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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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Keywords: Nuclear glasses; glass structure; EXAFS; XANES; neutron diffraction

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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 SiO_4 and AlO_4 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 indicate a limited distribution of cation-oxygen distances in glasses, also an indication of the existence of well-defined sites. In the last two decades, a wealth of information has demonstrated a specific structural behavior of cations in glasses, such as the presence of original coordination states or a heterogeneous distribution of cations at a mesoscale. The interplay between cations and the polymeric network or the competition between various structural environments of cations is at the origin of the modification of glass properties, an illustration of the structure-property relationships in glasses. Chemical selectivity of spectroscopic methods allows a direct comparison between model glasses of simplified composition and chemically complex technological glasses.

3.1. The existence of well-defined cation sites

Evidence for well-defined cation sites is provided by two pieces of information: the existence of a coordination shell, for which it is possible to get interatomic distances, and spectroscopic properties that are similar to those encountered in crystals or aqueous solutions. An example is provided by Zr in SON68 glass [Galoisy et al., 1999]. In addition to its interest in glass technology, as Zr controls glass stability during alteration or crystalline nucleation during glass-ceramics elaboration, Zr is an interesting structural probe of glasses, due to a versatile geometry of Zr-sites, including coordination numbers ranging between 6 and 8. Zr-$L_{2,3}$ XANES spectroscopy directly probes the empty 4d-states of Zr^{4+}. It is sensitive to crystal-field effects, which have been numerically simulated and hence to Zr-site geometry (Figure 1). The spectra of crystalline references illustrate the influence of the diversity of Zr-coordination, which directly affects the splitting of the empty 4d-levels. The Zr-$L_{2,3}$ XANES spectra of SON68 and model borosilicate glasses are characterized by Lorentzian shape components. The absence of further splitting of the crystal-field split 4d-levels is consistent with an Oh symmetry, which indicates that Zr occurs in a regular octahedron. This coordination number is consistent with EXAFS-derived Zr-O distances of 2.08 Å. The comparison with crystalline references provides a tool to quantify the coordination changes of Zr during glass alteration, in relation with the role of this element in the alteration layer [Pélegrin et al., 2010].

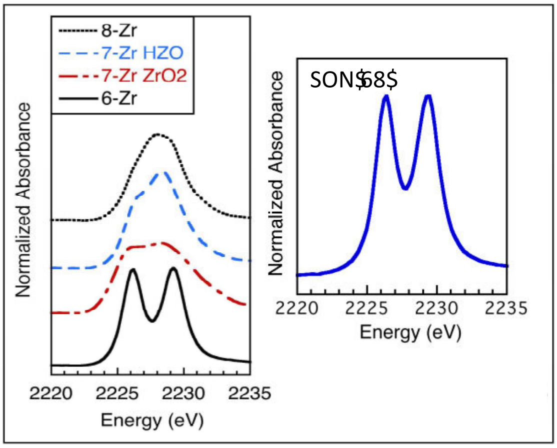

Fig. 1. Left. Zr-$L_{2,3}$ XANES spectra of crystalline references, lemoynite ($(Na,K)_2CaZr_2Si_{10}O_{26}$, 5–$6H_2O$) ($^{[6]}Zr$), baddeleyite (m-$ZrO_2$) and hydrous zirconia (HZO) (both with $^{[7]}Zr$) and $ZrSiO_4$ ($^{[8]}Zr$). Right. Zr-$L_{2,3}$ XANES spectrum in SON68 glass.

