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**HIGH-PRESSURE GLASS-CERAMICS FOR IODINE NUCLEAR WASTE
IMMOBILIZATION: PRELIMINARY EXPERIMENTAL RESULTS**

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29

30 Abstract

31 Several matrix types have been considered for the immobilization of iodine radioisotopes
32 from which glass-ceramics represent a serious candidate; however, I-bearing glass-ceramics
33 are challenging owing to the iodine volatility. We have synthesised glass-ceramics from the
34 partial crystallization of a parental glass enriched with different iodine sources (I_2 and I_2O_5)
35 under high-pressure conditions (up to 1.5 GPa). The samples were characterized using
36 Scanning and Transmission Electron Microscopy and X-ray Diffraction. Using standard
37 synthesis protocol: melting, nucleation and crystal growth, we have obtained glass-ceramics
38 showing the coexistence between I-bearing glass (<0.8 mol.% I), nepheline ($NaAlSi_3O_8$) and
39 iodosodalite ($Na_8Al_6Si_6O_{24}I_2$ with up to 14 mol.% I). For several samples, we observed also
40 the presence $NaPt_3O_4$ witnessing a chemical reaction between the container walls and the
41 inside experimental charge. The structure of iodosodalite is entirely resolved by Rietveld
42 refinement of the XRD pattern for I_2 experiments whereas it cannot be solved for I_2O_5
43 experiments suggesting a change in the iodosodalite structure probably due to the β cage
44 filling by IO_3^- clusters instead of I^- . Our present work could represent a potential solution to
45 tackle the problem of iodine radioisotopes immobilization.

46

47 Keywords: glass-ceramics, iodosodalite, high-pressure, nuclear waste immobilization

48

49 1. Introduction

50 Iodine radioisotopes are by-product of the nuclear plant industry and is of major concern in
51 the nuclear waste immobilization [1,2]. In particular, ^{129}I is a major troublesome isotope due
52 to its high mobility in the environment and its long half-life (15.7 My) [3-8]. Moreover, ^{129}I is
53 shown to be the main contributor of radioactive dose at the outlet of a geological disposal site

54 [9,10]. For these reasons, ^{129}I represents an immediate environmental hazard and a societal
55 risk that needs to be addressed. As a matter of fact, radioactive iodine can be incorporated into
56 human body involving metabolic damages to the long term [11-14]. However, due to its high
57 volatility, iodine cannot be immobilized using classical vitrification of nuclear waste bearing
58 glass at ambient pressure [15-17]. In a recent landmark work, Riley et al. [1] reviewed this
59 problematic and enumerated possible matrix able to efficiently immobilize iodine
60 radioisotopes such as: crystalline phases (e.g. [18-21]), glass (e.g. [22-24]) or cement (e.g.
61 [25]). They also pointed out that glass-ceramics could be a good candidate for the
62 immobilization of ^{129}I with the difficulty to find a glass binder that is compatible (i.e. in
63 equilibrium) with the I-bearing crystalline phases. From the general viewpoint, there is a
64 growing interest in the formulation of glass-ceramics for nuclear waste immobilisation (e.g.
65 [26-30]). Glass-ceramics have several advantages over pure crystalline or pure glass
66 immobilization matrix: 1) higher mechanical resistance with a lower fracture propagation
67 [31], 2) multiple barrier offering a better chemical stability [32,33] and 3) higher
68 incorporation of nuclear waste [34,35]. Several studies [36-40] have developed experimental
69 protocols for synthesising I-bearing glass-ceramics using iodosodalite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{I}_2$) as the
70 I-bearing crystalline phase embedded in a sodium aluminoborosilicate glass binder. Although
71 the developed approach involves the consolidation with a glass binder, this latter phase does
72 not contain iodine, therefore the question remains on the thermodynamic stability through
73 time in between the I-bearing crystalline phase and the I-free glass matrix. Although,
74 iodosodalite crystalline phase has not been studied extensively, it appears as an appropriate
75 crystalline phase for immobilizing radioactive iodine as 1) it incorporates a large quantity of
76 iodine (>10 mol.% I) in its cage structure, 2) it is stable at high-temperature (up to at least
77 950°C , [40]), 3) it incorporates iodine under different forms, either I^- or IO_3^- [41], 4) it can be
78 obtained using different methods (i.e. aqueous, hydrothermal and sol-gel syntheses, [40]) and

79 5) several studies measured the dissolution rate of iodosodalite [42,43], which showed good
80 chemical resistance to standard leaching tests.

81 Obtaining a glass-ceramics requires the crystallization from a parent glass held at high
82 temperature and cooled down to a temperature that allows nucleation and crystallization
83 processes [44,45]. As mentioned earlier, the main difficulty with iodine is its high volatility at
84 ambient pressure and high-temperature that prevents from iodine retention. For instance, at
85 best the I solubility at ambient pressure in low activity waste glass compositions does not
86 exceed 0.7 mol.% I [22]. An alternative to that problem has been developed recently by using
87 high-pressure conditions for synthesising aluminoborosilicate glasses. The recent works [46-
88 48] showed that the confinement pressure strongly enhances the I solubility in nuclear waste
89 glasses. Although, this approach represents a potential solution, the chemical durability of
90 those I-bearing matrices will remain to be determined in future studies [49].

