serve as a cautionary tale— especially with regard to the handling of ^{137}Cs immobilized as CsCl.



ESR Evidence for Decomposition of HLW Glasses and Related Materials under Irradiation

NRL

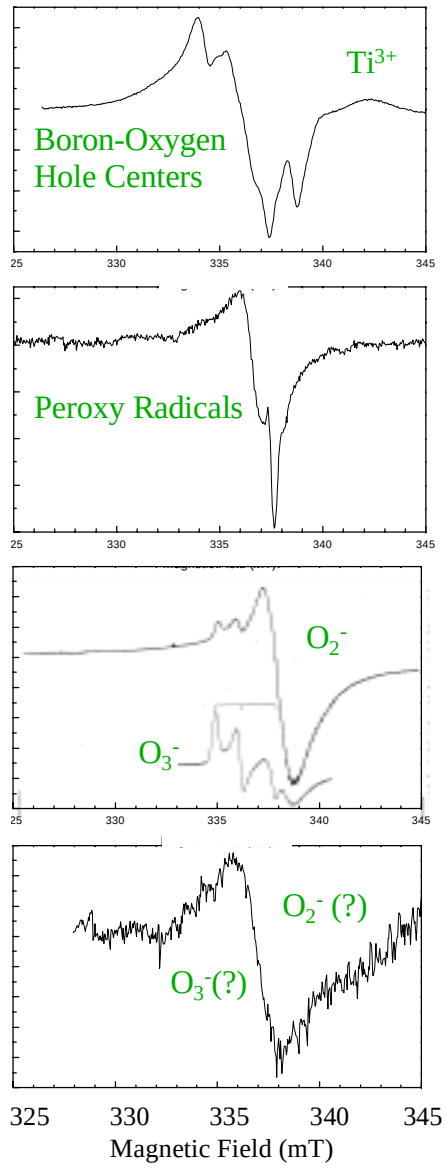
- **HLW Simulant**: Composition CSG
- **Simple Binary Silicate Glass**: $44K_2O$-$66SiO_2$
- **Geologic Glass**: 65-Myr-Old Calcium Aluminosilicate Tektite Glass

Gamma irradiation

He ion implantation

Gamma irradiation

^{238}U & ^{232}Th a decays



- Trapped-electron and hole centers recorded in iron-free CSG glass under g irradiation.
- Only peroxy radicals are observed in He^+-implanted sample, owing to local heating in collision cascades.
- Interstitial superoxide and ozonide ions indicate radiolytic decomposition.
- This glass survived 65 million years of ground water attack but shows signs of decomposing under a decays of contained radionuclides