3.2. The diversity of cation sites

The sites occupied by cations in nuclear glasses have been determined by EXAFS and neutron/x-ray diffraction. Appendix 1 provides cation-oxygen distances and, for most elements, cation coordination numbers. A general property of the cation sites in glasses is that interatomic distances are usually smaller than those observed in crystals, which corresponds to smaller coordination numbers (see below). The cation-oxygen distances are usually more accurate than cation coordination numbers, especially in the case of a broad distribution of interatomic distances, as observed for large alkalis or alkaline earths. For these elements, the definition of an average coordination number would be questionable due to the broad distribution of the geometry of cation sites. Even for Na, the distribution of $d_{Na\text{-}O}$ distances is not symmetric, showing a long tail at large r-values. However, the average coordination number of Na and the $d_{Na\text{-}O}$ distances, obtained by coupling neutron/x-ray diffraction data coupled with numerical simulations, are smaller in alkali silicate than in borosilicate glasses [Cormier et al., 2000; Weigel et al., 2008]. This may indicate a different structural role of Na in these glasses. Indeed, as predicted by bond valence rules and as observed in crystals, $d_{Na\text{-}O}$ distances are smaller when a Na modifier is bound to non-bridging oxygen neighbors than when a Na charge-compensator is bound to a bridging oxygen. Some of structural characteristics commonly present in glasses, such as 5-coordination and more generally small coordination numbers, may be inherited from the peculiar dynamics of silicate melts.

Transition elements form a homogeneous group of glass components, for which it is generally possible to combine radial information with data from symmetry-sensitive spectroscopic techniques. These cations often occupy unusual sites in oxide glasses: in this case, crystalline models need to be used with caution. A general observation is the trend towards lower coordination numbers in glasses relative to crystals. For instance, 5-fold coordinated sites are encountered for transition element cations such as Ti^{4+}, Ni^{2+}, Fe^{2+} or Fe^{3+}. The same transition element cations may also occur in tetrahedral sites showing various degrees of distortion. The relative proportion of 4-and 5-coordinated sites usually exhibits a strong chemical dependence, due the different structural role of these local environments (see 4.1).

Tetrahedral coordination of transition elements may also correspond to a sp^3 hybridization, a situation often encountered in extreme oxidation states, such as for Mo(VI). However, as discussed in Section 4.1, the relationships with the silicate framework are very different between these two groups of tetrahedral cations, explaining the contrasted structural role that these elements play in the stability of the glass. Finally, as shown in Section 3.2 for Zr^{4+}, some transition element cations may be octahedrally coordinated, but this coordination arises from peculiar relationships between cation sites and the silicate framework in presence of charge compensating cations (see 4.1). However, this coordination state appears less frequent than in crystals, where octahedral sites are encountered in most crystalline silicates, and are generally preferentially occupied by transition elements.

Among actinides, uranium and neptunium have been investigated in SON68 glasses. Both elements exist in their most oxidized state, with a similar geometry. U is present in a UO_3-type environment, with U–O distances and U-coordination number similar over a broad uranium concentration range [Jollivet et al., 2002]. The coexistence of short axial bonds, due to linear actinyl groups, with larger equatorial bonds, is observed for neptunyl groups, the equatorial Np-O bond lengths being larger than the corresponding U-O distances [Petit-Maire et al., 1989].

3.3. Five-coordination: a frustrated octahedron?

The frequent occurrence of 5-coordinated transition metal ions in glasses may be seen as a witness of the importance of atomic motions in the molten stage. 5-coordinated ions indicate the presence, in the melt, of reactive intermediate species, resulting from the permanent reorganization of octahedral complexes through associative/dissociative reactions. It is a major difference with liquid water, in which the sites occupied by transition metal ions retain a high symmetry, as a result of the minimization of the local entropy and the additional driving force provided by their crystal field stabilization energy. Indeed, silicate melts behave as a highly organized solvent: as the O neighbors of transition metal ions are linked by strong Si-O covalent bonds to silicate tetrahedra, the motion of silicate groups, associated with the viscous flow and atomic diffusion, will easily destroy the weakly bound cation sites. This mechanism has been evocated to explain the presence of minority $^{[5]}$Si and $^{[5]}$Al in the glassy polymeric network [Farnan and Stebbins, 1994; Massiot et al., 2008]. In multicomponent glasses, an easier cation-oxygen bond breaking ability explains why, by contrast to $^{[5]}$Si species, which only affect a minority of Si atoms, 5-coordinated sites are a major coordination state for cations in oxide glasses.

4. The structural role of cations

The presence of stable local topologies is a remarkable property of the surrounding of some elements when considering the importance of disorder at larger distances. Indeed, there is usually a loss of information over the medium-range structure scale, beyond the coordination shell. The causes are multiple. The distribution of cation-oxygen distances is a primary cause of disorder. But distribution in the dihedral angles between cation polyhedra and their structural surrounding is an efficient cause for loss of information, as observed in framework glasses such as silica, in which the presence of rigid tetrahedra limits disorder effects on the first coordination shell.