91 In the present study, we demonstrate for the first time the possibility to synthesise I-bearing
92 glass-ceramics obtained from the crystallization of a parent aluminoborosilicate glass under
93 high-pressure conditions. The experiments were conducted with a standard thermal path
94 involving melting-nucleation-crystallization steps, leading to the formation of a stable I-
95 bearing silicate phase (i.e. iodosodalite) in equilibrium with a I-bearing aluminoborosilicate
96 glass and showing no apparent open porosity. From electron microscopy and X-ray
97 Diffraction we were able to quantify the relative crystalline phase proportions. We used
98 different iodine sources in order to investigate the change in the iodine retention in the glass
99 and crystals, which appears to influence the chemistry of the iodosodalite. We then discuss
100 how iodine is incorporated qualitatively and quantitatively into our glass-ceramics; and we
101 propose several solutions to improve the iodine assimilation into glass-ceramics.

102 2. Experimental and analytical methods

103 2.1. Starting material and high-pressure syntheses

104 In the present work, we studied two starting compositions noted NH and SoNH, both prepared
105 in the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-CaO-Na}_2\text{O}$ system. In the investigated compositions, we did not add
106 any nucleating agents. The glass compositions are reported in Table 1 and were chosen such
107 as to represent close analogues to the low activity waste aluminoborosilicate glass
108 compositions [50]. In between NH and SoNH, we changed the Na_2O content in order to see if
109 the addition of Na promotes the formation of sodalite that is a Na-rich crystalline phase. The
110 powders were prepared from a mixture of oxides for SiO_2 , Al_2O_3 , B_2O_3 and CaO and Na_2CO_3
111 for the source of Na_2O . The starting powders were grinded in an agate mortar under ethanol.
112 The dried powders were melted in a Pt crucible at 1250°C for 2h in a box furnace and then
113 quenched in a cold-water bath. The recovered glasses were characterized for major element
114 concentration and glass transition temperature (T_g , see Table 1).

115 For the high-pressure experiments, the volatile-free glass powders were loaded into 2.5-2.9
116 mm Pt capsules along with I_2 or I_2O_5 powders as a source of iodine during the experiments.
117 The solid iodine source was loaded at the bottom of the capsule prior filling with the glass
118 powder. The Pt capsule were welded shut at both ends using arc-welder. The initial loaded I_2
119 or I_2O_5 range from 4.0 to 11.5 mol.% ensuring an excess iodine fluid phase during the high-
120 pressure experiments for comparable glass compositions [46-48]. The use of different iodine
121 sources has been shown to have a significant effect on the resulting I solubility; hence, we
122 wanted to test if it could have an effect on the incorporation of iodine into glass-ceramics. At
123 high temperature, the I_2O_5 dissociates into I_2 and O_2 that will impose high-oxidation state
124 during the experiment [47]. The high-pressure experiments were conducted using piston-
125 cylinder apparatus at 1.0 and 1.5 GPa. We used $\frac{3}{4}$ inch talc-Pyrex high-pressure assemblies in
126 which the sample capsules were placed into MgO base ceramics. For each run, two capsules
127 could be experimented with I_2 and I_2O_5 , respectively. During the experiments, the temperature
128 is controlled using a Eurotherm that is accurate to $\pm 1^\circ\text{C}$ and temperature is measured using a

129 type S thermocouple PtRh₁₀/Pt located at the top of the Pt capsules. The pressure during the
130 experiments has been controlled automatically using a Stigma© needle pump.

131 During the high-pressure experiments, we adopted a thermal path based on the results
132 obtained by Differential Scanning Calorimetry (DSC) to determine T_g . The experimental
133 protocol is described in Figure 1 and is consistent with current knowledge [45]. The main
134 difference from existing experimental work is that high-pressure conditions are applied during
135 the whole experiment duration. The samples held under high-pressure conditions (1.0 and 1.5
136 GPa) were heated up between 1200 and 1300°C for melting the experimental charges during
137 1h. A cooling step of 15°C/min is applied to decrease the temperature down to ~550°C that is
138 supposed to correspond to the nucleation temperature (T_n , 50°C above T_g , [51]). The T_n
139 duration was set to 24h; then temperature is increased to ~790°C corresponding to the
140 crystallization temperature (T_c) as determined by DSC measurement. The T_c duration was set
141 also to 24h then followed by the rapid isobaric quench of the high-pressure experiment
142 (~60°C/sec) by cutting of the power. It should be emphasised that the T_n and T_c were
143 determined from the DSC results obtained on I-free glasses prepared at ambient pressure and
144 I-bearing pure glasses recovered from high-pressure experiments (see Table 1), therefore,
145 those temperature conditions are only approximate considering that the obtained T_n and T_c are
146 not determined in-situ under high-pressure conditions. Moreover, in our experiments, the
147 temperature is measured by the thermocouple at the top of the capsules and temperature
148 gradient is occurring on the capsule length (~50°C over ~10 mm capsule length, [52]). After
149 the experiment, most of the recovered glass-ceramics are covered with a I₂ black residue that
150 is removed in ethanol bath. Although we did not quantify the iodine coating, it suggests that
151 an excess fluid phase was always present during the experiments. The glass-ceramics were
152 scrutinized using optical microscope to confirm the presence of both glass and crystalline
153 materials.

