

Project ID: **60313**

Project Title: **Radiation Effects on Transport and Bubble Formation in Silicate Glasses**

DOE Report Number: 60313

**Lead Principal Investigator:**

Dr. Alexander D. Trifunac  
Group Leader, Senior Scientist  
Chemistry Division  
Argonne National Laboratory  
9700 South Cass Avenue  
Argonne, Illinois 60439  
Telephone: 630-252-3483  
e-mail: [trifunac@anl.gov](mailto:trifunac@anl.gov)

## RESEARCH OBJECTIVE

This project aims to discover the chemistry induced by fast electron, gamma, and neutron irradiation of mixed oxide glasses. The fundamental knowledge gained will provide the scientific basis for extrapolating long-term behavior of radioactive waste glass forms.

## RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes work after 2 years of this project. Over the last 6 months, we completed our studies of spin-1/2 radiation-induced defects in silicate and borate glasses. Several classes of the such defects were examined and their structure and the formation mechanisms determined. Three papers were submitted to the Journal of Non-Crystalline Solids and the Journal of Chemical Physics.

*Alkali borate glasses. (paper 1)* Metastable electron and hole centers in boron trioxide and alkali borate glasses were studied using EPR and modeled with semi-empirical and *ab initio* methods. It was shown that electrons and holes in these glasses are trapped on valence alternation (VA) defects, under coordinated oxygen (holes) and over coordinated oxygen (electrons). This is the first experimental demonstration of the VA defects in any oxide glass. Before, the wisdom was that all radiation-induced defects in such glasses are coordination defects.

The local environment around these defects has major effect on spin parameters of the corresponding spin centers:

All variants of oxygen hole centers are holes trapped on the nonbridging oxygen in a  $\text{BO}_3^-$  unit. Alkali cations and protons are excluded from this center; the hole is trapped on under coordinated oxygen (the " $\text{O}_1^-$ " defect). There is no clear distinction between different variants of the hole centers in alkali borate glasses. The observed difference in the spin parameters is due to variations of the immediate environment of the  $\text{BO}_3^-$  unit.

The dangling bond center is an electron trapped on over coordinated oxygen (the " $\text{O}_3^+$ " defect). If the central oxygen is coordinated with borons, the neutral center is formed. If it is coordinated with an alkali cation or a compensated  $\text{BO}_3^-$  unit, a charged center is formed. The " $\text{O}_3^+$ " defect is a deeper trap for electrons than an isolated network-bound alkali cation. Only clusters of alkali cations and network-bound protons can compete with this deep Coulombic trap.

Three other spin centers were found in borate glasses: the B E" centers, alkali electron centers, and peroxy radicals. The B E" center is a variant of the B E' center in which one of bridging oxygens is replaced with boron. This center is likely to be an electron trapped by the " $\text{O}_3^+$ " center adjoining the B-B bond. The formation of the B E" center is indicative of the presence of oxygen deficiency centers in borate glasses; the peroxy radicals are likely to be formed by hole trapping at the  $\text{B}_4^- \text{OOB}_4^-$  linkages.

Alkali-related electron centers are shown to form upon electron trapping by a cluster of alkali cations loosely associated with  $\text{BO}_4^-$  groups. Thermally activated migration of alkali cations to a precursor defect is necessary for the formation of this center.

*Alkali silicate glasses. (paper 2)* O- and Si-centered radicals in Li, Na, K and Cs silicate glasses were studied experimentally and theoretically. Several structural and mechanistic insights were obtained:

Irradiation of alkali silicate glasses results in the formation of oxygen hole centers ( $\text{HC}_1$  and  $\text{HC}_2$ ), silicon peroxy radicals, and a silicon dangling bonds. It was shown that

in a subset of the  $HC_1$  centers the  $\bullet SiO^\wedge$  radical is strongly coupled to a single alkali cation. Thermally-activated swinging motion of this cation causes asymmetric spin relaxation. It was shown that trapping of the hole by nonbridging oxygen atoms does not result in the release of the compensating alkali cation, in contrast to the previously accepted scenario. The implication of this result is that irradiation of the waste forms will not result in the degradation of the glass via mass migration of the modifier cations, as was speculated by some researchers.