4.1. Structural connections with the silicate framework

A network-forming position does not just correspond to a cation in tetrahedral coordination. This property arises from a structurally stable connection between the cation tetrahedral site and the silicate framework. Nuclear glasses and their inactive analogs contain cations in a network-forming position, such as Fe^{3+} or Zn^{2+} (Figure 2a). This explains the role of Zn in improving the mechanical properties and the chemical durability of glasses [Calas et al., 2002]. Na^+ and other alkalis play a charge-compensating role. Zn-O-Si angles are smaller than Si-O-Si angles in vitreous silica, due to lower cation-cation repulsion, resulting in a decrease of the size of the rings in the glassy polymeric network. Bond valence models show that two Na^+ ions charge compensate the oxygen atoms bound to both Zn and Si. Such an environment has been recently modeled for network-forming $^{[4]}Fe^{3+}$ in aluminosilicate glasses, with Na^+ ions acting as charge-compensators [Weigel et al., 2008].

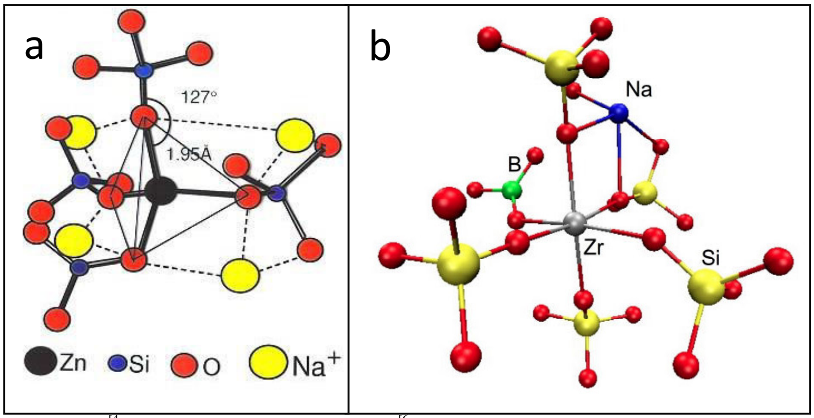

Fig.2. Network-forming position of $^{[4]}$Zn (a) and networking position of $^{[6]}$Zr (b) in SON68.

Another stable connection with the silicate network is illustrated by octahedral Zr, as demonstrated by the presence of Si second neighbors shown by EXAFS in SON68 [Galoisy et al., 1999]. Zr-O and Zr-Si distances indicate regular ZrO_6 octahedra, linked by corners to SiO_4 tetrahedra, in a similar position as observed in crystalline zirconosilicates (Figure 2b). MD simulations, coupled with Zr K-edge EXAFS in glasses of simplified composition, indicate charge compensation by Na^+ ions. The high symmetry of the Zr-sites and its immediate surrounding adds support to a networking role of Zr, i.e. a structural position that strengthens the glassy network [Ferlat et al., 2006].

4.2. The peculiar case of polyanions

Under oxidizing and mildly reducing conditions, Mo occurs as tetrahedral molybdate polyanions. However, the environment beyond the first shell is different from that observed for Zn^{2+} or Fe^{3+}. EXAFS data do not indicate contributions beyond the coordination shell and there is no apparent connection of molybdate groups to the borosilicate framework. The combination of EXAFS data with a bond-valence model and MD simulations indicates that molybdate groups are located within alkali and alkaline-earth rich domains in the glass. This is confirmed by recent NMR data that show a high similarity of the environment of Mo in crystalline Na_2MoO_4 and in a sodium silicate glass (Angeli et al., 2011). Local charge compensation is provided by alkalis and alkaline earth cations [Calas et al., 2003]. The composition of crystalline molybdates crystallizing from borosilicate glass/melts seems consistent with this model. This behavior illustrates the heterogeneous structure of the glassy state. In addition, the competition for charge compensating between B and Mo sites explains the different nature of the molybdates formed by phase separation in the melts or by crystallization of heated glasses. This modification of molybdate composition as a function of the thermal history arises from temperature-induced coordination changes of B in borosilicate glass/melt systems [Michel et al., 2013; Stebbins and Ellsworth, 1996]. This modifies the activity of cations, as shown by the reaction:

