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The structural properties of cations in nuclear glasses

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Abstract

The structure of nuclear glasses and of simplified surrogates has been investigated using complementary diffraction and spectroscopic methods, together with numerical modeling. The diversity of structural surroundings of cations in glasses is reviewed at various scales. Cations usually occur in smaller sites in glasses than in crystals, with unusual site geometries such as 5-coordination. These sites may correspond to different structural positions. Network forming and networking situations illustrate the existence of a well-defined relationship with the glassy network, with cations improving glass stability. The complementary charge-compensation may sometimes give rise to a competition between cations. In that case, the cation may lose its stabilizing character and become a nucleating agent, as observed for "chameleon" elements, the coordination of which and hence the structural properties may change as a function of glass composition. Eventually, at the mesoscale, the heterogeneous distribution of cations has been recently visualized, providing keys to understand the nucleation processes in glasses.

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1. Introduction: from an ill-defined to a self-organized structure

Vitrification of high-level radioactive waste in borosilicate glasses is used in several countries. The fundamental properties of the waste forms are their chemical and mechanical durability against the forcing conditions represented by chemical alteration or internal/external irradiation. The waste immobilized in glass is composed of over 30 different nuclear fission and activation products, as well as minor actinides (Am, Np, Cm). Among other parameters,

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the nature and concentration of cations control glass properties, such as homogeneity or chemical stability under forcing conditions (alteration, irradiation). We present an overview of the local structure around cations in the inactive French nuclear glass, combining direct structural information and numerical simulation.

Information about the structure of silicate glasses and melts at a molecular-scale helps rationalize and understand their properties. This task is a challenge, because silicate glasses possess no long-range structural periodicity or symmetry, which limits the information available. However, a short-range order exists, usually manifested through the occurrence of polyhedral units such as 4-, 5-, or 6-coordinated cation sites. Cations may occur as modifiers, playing either a depolymerizing role for the polymeric framework, or as charge compensators, in the vicinity of charge-defective sites, such as trivalent or divalent tetrahedral cations. Some cation sites may occur in a network-forming (for tetrahedral sites) or similar networking position (for non-tetrahedral sites), with well-defined topological relationships relative to the polymeric network. These structural properties govern glass stability under forcing conditions. Rationalizing the short- and medium range organization around cations is constrained by the limited information due to the local and the non-directional, ionic nature of the cation-oxygen bonds. However, experimental observations and numerical simulations indicate that the structure of multicomponent oxide glasses and melts, in contrast to silica and other network glasses is not simply a continuous random network, but also shows the presence of well-defined cation sites and medium-range organization around cations, that obey the basic crystal chemical principles (e.g., Pauling rules).

We will mostly focus on the structural data that exist on the surrounding of cations in SON68, the nonradioactive glass surrogate of the French technological R7T7 glass. Various questions are centered on *structure-properties relationships* [Calas et al., 2002] and address specific questions during glass processing, such as the solubility of actinides, the influence of the formation of platinum group elements and spinels on glass properties or the presence of low-solubility elements such as Mo. Over the medium and long term, the control of glass structure on the stability of waste forms during heating, irradiation and alteration are major issues in nuclear waste management on which structural approaches shed light to rationalize the properties observed.

2. Experimental approach

Structural information on the surrounding of cations in glasses is primarily derived from x-ray and neutron diffraction (=wide angle scattering) and a broad range of spectroscopic methods (see e.g. Greaves and Sen, 2007). These techniques have benefited from the development of large user facilities, as synchrotron and neutron sources. Structural parameters, interatomic distances, bond angles and coordination numbers, may be derived from the pair distribution functions (PDF) provided by neutron and X-ray diffraction [Brown et al., 1995]. Chemical selectivity of PDF's may be obtained by coupling neutron scattering with isotope substitution. In most cases, the local structure around a given cation is obtained by using synchrotron Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. Complementary information on the sites occupied by cations is obtained by spectroscopic methods. Owing to the large diversity of cations in glasses, chemically selective methods are usually preferred, such as X-ray Absorption Near Edge Structure (XANES) spectroscopy, optical absorption/emission spectroscopy, Electron Paramagnetic Resonance (EPR), Nuclear Magnetic Resonance (NMR) or Mössbauer spectroscopy. These spectroscopic methods are sensitive to the local geometry, site symmetry and to the nature of the chemical bond. In addition, adequate detection may provide selective information on the structure of glass surfaces, e.g. using electron detection in X-Ray absorption spectroscopic techniques. Numerical simulations, such as classical or Ab Initio Molecular Dynamics (MD), are used to gain insight into the atomic level structure of glasses and embedding local structures within a larger topological landscape. In addition, Reverse Monte Carlo (RMC) or Empirical Potential Structure Refinement (EPSR) simulations provide 3D atomic-scale models consistent with the experimental data.

3. The specificity of cation sites in glasses

The classical random-network model of Zachariasen depicts cations such as Na, K, and Ca fitting into the voids created by a random network of corner-linked SiO₄ and AlO₄ tetrahedra (i.e., through bridging oxygens) and serving to balance bond valences within the glassy network. This oversimplified picture does not correspond to the experimental observations. For instance, in transition element-bearing glasses, glass coloration often, corresponds to a specific speciation of transition elements, indicating the presence of well-defined sites. On the other hand, PDF's

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