Radiation Effects in Silicate HLW Glass Simulants: Conclusions and Future Plans

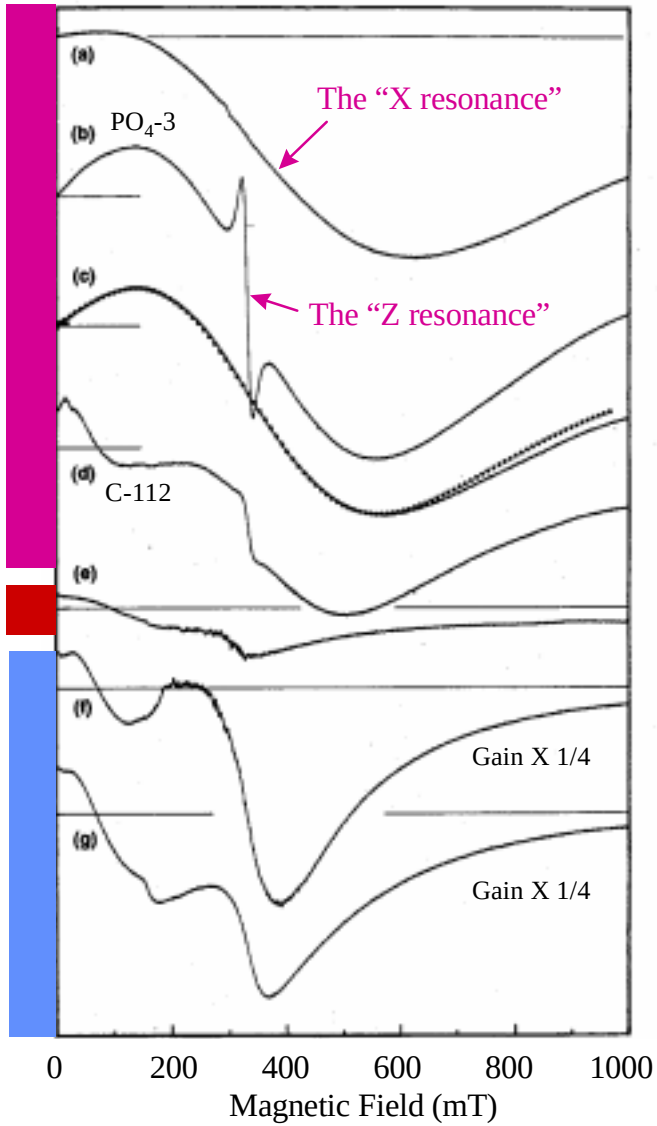
	ã Irradiation	Ion Implantation	á Decays of Contained Radionuclides
Iron-free binary potassium silicate glass	(a) Several types of color centers which anneal below 300 C (b) O_2^- and O_3^- ions stable above 300 C	No data	No data
Iron-free complex borosilicate glass (simplified HLW glass simulant)	(a) Several types of color centers which anneal below 300 C (b) Peroxy radicals stable above 300 C	Peroxy radicals stable above 300 C. Further studies planned.	No data
Fe^{3+}-containing borosilicate HLW glass simulant (DWPF)	No measureable effect for dose=30 MGy	Planned future studies	Planned future studies
Fe^{3+}-containing aluminosilicate natural glass (tektite)	No data	No data	Possible O_3^- and/or O_2^-
Aluminosilicate glass with nearly all iron in 2+ state (simulated lunar glass)	No measureable effect for dose=2 MGy	Clear evidence of disproportionation into Fe^0 and Fe_3O_4	No data

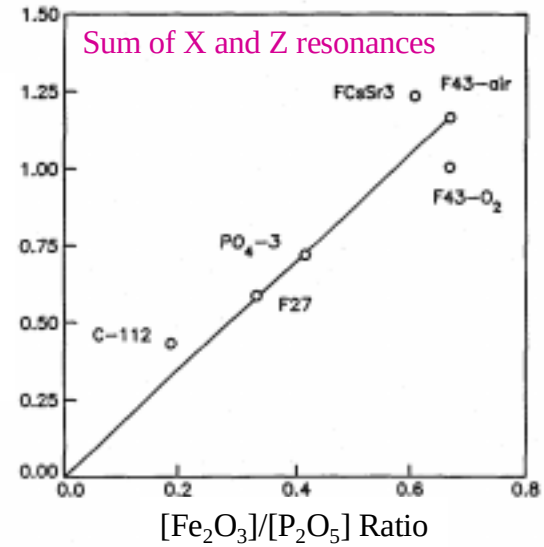
High-Iron Phosphate Glasses

- Glasses with approximate compositions $40Fe_2O_3$-$60P_2O_5$ possess chemical durabilities higher than that of the Savannah River DWPF borosilicate glass and are apparently capable of incorporating high HLW loadings without much change in durability.
  (See G.K. Marasinghe et al., J. Non-Cryst. Solids 222, 144 (1997) and references therein.)
- In the present study (following slides) a variety of such high-iron phosphate glasses were investigated by electron spin resonance, Mössbauer, thermal analysis, and evolved-gas mass spectroscopy.
  (See D.L Griscom, C.I. Merzbacher, N.E. Bibler, H. Imagawa, S. Uchiyama, A. Namiki, G.K. Marasinghe, M. Mesko, and M. Karabulut, Nucl. Inst. & Methods B, in press, 1998.)