154 In addition, ambient pressure crystalline iodosodalite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{I}_2$) has been synthesised
155 using the protocol described in Warner et al. [53]. We used zeolite A ($\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$) and
156 NaI as precursors, mixed in 1:16 molar proportions. The powder has been homogenized in a
157 ball milling at 400 rpm for 6h under ethanol, dried overnight at 80°C. The reaction is finalized
158 by heating the powder at 900°C for 8h in box furnace. The obtained iodosodalite powder
159 serves as a fingerprint for the characterization of the high-pressure glass-ceramics with X-ray
160 Diffraction.

161 2.2. Characterization methods

162 Several chips were mounted in epoxy plugs, polished under glycerol to avoid crystalline
163 phase reaction and coated with carbon for Scanning Electron Microscopy (SEM) analyses.
164 We used two types of SEM (IMN Jean Rouxel): a JEOL JSM 5800LV equipped with an
165 Energy Dispersive Spectrometer (EDS) for the major element (including iodine) quantitative
166 analyses, a JEOL JSM 7600F for obtaining high-resolution imaging of the crystalline phases
167 as well as a mapping of the elemental concentration. For the JEOL JSM 5800LV SEM EDS
168 analyses, the analytical conditions were 15 kV for voltage and 0.5 nA for current. We
169 conducted the acquisitions on a 10 μm spot size to avoid Na loss under the electron beam.
170 Five scans of 1 min were collected on each sample at different location on the glass chip. For
171 the JEOL JSM 7600LV SEM mapping, the analytical conditions were 10 kV for voltage and
172 0.5 nA for current. The high-resolution mapping was acquired using backscattered electron.
173 The dot mapping was acquired on 800 x 600 pixels (24 x 18 μm) at a dwell time of 15 μs per
174 pixel and corresponding to a 20 min data collection. The element quantification was
175 conducted using the following internal standard on the SEM EDS: corundum for Al_2O_3 ,
176 wollastonite for SiO_2 and CaO , NaCl for Na_2O , RbI for I. Due to the low boron mass, we did
177 not analyze B_2O_3 that is not correctly quantified using SEM EDS analyses. The mol.% B_2O_3
178 reported in Table 1 corresponds to the shortfall obtained from SEM EDS analyses. The error

179 calculated on the determined mol.% major element oxides in both the I-free and I-bearing
180 glasses and the matrix of the glass-ceramics is on the order of ± 0.5 mol.% based on the
181 standard deviation of replicated measurements (Table 1). We also could analyze the chemical
182 compositions of iodosodalite crystals. The I content of the iodosodalite crystals is provided in
183 Table 2; however, it should be pointed out that, owing to the small size of this crystalline
184 phases, the error on the reported mol.% I in Table 2 is probably large. Even though the
185 iodosodalite mol.% I is based on multiple measurements (at least five different crystals), we
186 cannot exclude to the measurement a potential contribution from the surrounding matrix
187 (glass + nepheline) with low I content.

188 We also conducted Scanning/Transmission Electron Microscopy (S/TEM) at 80 kV on a Cs
189 probe corrected Themis Z G3 (Thermo Fisher Scientific) using the High Angle annular Dark
190 Field (HAADF) detector (with 33-197° collection angle range) and the 4-SDD detectors
191 (Super-X system) for EDS analysis. Samples were previously prepared by dispersing the
192 grinded powder in ethanol and depositing a drop of this solution on a holey-carbon-coated
193 copper grid.

194 We performed the Differential Scanning Calorimetry (DSC) on two different apparatus to
195 determine T_g and T_c : a Q20 TA Instruments and a Sensys Evo SETARAM, at IMN Jean
196 Rouxel. The DSC was calibrated against the melting enthalpy of lead. The blank was
197 performed using an empty reference alumina crucible. The samples were crushed and ~20 mg
198 of glass sample was analysed each time. The heating profile was a heating ramp from ambient
199 temperature to 850°C at 5°C/min. The furnace was purged with inert gas (N_2) with a flow of
200 20 mL/min during the heating cycle. The T_g value was determined using the variation of the
201 measured heat flow (mW) and the two tangents method using the implemented software
202 procedure in Universal Analysis 2000© for the Q20 TA Instruments and Calisto© software

203 for the Sensys Evo SETARAM. The T_c value is extracted from the exothermic peak on the
204 DSC curves.