In the oxygen hole center  $HC_2$ , there is rapid tunneling of the electron between two degenerate sites with rate  $(0.2-50) \times 10^{11} \text{ s}^{-1}$  and activation energy ca. 10 MeV. This center is a hole trapped on a tetrahedral  $=SiO_2^{2-}$  unit or a planar  $-SiO_2^-$  unit.

It is demonstrated that silicon peroxy radicals are formed by decay of self-trapped excitons; the same process yields Si dangling bonds. In the latter, it is shown that the alkali cation is not coupled to the dangling bond. In phase-separated alkali silicate glasses, Si dangling bonds are mainly formed in the Si-rich phase. Our results identify the decay of self-trapped excitons as the source of oxygen that eventually coalesces to form microscopic bubbles in irradiated glasses.

Contrary to the previous reports, no intrinsic spin-1/2 electron centers were identified in pure alkali silicate glasses. Either the electrons are trapped by traces of metal impurity ( $Fe^{II}$ ,  $Ti^{IV}$ ) or the electron centers are diamagnetic.

H atoms in oxide glasses. Radiolytic H atoms play an important role in annealing the radiation damage. We were first to identify the formation mechanism for the H atoms in room-temperature glasses.

Trapped H atoms generated in radiolysis of  $B_2O_3:OH$  glass below 140 K were studied using pulsed EPR. Two types of trapped H atoms were present in this glass: one was an interstitial atom located in a void between several  $>BOB<$  fragments, another was the atom trapped in a cage between two hydrogen-bonded boroxol rings.

Mobile H atoms were observed at 300-500 K. Lifetimes of the H atoms were controlled by  $\gg 10^{18} \text{ cm}^{-3}$  of metastable spin centers (10-100  $\mu\text{s}$ ). The H atoms migrated with diffusion constant of  $1.5 \times 10^7 \text{ cm}^2/\text{s}$  (activation energy of 0.13-0.16 eV), residence time at the site of 4-5 ns and a jump length of 0.56 nm (at 300 K). This site-to-site migration causes rapid spin relaxation due to modulation of anisotropic magnetic interactions.

No H/D kinetic isotope effect was found on the decay/diffusion of the hydrogen atoms, but there was a significant isotope effect on the H atom yield ( $\approx 1.5-1.6$ ). This effect is comparable to the one observed in  $SiO_2:OH$  and aqueous acid glasses. This similarity indicates that in the room-temperature "wet"  $SiO_2$  and  $B_2O_3$  glasses, mobile H atoms are generated via electron trapping at the proton(s) associated with 3-fold coordinated oxygen ( $-OH_2^+$  and/or  $>OH^+$  centers). Semi-empirical simulations were used to estimate energetics of these electron trapping reactions.

## PLANNED ACTIVITIES.

Currently, we are carrying out systematic magnetic resonance studies of technologically relevant alkali borosilicate glasses.

## INFORMATION ACCESS

- 1 I. A. Shkrob, B. M. Tadjikov, and A. D. Trifunac *Magnetic Resonance Studies on Radiation-Induced Point Defects in Mixed Oxide Glasses. I. Spin Centers in  $B_2O_3$  and Alkali Borate Glasses*, submitted to J. Non-Cryst. Solids.

2. I. A. Shkrob, B. M. Tadjikov, and A. D. Trifunac, *Magnetic Resonance Studies on Radiation-Induced Point Defects in Mixed Oxide Glasses. II. Spin Centers in Alkali Silicate Glasses*, submitted to J. Non-Cryst. Solids.
3. I. A. Shkrob, B. M. Tadjikov, S. Chemerisov, and A. D. Trifunac, *Electron Trapping and Hydrogen Atoms in Oxide Glasses*, submitted to J. Chem. Phys.