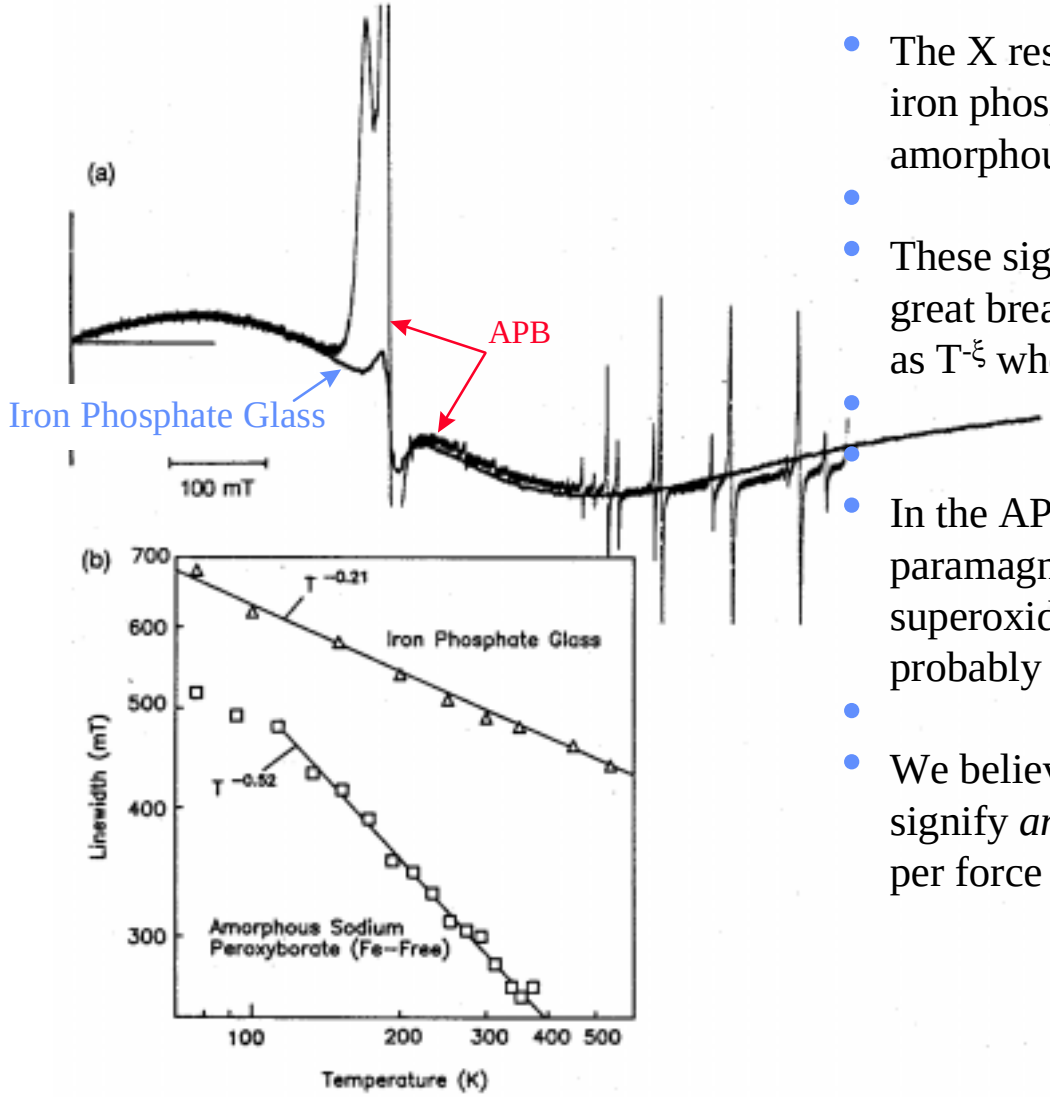
ESR Spectra of Some Proposed and Actual HLW Glasses before Irradiation

- Iron Phosphate Glasses: (a) FCsSr3, (b) PO_4-3, (c) F27, (d) C-112.
  N.B. Glass C-112, containing 18 wt% UO_2, was devised as a means of vitrifying phosphorus-rich HLWs from Hanford tank C-112.
- A Lanthanum Silicate Glass: (e).
- Defense Waste Processing Facility HLW Glass Simulants: (f) and (g).
  N.B. No significant changes in these Fe^{3+}-related ESR signals were noted upon γ irradiation to a dose of 30 MGy.