205 For all the glass ceramic samples, the X-ray Diffraction (XRD) patterns have been obtained
206 using and INEL XRG3500 operating at 40 kV and 20 mA at IMN Jean Rouxel allowing small
207 sample size using capillary and Debye-Scherrer geometry. The simultaneous acquisitions
208 were performed on a 120° angle with a step of 0.03° in 2θ . We used the Cu $K\alpha_1$ wavelength
209 at 1.5406 \AA monochromated using quartz crystal. Sample acquisitions were conducted in 0.2
210 and 0.3 mm in diameter capillary. The acquisition duration was between 6 and 24h with a 2s
211 time per step. As we obtained a large quantity of iodosodalite synthesised at 1 bar pressure
212 (see Table 2, Iodo 1bar), the XRD acquisition was performed on a Bruker D8 II with a Bragg-
213 Brentano geometry equipped with a Cu $K\alpha_1$ wavelength at 1.5406 \AA and monochromated
214 using germanium (111). The obtained diffractograms were pre-treated using
215 DIFFRAC.EVA© software and the PDF-2 database to find the association of crystalline
216 phases present in our material. We then conducted the Rietveld refinement [54] with
217 JANA2020© software [55] for determining the crystallographic structure of the mineral
218 phases and their proportions (see Table 2).

219 3. Results and discussion

220 3.1. Thermal analyses as a function of experimental conditions and iodine content

221 Typical DSC curves are shown in Figure 2 and are obtained for 1) ambient pressure I-free NH
222 and SoNH glasses and 2) I-bearing glasses synthesised at 1 GPa and 1300°C equilibrated with
223 either I_2 or I_2O_5 fluid phase, SoNH_I₂-0 and SoNH_I₂O₅-0, respectively. The I content in the
224 glasses is reported in Table 1: 0.6 mol.% and 1.2 mol.% for SoNH_I₂-0 and SoNH_I₂O₅-0,
225 respectively. The present result can be compared to the results obtained in Jolivet et al. [46]
226 for low activity waste glasses synthesised at identical pressure ($\sim 1.5 \text{ mol.\% I}$ at 1.5 GPa). The

227 obtained T_g is ranging from 510 to 531°C determined from the double tangent method. We
228 observe that the T_g is only weakly affected by either the high-pressure conditions or the
229 presence of dissolved iodine in agreement with the results shown in Jolivet et al. [56]
230 suggesting that increasing I dissolution slightly decreases T_g values. It is assumed that T_n
231 value is close to T_g value ($\sim+50^\circ\text{C}$). In our case, the curves shown in Figure 2 suggest a T_n
232 value close to 560 and 590°C for SoNH_1b and NH_1b, respectively. As the crystallization
233 corresponds to an exothermic phenomenon, the T_c is represented by the positive peak
234 observed in Figure 2 and is estimated to be close to 790°C. Those derived T_n and T_c values
235 were used in our experimental protocol shown in Figure 1 for synthesising the glass-ceramics.
236 However, as emphasised previously, the adopted protocol constitutes a first approach and
237 further improvements in the temperature path and constraints are required during the high-
238 pressure experiments. This aspect will be further discussed in the following sections.

239 3.2. Iodine incorporation into glass and glass-ceramics at high-pressure

240 We present in Figure 3 two typical SEM element mapping images obtained on a JEOL JSM
241 7600LV for NH_I₂-2 and NH_I₂O₅-2 synthesised at 1.0 GPa with $T_n = 594^\circ\text{C}$ and $T_c = 813^\circ\text{C}$
242 both temperature for 24h run duration, respectively. The images in Figure 3 show the
243 coexistence between a glass matrix in grey and disseminated euhedral crystals in bright. It
244 should also be emphasised that there is no apparent porosity in the obtained samples that is
245 compulsory for the glass-ceramics durability [45]. The change in brightness in between the
246 crystals and glass suggests that the observed crystalline phases are enriched with respect to
247 heavier elements (i.e. iodine) as compared to the matrix. In Figure 3, we have reported the
248 elemental distribution for Si, Al, I and Pt; however, we also obtained the Ca and Na elemental
249 mapping for the same samples but not provided here for clarity. For both samples, we observe
250 that Al is more concentrated in the observable crystalline phase than in glass matrix; and I is
251 much more concentrated in the observed bright euhedral crystals than in the surrounding

