

# THE EFFECT OF IODINE ON THE LOCAL ENVIRONMENT OF NETWORK FORMING ELEMENTS IN ALUMINOBOROSILICATE GLASSES: AN NMR STUDY

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Among radioisotopes produced by nuclear power plants, halogens (<sup>129</sup>I and <sup>36</sup>Cl) represent a major trouble as their high volatility makes them impossible to immobilize through classical nuclear waste vitrification. The approach we have recently developed using high-pressure synthesis conditions is able to incorporate large quantities of iodine (I) in aluminoborosilicate glass that could potentially be used as a matrix for <sup>129</sup>I immobilisation.

The I incorporation in the structure of aluminoborosilicate glasses is strongly dependent on the presence of alkali or alkaline-earth cations needed to charge compensate the iodide (I<sup>-</sup>) and/or iodate (IO<sub>3</sub><sup>-</sup>) molecular groups. It is currently accepted that the incorporation of volatile species in the glass structure may induce large structural change that, by extent, could influence the physical properties of the glass (i.e. chemical durability). This aspect is of prime importance for nuclear waste that requires a geological disposal for a long period of time. However, the effect induced by I dissolution on the glass structure is actually not apprehended.

We have investigated the change in the glass network structure as a function of I content. We conducted a series of high-pressure experiments (1.0 GPa) on several aluminoborosilicate glasses in the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O system. The starting glass was equilibrated with an iodine fluid phase using either I<sub>2</sub> or I<sub>2</sub>O<sub>5</sub> as a starting source. XPS analyses revealed that iodine in the recovered glass (reaching up to 1 mol.%) appears mainly under I<sup>-</sup> form, co-existing with I<sup>5+</sup> when samples were loaded with I<sub>2</sub>O<sub>5</sub>.

The I-bearing glasses were characterized by <sup>11</sup>B, <sup>23</sup>Na and <sup>27</sup>Al Solid-State NMR. Aluminium in the glass is mainly present as AlO<sub>4</sub> 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 N<sub>4</sub> value (BO<sub>4</sub>/[BO<sub>4</sub>+BO<sub>3</sub>]); the I effect remains weak. In detail, the I incorporation (either I<sup>-</sup> or IO<sub>3</sub><sup>-</sup>) does not seem to affect the N<sub>4</sub> value. In contrast, the <sup>23</sup>Na NMR parameters (δ<sub>iso</sub> and C<sub>q</sub>) exhibit a shift towards values indicating a more compensating role for Na<sup>+</sup> cations. Therefore, Na<sup>+</sup> acting as network modifiers are scavenged by I species for charge compensation (*figure 1*). It also suggests that the role of Na<sup>+</sup> cation for charge compensation of AlO<sub>4</sub> and BO<sub>4</sub> unit prevails on its role of network modifiers.

Further additional work is required for investigating the iodine impact on more extended range of glass compositions. Nonetheless, in the present investigated glasses, only little changes are observed on the glass structure upon I dissolution.

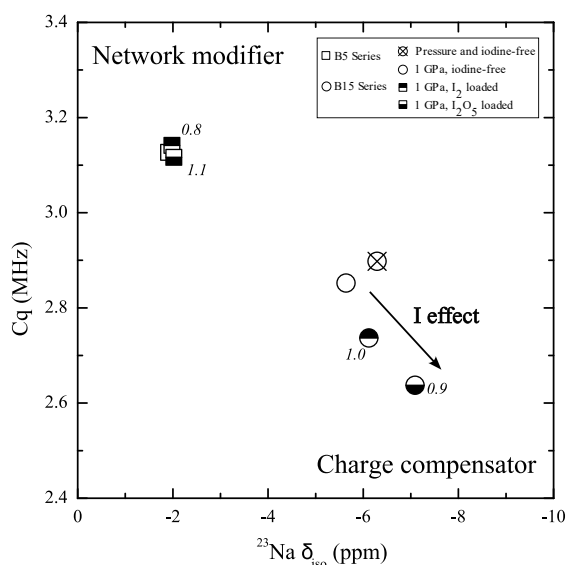


Figure 1: Evolution of the <sup>23</sup>Na parameters as function of iodine source and pressure.