Properties of the X Resonance



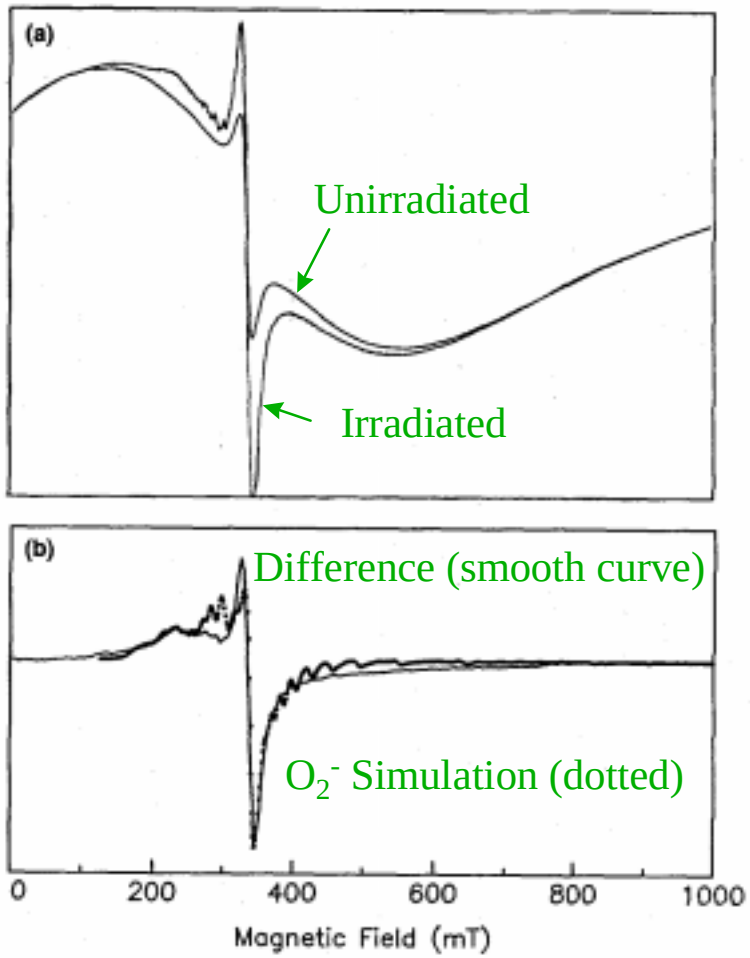
- The X resonance has so far been reported only in iron phosphate glasses and in the (iron-free) amorphous peroxyborates (APBs).
- These signals comprise Lorentzian line shapes of great breadths, ΔH, which depend on temperature, T, as $T^{-\xi}$ where $0<\xi<1$.
- In the APBs, the X resonance arises from paramagnetic states of oxygen, almost certainly superoxide ions. In the iron phosphate glasses it is probably due to Fe^{3+} and Fe^{2+} ions.
- We believe that all occurrences of the X resonance signify *amorphous antiferromagnetic ordering* — per force implying very special glass structures.