252 matrix. The I-bearing crystalline phase is interpreted as iodosodalite (Is.) and also confirmed
253 by XRD measurements. Those results are consistent with our knowledge of the iodosodalite
254 chemical composition that has high Al₂O₃ content (20 mol.%) and high I content (13.3 mol.%
255 I) that are contrasting with the glass Al₂O₃ and I contents: ~10 mol.% and <1 mol.%,
256 respectively. We also observe from the Al and I mapping images in NH_I₂O₅-2, a crystalline
257 phase that is enriched with respect to Al and that does not contain I and is interpreted as
258 nepheline crystal (Neph.). Interestingly, this crystal is not observed in the backscattered image
259 suggesting that the contrast in elemental mass in between the glass matrix and the nepheline
260 crystals is low. This represents a major problem as the quantitative analysis of the glass-
261 ceramics phase proportions (i.e. glass, nepheline and iodosodalite) is not possible from image
262 analysis. Consequently, in Table 1, we refer to the matrix composition as an association
263 between nepheline and glass instead of the glass composition. As shown in Table 2, the
264 nepheline has been identified in several samples, regardless of the initial iodine source. The
265 presence of nepheline is a negative aspect for the formulation of a reliable glass-ceramics
266 immobilizing iodine radioisotopes. Previous studies showed that the nepheline crystallization
267 is particularly detrimental for the durability of the nuclear waste form [29,57,58]. The
268 presence of nepheline could have several explanations. It is possible that local iodine
269 depletion prevents from the crystallization of additional iodosodalite crystals. Although the
270 experiments were conducted above T_g and the system is supposed to behave like a liquid (i.e.
271 instantaneous change in the physical properties; [59]), it might be possible that the I diffusion
272 is not fast enough and the crystallization of nepheline occurs well before an equilibration of
273 the I content could occur. Another explanation is that the adopted experimental conditions,
274 especially pressure conditions (1.0 and 1.5 GPa), are, at some stage, outside the
275 thermodynamic stability field of iodosodalite and nepheline becomes the more stable
276 crystalline phase. We also identified the presence of a Pt-rich phase that appears very bright in

277 the backscattered image of the NH_I₂O₅-2 sample. The XRD analysis revealed that it
278 corresponds to NaPt₃O₄ suggesting that there is a chemical reaction between the Pt capsule
279 walls and the sample charge during the experiment.

280 The SEM EDS results are given in Table 1 for 1) the pure glass either I-free or I-bearing and
281 2) the matrix composition of the glass-ceramics and considered to be an association between a
282 I-bearing glass and I-free nepheline crystalline phase. The error bars on the I content based on
283 the standard deviation of the replicated measurements is on the order of ±0.2 mol.%. For pure
284 glass samples, we observe that I content in the glass is higher in the case I₂O₅ is the I source
285 as compared to I₂. For instance, we measured 0.7 and 1.5 mol.% I in NH_I₂-0 and NH_I₂O₅-0
286 glass loaded with I₂ and I₂O₅, respectively. The same applies to the SoNH glass composition
287 in which we measured 0.6 and 1.2 mol.% I for SoNH_I₂-0 and SoNH_I₂O₅-0, respectively.
288 The higher I content measured in glasses with initial I₂O₅ source is consistent with the recent
289 results from Morizet et al. [47] suggesting that I solubility is enhanced in that case owing to
290 the stabilization of IO₃⁻ molecular groups within the glass structure. In the present work for I₂
291 experiments, the measured I solubility (0.6 and 0.7 mol.% I for SoNH_I₂-0 and NH_I₂-0,
292 respectively) is significantly lower than the one reported in Jolivet et al. [46] (~1.5 mol.% I)
293 for identical intensive conditions. Despite the higher Na₂O content in SoNH (~24 mol.%)
294 compared to NH (19 mol.%) the measured mol.% I is lower in SoNH. Such result was not
295 expected considering that recent studies have shown that I solubility is positively affected by
296 the alkali concentration [47,60]. There is also a difference in the run duration in between both
297 glass compositions: 3h for NH and 10h for SoNH. We wanted to check if changing the run
298 duration could induce a change in the I solubility and by extension could impact the I
299 dissolution for glass-ceramics, which are equilibrated with longer run duration. As observed
300 in Table 1, we suggest that there is no change in the I solubility with increasing run duration.

301 This implies that the equilibrium between the I-rich fluid phase and the melt at high
302 temperature is reached early in the experiment.

303 Globally, the I content measured in the matrix of the glass-ceramics appears lower than the
304 pure equivalent glass. This is especially true for the NH glass ceramic samples in which the I
305 content does not exceed 0.5 mol.% I (see Table 1). This observation is less obvious for SoNH
306 glass ceramic samples. For instance, 0.8 mol.% I has been determined the glass matrix for the
307 SoNH_I₂-1 whereas 0.6 mol.% I has been measured in the pure glass SoNH_I₂-0 in
308 equilibrium with I₂ fluid phase and for identical pressure conditions (1.0 GPa). The decrease
309 of the I content in the glass matrix is more pronounced for the samples equilibrated with I₂O₅
310 fluid phase: 0.7 mol.% I is measured in the SoNH_I₂O₅-2 glass ceramic whereas 1.2 mol.% I
311 is determined for the equivalent pure glass SoNH_I₂O₅-0. Moreover, in between those
312 samples, there is a difference in pressure synthesis: 1.5 GPa for the SoNH_I₂O₅-2 glass
313 ceramic and 1.0 GPa for the SoNH_I₂O₅-0 glass; that would induce higher I dissolution in the
314 glass-ceramics than in glass as pressure is thought to have a positive effect on the I dissolution
315 [46,48,61,62]. Nonetheless, the decrease in I content in the matrix for the glass ceramic
316 samples is explained by the fact that the crystallization of I-bearing crystalline phases depletes
317 the bulk composition with respect to iodine. Another explanation is the presence of nepheline
318 crystals that are I-free and are not observed using SEM. Therefore, the analysis of the matrix
319 glass-ceramics composition will result in an even lower I content. The presence of
320 iodosodalite crystals that are Na-rich crystalline phases also points towards the depletion of
321 Na₂O in the chemical composition of the glass ceramic matrices. As can be seen in Table 1,
322 the matrix compositions are systematically depleted in Na₂O (~21.0 mol.% Na₂O) for SoNH
323 glass-ceramics as compared to the pristine SoNH glass (~24.0 mol.% Na₂O). As inferred
324 earlier, the decrease in Na₂O content of the glass matrix does not favour I dissolution

