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# Uranium speciation in binary alkali-borate glasses: a multispectroscopic study

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## Abstract

During centuries, uranium has been used as an efficient coloring agent in glasses. It is also used as a surrogate of transuranic elements in nuclear waste matrices. In glasses and ceramics, U is mainly present in the forms of U(VI) and U(IV), with minor amounts of U(V). Silicate glasses show uranyl sites U(VI) with an original geometry, based on shorter distances between U and equatorial oxygens than in most uranyl complexes found in crystals and aqueous solutions. This intermediate speciation of U(VI) in glasses is also illustrated by their color, which may vary between green to brown, depending on the glass composition. Uranium speciation has been investigated since years in complex technological borosilicate glasses using XANES, EXAFS and neutron/x-ray diffraction data. However, there has been no investigation of the more simple alkali borate glasses, despite they show a large diversity of cation sites as a function of the presence of various structural superunits. Here we report the study of uranium speciation in binary borate glasses using U optical and L3-edge X-ray absorption spectroscopies to determine the valence and local structure of U. Our results show that the alkali content and nature drastically influence uranium speciation: the color change from pale green to deep yellow with increasing alkalinity reflects the change of the redox ratio between co-existing U(IV), U(V) and U(VI). In addition, changes in the 5f-electron localization causes the transformation from uranyl to uranate speciation. The relation between the uranium species and the glass network will be discussed in light of the composition-dependent structural changes of the borate glass.

**Keywords:** uranium, borate, EXAFS, nuclear waste storage

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