ESR-Detected γ-Ray Damage in an Iron Phosphate Glass

FeP

NRL

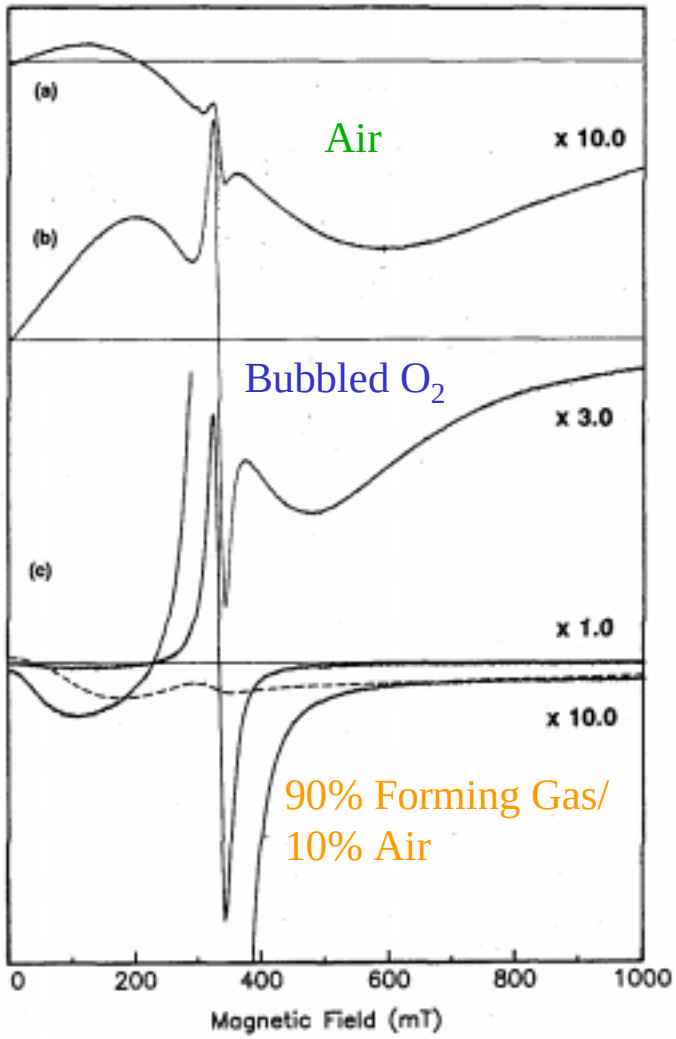
- The studied material was glass PO_4-3.
-
- The ESR difference spectrum was computer fitted using the theory of Känzig and Cohen for O_2^- ions in solids.
-
- We conclude that O_2^- (superoxide) ions are products of γ radiolysis in this high-alkali (23 mole %) glass, as has been found to be the case in the binary K_2O-SiO_2 glass system. (This result has not been duplicated in alkali-free high-iron phosphate glasses.)

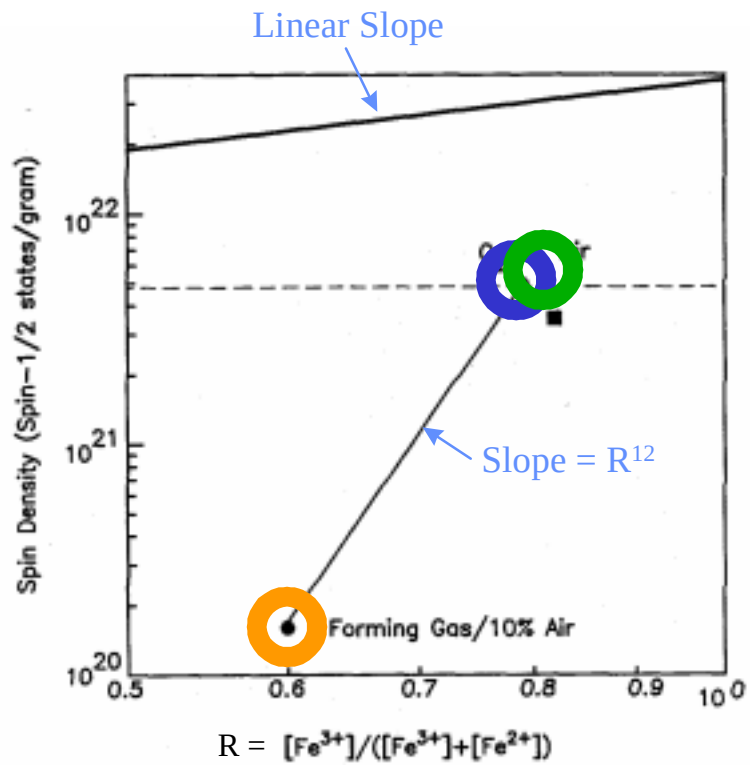


Effects of Melt Atmosphere on Some Properties of a Binary Iron Phosphate Glass (F43)