325 [24,48,60]; however, Na₂O decrease will induce an increase in the degree of polymerization
326 of the glass matrix network and therefore potentially increase the glass durability [29,48,63].

327 We have pushed further the analysis of the glass-ceramics by conducting S/TEM mapping at
328 nm scale as shown in Figure 4 on NH-I₂-2. We found sample chips exhibiting different
329 compositions that can be attributed to the identified coexisting phases: nepheline, iodosodalite
330 and glass. The nepheline and iodosodalite are Ca-free whereas the glass is Ca-bearing. A
331 small amount of Ca (~1 at.%) is present in the area assigned to nepheline. This could be
332 explained by the superposition of this phase with the glass. The iodosodalite has the following
333 composition (with an associated error of ±20% in relative): 25.0 Na₂O, 19.2 Al₂O₃, 44.5 SiO₂
334 and 11.3 mol.% I; that is very close to the theoretical composition: 26.7 Na₂O, 20.0 Al₂O₃,
335 40.0 SiO₂ and 13.3 mol.% I. The measured glass composition is: 16.3 Na₂O, 12.7 Al₂O₃, 61.1
336 SiO₂ and 10.0 mol.% CaO; the I content of the glass could not be determined due to the
337 overlapping between the I L α and Ca K β lines and the low I concentration in glass. The
338 derived glass composition is strongly enriched in SiO₂, depleted in Na₂O and slightly enriched
339 in CaO as compared to the initial starting glass composition (see Table 1). The crystallization
340 of iodosodalite and nepheline will decrease significantly the Na₂O of the matrix considering
341 that those phases are Na-rich.

342 Although the presented results provide a proof-of-concept, substantial improvements in the
343 syntheses method are required in order to 1) avoid the crystallization of nepheline crystals
344 during the high-pressure synthesis that is a low durability phase, 2) increase the proportion of
345 iodosodalite crystals that are known to incorporate large amount of I under either I⁻ or IO₃⁻
346 into the β -cage and 3) increase the size of the iodosodalite crystals for better characterization.
347 Nevertheless, we propose the first attempt for glass-ceramics obtained from heterogeneous
348 nucleation from the parental glass under high-pressure conditions showing the coexistence
349 between an I-bearing glass matrix and an I-bearing crystalline phase.

350 3.3. Iodosodalite crystal-chemistry

351 We focused on the crystal-chemistry of the obtained iodosodalite using XRD and Rietveld
352 refinement. In Figure 5, we show one diffractogram obtained for NH_I₂-2 equilibrated at 1.0
353 GPa. Additional diffractograms are also provided in the Suppl. Mat.. The identified
354 diffraction peaks for NaPt₃O₄, nepheline and iodosodalite are indicated. We observe a strong
355 non-linear background that is assigned to the contribution of the glass amorphous phase.
356 Unfortunately, without calibration compound, we are not able to determine the proportion of
357 the amorphous glass in the glass ceramic samples. The peaks for NaPt₃O₄ are strong in
358 intensity due to the high cubic symmetry (space group O_h³ – *Pm-3n*, [64]). We give in Table 2
359 the lattice parameters derived from Rietveld refinement for crystalline phases, the associated
360 space group and the wRp parameter. This latter parameter represents the reliability parameter
361 with respect to the structure refinement. We also reported the I content in iodosodalite as
362 measured from SEM EDS and based on at least 5 measurements on different crystals. It
363 should be emphasised that, for iodosodalite structure, the Rietveld refinement has been
364 adequately conducted for I₂ samples whereas it is only partially resolved for I₂O₅ samples (see
365 Table 2).

