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Radiation Effects on Transport and Bubble Formation in Silicate Glasses

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Lead Principal Investigator: A. D. Trifunac, tel. 630-252-3483, trifunac@anl.gov
Co-Investigators: I. A. Shkrob, tel. 630-252-9516, shkrob@anchim.chm.anl.gov
D. W. Werst, tel. 630-252-3474, werst@anchim.chm.anl.gov
Radiation and Photochemistry Group, Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

Number of Postdocs involved in the project: 1.

Problems and Relevance

Vitreous borosilicate forms will be used for storage of HLW within the DOE complex. Our research aims to discover the chemistry induced by β and γ irradiation of mixed oxide glasses. The effects of radiation are studied from the standpoint of defect formation and transport properties. Special emphasis is made on aggregation of defects and formation of oxygen bubbles. The fundamental knowledge gained provides the needed scientific basis for extrapolating long-term behavior of stored radioactive waste glass forms.

Research Objectives

To understand the effect of ionizing radiation on point defect formation, to discover the mechanism for radiation-induced volatilization and devitrification, to determine the temperature, dose, and dose-rate effects, to assess the role of relaxation processes and diffusion.

Research Progress and Implications

This report summarizes work after two years of a three-year project. Over this time, we carried out a comprehensive EPR study of paramagnetic radiation-induced defects in borosilicate, silicate, and borate glasses. Several classes of such defects were examined and their structure and mechanisms for formation determined. Two papers were published in the Journal of Non-Crystalline Solids and one in the Journal of Chemical Physics.

Alkali borate glasses. Metastable electron and hole centers in boron trioxide and alkali borate glasses were studied using pulsed 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 defects, undercoordinated oxygen (holes) and overcoordinated oxygen (electrons). This is the first experimental demonstration of such defects in oxide glasses. 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 BO_3^- unit. Alkali cations and protons are excluded from this center; the hole is trapped on undercoordinated oxygen (the "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 BO_3^- unit. The dangling bond center is an electron trapped on overcoordinated oxygen (the "O_3^+" defect). When the central oxygen is coordinated with borons, the neutral center is formed. If it is coordinated with an alkali cation or a

compensated BO_3^- unit, a charged center is formed. The "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.

Alkali silicate glasses. O- and Si-centered radicals in Li, Na, K and Cs silicate glasses were studied experimentally and theoretically. Irradiation of alkali silicate glasses results in the formation of oxygen hole centers (HC_1 and HC_2), silicon peroxy radicals, and a silicon dangling bonds. It was shown that in a subset of HC_1, the ≡SiO• radical is strongly coupled to a single alkali cation whose swinging motion causes asymmetric spin relaxation. It was shown that trapping of the hole by nonbridging oxygen atoms do not result in the release of the compensating alkali cation. **The implication is that irradiation of HLWF will not lead to mass migration of the modifier cations, as suggested by some researchers**. In the oxygen hole center HC_2, there is rapid tunneling of the electron between two degenerate sites; this center is a hole trapped on a tetrahedral $=SiO_2^{2-}$ unit.

It is demonstrated that silicon peroxy radicals are formed by decay of self-trapped excitons; the same process yields Si dangling bonds. Our results identify this reaction as the main source of O_2 that eventually coalesces to form microscopic bubbles. **The yield of oxygen is 10^2 to 10^4 times less than previously estimated. Radiation-induced volatilization of the glass appears to be much less a problem than was suggested in the past.**

H atoms in oxide glasses. Radiolytic H atoms play important role in annealing the radiation damage. We were first to identify the formation mechanism for the H atoms at 300-500 K. The lifetimes of the H atoms were controlled by metastable spin centers. The H atoms migrated with diffusion constant of 1.5×10^7 cm^2/s (300 K) and activation energy of 0.13-0.16 eV). No kinetic isotope effect was found on the decay/diffusion of the H atoms, but there was a significant isotope effect on the H/D atom yield. This effect is comparable to the one observed in SiO_2:OH and aqueous acid glasses. This similarity indicates that in all of oxide glasses, mobile H atoms are generated via electron trapping at the proton(s) associated with three-fold coordinated oxygen. Semi-empirical simulations were used to estimate energetics of these electron-trapping reactions.

Planned Activities

Currently, we are focusing on two remaining problems: (I) the exact nature of spin centers in alkali borosilicate glasses and (II) the structure of hole centers in borate glasses with high modifier content (the latter is present as an inclusion phase in borosilicate forms). To address these problems, we will study ESEEM, ENDOR and high-frequency EPR of spin defects in several such glasses and reference crystals.

Information Access

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