FeP

NRL

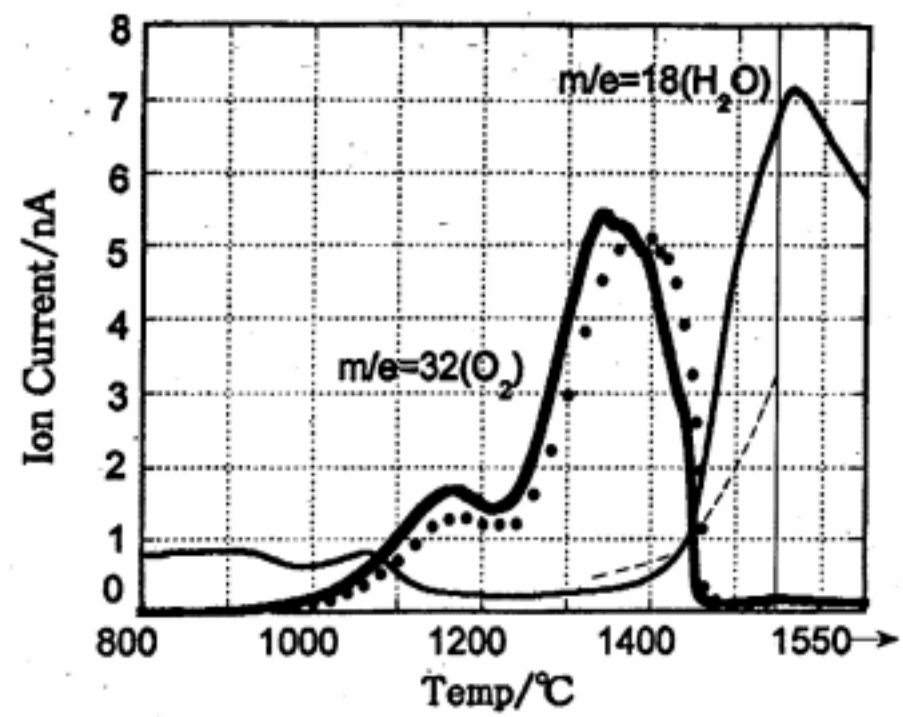




Spin densities measured by ESR are plotted as a function of the redox ratio, R, determined from Mossbauer. The structure and properties of these glasses appear to be critically dependent on R.