366 The nepheline structure shows a hexagonal lattice with a space group P6₃. We calculated an
367 average value for the cell parameters and we obtained 9.940±0.012 and 8.320±0.013 Å for a
368 and c, respectively. The small standard deviation in the cell parameters suggest that the
369 structure of nepheline is roughly constant in between the glass ceramic samples. The
370 nepheline structure has been investigated a long ago [65-67]. Buerger et al. [65] reported
371 10.05 and 8.38 Å for the lattice parameter values, which is significantly higher than the ones
372 we obtain. We explain the lower a and c values in our nepheline by the high-pressure
373 synthesis conditions. It is currently known that increasing pressure conditions induces a
374 decrease in the lattice volume and parameters. Recent work by Diego Gatta and Angel [68]

375 showed that increasing pressure decreases the cell parameters for nepheline (i.e. K- and Na-
376 bearing natural nepheline). In their work, the a and c parameters change from 9.9995 and
377 8.3766 Å to 9.8499 and 8.2838 Å between ambient and 2.0 GPa pressure.

378 To conduct the Rietveld refinement for idosodalite structure, we used the CIF reference
379 1534899 from the Crystallographic Open Database and reported in Beagley et al. [69]. The
380 obtained lattice parameter is on the order of 9 Å with a cubic space group I-43m that is
381 consistent with previous results [41,70,71]. For instance, Chong et al. [71] gives a cell
382 parameter at 9.009 Å for idosodalite crystals obtained by hydrothermal synthesis.
383 Systematically, the derived cell parameter for the high-pressure idosodalite is lower (on
384 average 9.007 ± 0.004 Å on the reported structures in Table 2) than the one obtained for the
385 ambient pressure idosodalite (9.0295 Å). As for nepheline, we suspect that the high-pressure
386 conditions explain the decrease in the lattice parameter for idosodalite.

387 We mentioned earlier that the Rietveld refinement was incomplete for I₂O₅ samples as
388 opposed to the I₂ samples in which the resolution of the idosodalite crystalline structure is
389 complete using standard crystalline model for the structure of idosodalite. We suspect that
390 this reference is not adapted for the idosodalite crystalline structure obtained in the I₂O₅
391 glass ceramic samples. One possible reason is that the idosodalite crystals obtained have β
392 cages occupied by IO₃⁻ instead of I⁻ clusters or a combination of both species. Currently, we
393 are unable to confirm the difference in cage occupancy.

394 3.4. Estimate of the iodine budget in glass-ceramics

395 In the absence of reliable quantification of the glass phase in the glass-ceramics, it is not
396 possible to constrain the I content in the glass-ceramics. It is even more complicated by the
397 fact that the concentration of nepheline crystals cannot be obtained from the SEM owing to
398 the low contrast difference in between the glass phase and the nepheline crystalline phase (see

399 Figure 3). Currently, the only information that can be obtained is the relative proportion of the
400 different crystalline phases. We have reported the proportion of the different phases in Figure
401 6 (data are provided in Table 2) as determined from XRD analyses. The wt.% for each
402 crystalline phases is represented for each glass ceramic sample and categorized as a function
403 of the initial iodine source (either I₂ or I₂O₅). It should be pointed out that, considering the
404 incomplete Rietveld refinement for I₂O₅ samples, the crystalline phase proportions are subject
405 to large errors. For the I₂-bearing glass-ceramics, we observe that the proportion of nepheline
406 seems more important in the SoNH samples (>70 wt.%) than in the NH samples (<50 wt.%),
407 for identical synthesis conditions (1.0 GPa pressure for NH_I₂-1 and -2 and SoNH_I₂-1).
408 Conversely, it corresponds to an increased proportion of iodosodalite in NH than SoNH
409 samples. It suggests that increasing the Na₂O in the starting composition (i.e. SoNH) does not
410 favour the crystallization of iodosodalite as initially thought. Instead, the higher Al/Na ratio in
411 the NH compared to SoNH is likely to enhance the stability of iodosodalite that is Al-rich.
412 Although it remains to be confirmed with additional experiments, it seems that the nepheline
413 proportion decreases and the proportion of iodosodalite increases in I₂O₅-bearing samples in
414 comparison to the I₂-bearing samples. The proportion of NaPt₃O₄ appears very low (<2 wt.%)
415 or even zero in the I₂-bearing samples. On the other hand, even with large associated errors
416 the NaPt₃O₄ is unambiguously identified in I₂O₅-bearing samples from XRD (see Figure 6). It
417 suggests that there is a chemical reaction in between the Pt walls of the sample container with
418 the inside fluid phase (I₂ and O₂) and the sodium of the matrix. This reaction has been clearly
419 identified for SoNH_I₂-0 and SoNH_I₂O₅-0 glasses and is described in the Suppl. Mat.. The
420 identified mass proportion of NaPt₃O₄ in the different samples (see Table 2) does not affect
421 the glass composition with respect to the Na incorporation. For instance, the 16 wt.% NaPt₃O₄
422 in NH_I₂O₅-1 corresponds to 0.5 wt.% Na incorporated into the NaPt₃O₄, which can be
423 considered as negligible with regards to the total Na₂O content within the glass matrix (~20

424 wt.%) and is likely to have a minor influence on the crystallization of the Na-bearing
425 crystalline phases (i.e. iodosodalite and nepheline).