$$Na_{CC} + BO_4 \leftrightarrow BO_3 + O_{NBO} + Na_{NM}$$

where Na_{CC} stands for charge compensating Na, O_{NBO} for non-bridging oxygen and Na_{NM} for network modifying Na. Alkali molybdates may form in borosilicate melts, as a result of a higher availability of alkali cations in the presence of predominately 3-coordinated B ($^{[3]}$B). By contrast, the partial transformation of B from a triangular to a tetrahedral coordination during cooling towards the glassy state will increase the proportion of Na^+ cations (and other alkalis: Cs…) involved in charge compensation of B sites, thus explaining the preferential formation of calcium molybdates during thermal aging of these glasses, as alkalis are no longer available.

4.3. Competition for charge compensation

Network forming or networking positions imply the need to ensure the overall neutrality of these sites. Generally, there is a charge deficit, when considering the balance between the formal positive charge of the cation and the sum of the negative charge of the cation-oxygen bonds. Alkalis and alkaline earths are then required to charge compensate this deficit. MD and RMC simulations of Na-Ca alumino-borosilicate glasses indicate a competition for charge-compensation between network forming or networking elements, with a decreasing preference in the order: Al, Zr, Zn and B [Cormier et al., 2000].

Most Na^+ ions compensate the charge deficit of network-forming $^{[4]}$Al or $^{[4]}$B, as $^{[6]}$Zr are charge-compensated by Ca^{2+}. Increasing the concentration of a more competitive cation will force a less competitive cation to change coordination. This explains the contrasted behavior of "chameleon" elements such as Zr, Zn, Ti, etc. Depending on glass composition and external parameters such as thermal history, these elements either improve glass durability or facilitate crystalline nucleation, providing a nice illustration of structure-property relationships in glasses.

4.4. Heterogeneous structure of glasses

Direct evidence of a medium-range order around cations has been brought by the presence of cation-cation correlations in second difference functions obtained from neutron scattering with isotopic substitution on transition element-bearing oxide glasses [Cormier et al., 1998, 2001]. At the nanometer scale, silicate glasses exhibit a heterogeneous structure, with domains enriched in alkalis and alkaline earth cations exhibiting stable cation–cation distrances and coexisting with the glassy polymeric framework [Majérus et al., 2004]. This vision is consistent with the Modified Random Network and Stereochemically Defined models of glass structure, as with a convergent set of experimental and numerical data, indicating an extensive medium range ordering in silicate glasses [Greaves and Sen, 2007].

Additional evidence of the heterogeneous structure of silicate glasses has been recently shown by Z-contrast scanning transmission electron microscopy (Z-STEM) [Dargaud et al., 2011]. In that case, a direct imaging of chemical fluctuations of transition elements (Zr, Zn) in glasses is possible with both a chemical and a spatial resolution. The length scale of Zr/Zn atoms segregation domains depends on the glass thermal history, suggesting either the beginning of phase separation or an intrinsic feature of the glass structure. These nanoscale heterogeneities may shed light on the processes involved during crystalline nucleation and further glass-to-crystal transformation and are explained in more detail in this issue [Cormier, 2014].

5. Conclusion

Amorphous solids such as glasses and gels have benefited from molecular scale approaches, which shed light on their structural organization and may be used to rationalize their properties. The local structure around key cations provides a unique harvest of results of scientific and technological significance: unusual coordination numbers, distribution of site geometry, site sensitivity to the chemical bond, medium-range organization, heterogeneous spatial distribution… Some structural characteristics may be inherited from the peculiar dynamics of silicate melts. Short-range order around cations in glasses shows that bond valence rules are operational in glasses, emphasizing the interdependence between structure and chemistry at the local scale. The chemical and mechanical durability of nuclear glasses against the forcing conditions represented by chemical alteration or internal/external irradiation is a unique application field of these concepts (Calas et al., 2010). With an increasing number and diversity of solid state spectrometers in hot zones and the presence of dedicated beamlines on user facilities (e.g. the MARS beamline on the SOLEIL synchrotron in France), the comparison of simplified inactive and active surrogates with the real nuclear glasses will be feasible. This will provide further basis for the analogy concept, at the basis of most models on active glasses, concerning either the structure of industrial, chemically complex glasses or the evolution of this structure during ageing under irradiation or alteration during decades and on which only a few structural data exist.