Quadrupole Mass Spectroscopy of Evolved Gasses

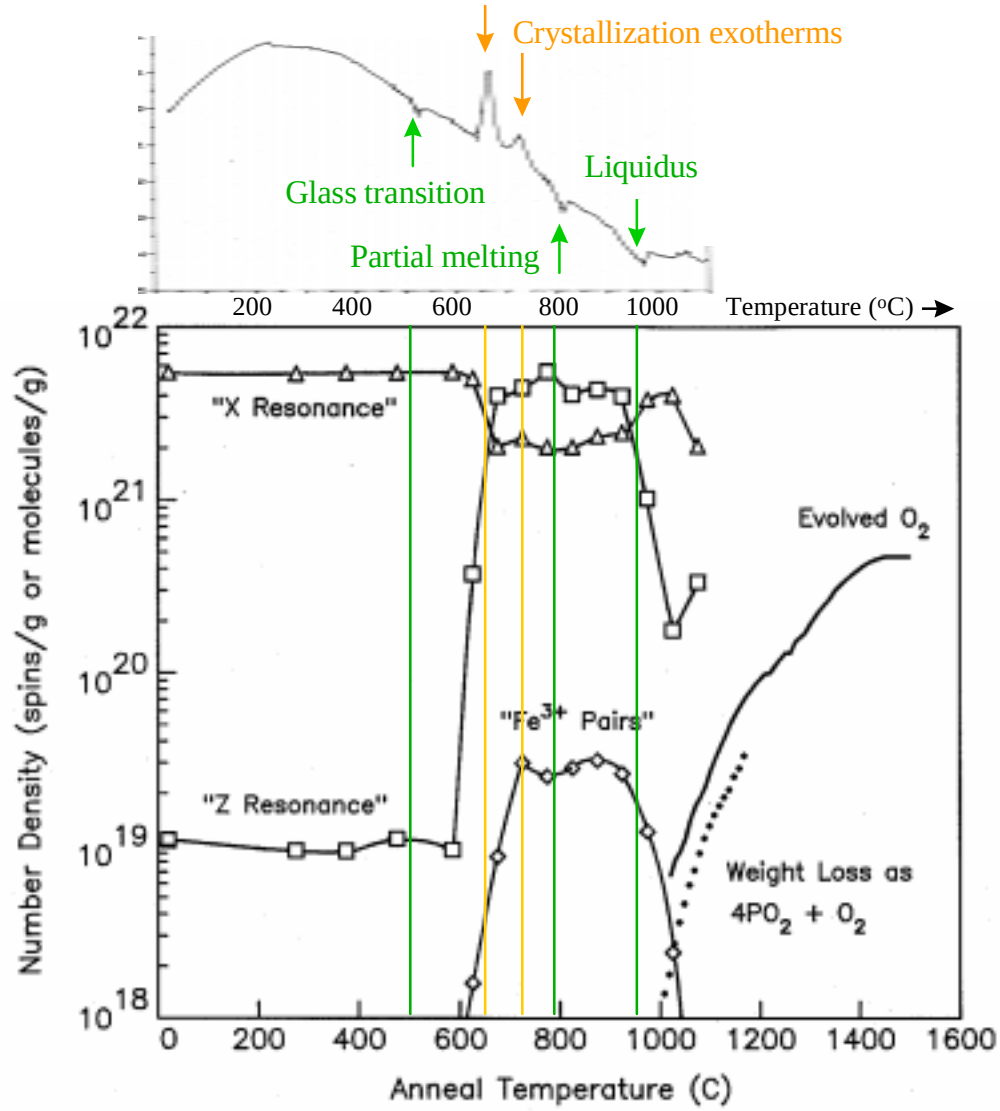
- Gas evolution was studied by quadrupole mass analyzer during ramped heating to 1550 ^{o} C at pressures ~10^{-5} Pa.
-
- Illustrated data are for glass PO_4-3 containing cerium. However, similar results were obtained for samples of glass F43 melted under various atmospheres.
-
- Unbroken curves show evolution of O_2 and H_2O from a sample γ irradiated to a dose of 30 Mgy. Dotted curve is O_2 evolution from an unirradiated sample. Dashed curve represents H_2 evolution.



Thermal Analyses of an Iron Phosphate Glass

- Differential Thermal Analysis (above right).
-
-
-
- Electron Spin Resonance Isochronal Anneal (symbols).
-
- Integrated Evolved O_2 at 10^{-5} Pa.
-
- TGA weight loss under Ar, expressed as numbers of PO_2 and O_2 molecules (dotted curve).

N.B. Data for γ irradiated glass PO_4-3. The appearance of "Fe^{3+} pairs" above 600 °C is a *latent* radiation effect not observed in the unirradiated material.



Summary: Iron Phosphate Glasses

- The X resonance observed in relatively oxidized (R≅0.8) iron phosphate glasses is an ESR property shared only with the iron-free amorphous peroxyborates (APBs). This observation means that either (a) the iron phosphate glasses, like the APBs, contain superoxide ions or (b) the two materials share a common amorphous antiferromagnetic order (e.g., linear chains of antiferromagnetically-coupled paramagnetic species). Possibility (a) has been considered in detail (Griscom et al., Nucl. Inst. & Methods B, in press, 1998.) and tentatively rejected since thermogravity and gas-evolution studies tend to show that the glasses contain too little oxygen to account for the model predictions.

- It is planned to pursue possibility (b) by neutron diffraction, further ESR studies, and modeling. One specific model to be considered (which could be responsible for the surprisingly high chemical durabilities of these glasses) postulates a nearly silica-like continuous random network of PO_4 and FeO_4 tetrahedra joined at all four corners in an alternating fashion.