THE EFFECT OF IODINE INCORPORATION ON THE CATION IN BOROSILICATE GLASSES

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Abstract

We have recently developed an approach using high-pressure synthesis conditions able to incorporate large quantities of iodine in aluminoborosilicate glass with the aim to propose a durable solution for the immobilisation of iodine radioisotopes such as 129I. For aluminoborosilicate glasses, it has been demonstrated that the incorporation of iodine is strongly dependent on the presence of alkali or alkaline-earth cations to form iodide (I-) or iodate (IO3-) molecular groups that are charge compensated by surrounding Na+ or Ca2+ for the most important. It is well-accepted that alkali or alkaline-earth cations in glasses act as a network modification role or as a compensation role to network species. The first case occurs in glasses enriched with respect to alkaline (or earth-alkaline) cations whereas the second case applies when additional positives charges are required for negative charge compensation of network units. In the particular case of the aluminoborosilicate glasses, two species require charge compensation to fulfil their charge neutrality: BO4 and AlO4 tetrahedrons. It has already been observed that the compensation of the AlO4 units prevails on the BO4 units compensation. This latter one is able to convert into BO3 that does not require charge compensation. However, even at low alkali content (i.e. peraluminous compositions), the amount of BO4 present in the glass is non-zero, indicating that depending on the composition, the aluminium priority for charge compensation is somehow limited. In the present work, the effect of the applied pressure on the structure of the quenched glasses is fairly apprehended; conversely, the effect induced by the incorporation of iodine on the glass structure is poorly known. This latter aspect is crucial in order to formulate a specific matrix composition able to immobilize iodine radioisotopes.

We have conducted a series of high-pressure experiments (1.0 GPa) on several aluminoborosilicate glasses in the SiO2-Al2O3-B2O3-Na2O system with 5 and 20 mol.% B2O3, 20 mol.% Na2O, 5 mol.% Al2O3 and 55 and 75 mol.% SiO2. The starting glass was equilibrated at high-pressure with an iodine fluid phase using either I2 or I2O5 as a starting source. Those investigated compositions were also enriched with 17O isotope in order to study the distribution of oxygen species (Bridging, Non-Bridging and Free Oxygen) within the glass. The iodine content in the recovered glass reaches up to 2 mol.% and appears to be more soluble under oxidized conditions (i.e. I2O5) in agreement with previous works. The I-bearing glasses were characterized by 11B, 17O, 23Na and 27Al Solid-State NMR.

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For the investigated compositions, Al is mainly present as AlO4 units in agreement with previous works for Na-bearing glasses. Whereas the pressure conditions produce a noticeable effect on the glass structure by increasing the N4 value (BO4/BO4+BO3); the effect of iodine remains weak. In detail, the incorporation of iodine as I- slightly decreases the N4 from 0.66 to 0.63; whereas the incorporation of iodine as IO3- (I5+) does not seem to affect the N4 value. The preliminary results obtained from 17O NMR do not reveal the presence of additional resonance that could be assigned or related to the dissolution of iodine. The most important change is observed on the 23Na diso of charge-compensating Na that appears to be affected by the iodine incorporation.
Our preliminary results show that the iodine dissolution into aluminoborosilicate glasses under high-pressure conditions does not dramatically influence the glass structure and the degree of polymerization appears to be roughly constant. Owing to the small change observed, the choice of a specific glass matrix for the immobilisation of iodine nuclear waste that is chemically durable seems not to be dictated by the iodine dissolution itself; at least for the strongly polymerized investigated glass compositions. Nevertheless additional work is required for investigating the iodine impact on more depolymerized glasses.

Keywords: Aluminoborosilicate, borosilicate, structure, pressure, solid, state, NMR, Nuclear, Radioactive, Waste, Immobilisation, Iodine