Radiation damages in nuclear waste glasses: a " NMR point of view "

Thibault Charpentier, S. Peuget, A. Le Gac, Bruno Boizot, C.L. Rountree, L. Martel, J. Somers

Radiation damages in nuclear waste glasses: a « NMR point of view »

T. Charpentier,[1] S. Peuget,[2] A. Le Gac,[2,3] B. Boizot,[3] C. L. Rountree,[4] L. Martel,[5] J. Somers[5]

1. CEA, IRAMIS, NIMBE, UMR CEA-CNRS 3685, F-91191 Gif-sur-Yvette, France
2. CEA, DEN, LMPA, 30207 Bagnols-sur-Cèze, France
3. CEA, IRAMIS, LSI, F-91191 Gif-sur-Yvette, France
4. CEA, IRAMIS, SPEC, CEA Saclay, CNRS UMR 3680, F-91191 Gif-sur-Yvette, France
5 European Commission, Joint Research Centre (JRC), Institute for Transuranium Elements (ITU), Postfach 2340, D-76125 Karlsruhe, Germany

Borosilicate glasses have been recognized as valuable materials for the conditioning of nuclear wastes. An important issue for their long-term behaviour is radiation effects which may impact their performance and stability. To address these concerns, a fundamental understanding of the origin *at the atomic scale* of the macroscopic property evolutions must be established. Over the last decade, magic-angle spinning nuclear magnetic resonance (MAS NMR) has firmly established itself as one of the most powerful tool to investigate a glass's structure. It offers several probes of the local structure, nuclei such as ^{11}B, ^{23}Na, ^{27}Al, ^{29}Si and ^{17}O, to probe changes either in the glass network or in the alkali distribution.

Recently, using external heavy ions irradiation (Xe, Au, Kr) to simulate alpha decays,[1-3] dramatic changes in the local network structure were evidenced : conversion of tetrahedral BO_4 units into planar trigonal BO_3 units (^{11}B), appearance of high-coordination aluminum units (AlO_5, AlO_6); glass depolymerisation (^{29}Si) and changes in the distribution of alkali cations (^{23}Na). Additionally, the spectra broaden globally which supports the hypothesis of an increased topological disorder after irradiation. All these structural changes are similar to those observed with increasing the glass temperature or quenching rate and support therefore the model of *ballistic disordering fast quenching events* which induce a new glassy state with higher fictive temperature. Effects of external electronic (beta) irradiations will be also discussed. If NMR spectra variations show similar trends -but much less pronounced- they are mainly engendered by alkali migration phenomena and formation of molecular oxygen.

Until recently, these studies were limited to externally irradiated samples (enabling the different components of irradiation to be dissociated for their precise investigation), but recently, the first MAS-NMR experiments could be performed on *radioactive* glasses (doped with 244Cm 0.1 % mol.) paving the way for future MAS NMR examinations of self-irradiation damages in glasses. Experiments were performed at the Joint Research Centre Institute for Transuranium Elements (JRC-ITU) where a commercial NMR spectrometer were integrated with a radioactive glovebox and a MAS commercial probe. First results will be presented. Competitive effects between the recoil nuclei and alpha decays were evidenced and the high resistance of the nuclear waste glasses corroborated.

[1] S. Peuget, C. Mendoza, E.A. Maugeri et al. Procedia Materials Science 7, (2014) 252-261
[2] C. Mendoza, S. Peuget, T. Charpentier et al., Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms 325 (2014) 5-65
[3] S. Peuget, E.A. Maugeri, T. Charpentier et al. J. Non-Cryst. Solids 378 (2013) 201-212.