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Appendix A.

Table 1. Chemical composition (wt%; 3% accuracy) and structural properties of the simulated surrogate glass SON68. Values obtained on SON68 glasses are designated by *a*. Other data are reported for model borosilicate glasses and other oxide glasses, designated by *b* and *c*, respectively.

Oxide	Wt%	Coordination Number	Averaged interatomic Distances	Reference
Glass frit components				
SiO_2	45.48	4	1.60Å (*b*)	Cormier et al., 2000
Al_2O_3	4.91	4	1.76Å (*c*)	Weigel et al., 2008
B_2O_3	14.02	3, 4	1.38 Å ($^{[3]}$B)-1.47Å ($^{[4]}$B) (*c*)	Majérus et al., 2003
Li_2O	1.98	4	1.99Å (*c*)	Zhao et al., 1998
Na_2O	9.86	8	2.2Å-2.55 (*b*)	Cormier et al., 2000
CaO	4.04		2.35Å (*c*)	Michel et al., 2013
ZnO	2.50	4	1.96Å (*a*)	Le Grand et al., 2000
Corrosion-derived elements				
Cr_2O_3	0.51	6 (Cr^{3+})	1.99Å (*c*)	Villain et al., 2010
Fe_2O_3	2.91	4 (Fe^{3+})	1.88Å (*a*)	Pélegrin et al., 2010
NiO	0.74	4, 5	1.95Å ($^{[4]}$Ni)- 2.0Å ($^{[5]}$Ni) (*c*)	Galoisy et al., 2005
Fission products				
ZrO_2	2.65	6	2.08Å (*a*)	Galoisy et al., 1999
Cs_2O	1.42		3.2-3.3Å (*c*)	Stefanovsky and Purans, 2012
SrO	0.33	6	2.62Å (*c*)	Cormier et al., 1999
Y_2O_3	0.20	6, 8	2.28Å ($^{[6]}$Y)-2.38Å ($^{[8]}$Y) (*c*)	Simon et al., 2013
MoO_3	1.70	4 (Mo(V))	1.78Å (*a*)	Calas et al., 2003
MnO_2	0.72	4, 5 (Mn^{2+})	2.07Å (*b*)	McKeown et al., 2003
CoO	0.12	4	1.94Å (*a*)	Hunault et al., 2014
Ag_2O	0.03		2.13-2.22Å (*c*)	McKeown et al., 2005
SnO_2	0.02	6 (Sn^{4+})	2.03Å (*b*)	McKeown et al., 2008
Sb_2O_3	0.01	3	1.95Å (c)	Youngman et al., 2003
TeO2	0.23	3, 4	1, 89Å ($^{[3]}$Te)-2.04Å ($^{[4]}$Te) (*c*)	Shimizugawa et al., 1995
BaO	0.60		2.72Å (*c*)	Taniguchi et al., 1997
La_2O_3	0.90	8	2.51Å (*b*)	Jollivet et al., 2007
Ce_2O_3	0.93	8	2.44Å (*b*)	Jollivet et al., 2005
Pr_2O_3	0.44	8	2.49Å (*b*)	Larson et al., 1990
Nd_2O_3	1.59	8	2.48Å (*b*)	Jollivet et al., 2005
Actinides (Total actinide content: 0.85 wt%)				
UO_2 (as U(VI))		2(uranyl)+5(equatorial)	1.78 and 2.25Å (*a*)	Petit-Maire et al., 1986
ThO_2		7-8	2.22Å ($^{[7]}$Th)-2.39Å ($^{[8]}$Th) (*a*)	Petit-Maire et al., 1986
Np(V)		6	2.25Å (*a*)	Petit-Maire et al., 1989

Pu^{4+}	6	2.25Å (*b*)	Lopez et al., 2005
Cm^{3+}	6-7	2.45Å (*b*)	Lopez et al., 2005

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