426 Further experiments are required in order to improve the iodine incorporation. For instance,
427 the percentage of I-bearing crystalline phase needs to be increased and the presence of
428 nepheline should be avoided. We suggest that the NH composition is probably more adequate
429 than the SoNH in the formulation of a glass ceramic for immobilizing ^{129}I nuclear waste due
430 to the higher Al/Na ratio in NH composition. We suggested that the presence of nepheline
431 could be due to the intensive conditions that are close to be outside the pressure and
432 temperature stability field of iodosodalite. For instance, previous works on Cl-bearing sodalite
433 [72,73] showed that the stability field of sodalite is located at low pressure and sodalite
434 becomes unstable above 0.8 GPa. As a result, we should consider performing experiments at
435 lower pressure (i.e. <0.5 GPa) that is likely to improve the stability of the iodosodalite phase.
436 Moreover, lowering the pressure condition is also beneficial as those pressure conditions can
437 be achieved industrially [1].

438 4. Summary

439 In the present work, we demonstrate the possibility to synthesise glass-ceramics that are able
440 to incorporate iodine content in both the glass and the crystalline phases with the objective to
441 propose a formulation for the immobilisation of ^{129}I radioisotopes. The glass-ceramics were
442 obtained from the nucleation and crystallization of a parent aluminoborosilicate glass under
443 high-pressure conditions (1.0 and 1.5 GPa) and using different iodine source: I_2 and I_2O_5 .

444 The glass ceramic analyses shows the coexistence between a glass matrix containing iodine
445 (up to 0.8 mol.%) and various crystalline phases. The crystalline phases are iodosodalite,
446 nepheline and NaPt_3O_4 . This latter phase is mostly present in the glass-ceramics equilibrated
447 with I_2O_5 source. The presence of nepheline is detrimental for the durability of the glass-

448 ceramics and further improvements in the experimental protocol are required. Experiments at
449 lower pressure might be of interest as we could avoid the crystallization of nepheline. For
450 now, due to the small crystal size ($<10\ \mu\text{m}$) we are only able to determine the local
451 environment of iodine into the idosodalite if it is filled with I^- species. When IO_3^- or both
452 species are present inside the cage (i.e. solid solution of iodate and iodide sodalite), the DRX
453 appears limited due to the lack of structural model in that case. The obtained results are
454 encouraging and request further experimental work for formulating a glass-ceramics able to
455 incorporate large iodine quantities in both the glass matrix and idosodalite crystalline phase
456 conferring mechanical durability, chemical durability through the double barrier, and higher
457 nuclear waste load advantages.

458

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465

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644 3-18.
- 645
- 646 Figure caption

647 Figure 1: Thermal history adopted in the experimental syntheses of the glass-ceramics under
648 high-pressure conditions. The temperature history is divided into three parts: 1) melting (T_f) at
649 $\sim 1250^\circ\text{C}$ for 1h, 2) nucleation (T_n) at $\sim 550^\circ\text{C}$ just above the glass transition temperature (T_g)
650 determined by DSC at $\sim 500^\circ\text{C}$ and 3) crystallization (T_c) at $\sim 790^\circ\text{C}$ as determined by DSC
651 measurements. The time for the T_n and T_c has been set to 24h. We used cooling and heating
652 ramp of $15^\circ\text{C}/\text{min}$. At the end of the experiment, the sample is rapidly quenched.

653 Figure 2: DSC curves obtained for ambient pressure glasses: NH_1b and SoNH_1b; and I-
654 bearing SoNH glasses: SoNH_I₂-0 and SoNH_I₂O₅-0. The reported T_g and T_n values were
655 determined using the double tangent method and the crystallization peak position,
656 respectively.

657 Figure 3: Elemental mapping obtained by high-resolution SEM on NH_I₂-2 and NH_I₂O₅-2
658 glass ceramic samples. The distribution of the element shows that most of the crystal are
659 enriched with respect to iodine and correspond to iodosodalite (Is.). We also identified the
660 presence of NaPt₃O₄ in NH_I₂O₅-2 and is a witness of a potential reaction in between the
661 experimental charge and the Pt capsule walls. The crystal size does not exceed 5 μm .

662 Figure 4: Element mapping collected from S/TEM acquisition and obtained on NH_I₂-2
663 sample showing the coexistence of iodosodalite, nepheline and glass. The Ca map witnesses
664 the presence of glass as Ca is absent from the structure of iodosodalite and nepheline.

665 Figure 5: X-ray Diffraction pattern obtained for NH_I₂-2 glass ceramic sample containing
666 iodosodalite, nepheline and NaPt₃O₄. The residual suggests that the Rietveld refinement has
667 been properly performed. We also added a β cage structure typical of the iodosodalite
668 structure.

669 Figure 6: The bar plot shows the proportion of each crystalline phase determined in the glass
670 ceramics from XRD treatment. Although, the refinement is incomplete for NH_I₂O₅-1

671 sample, there seems to be an increase in the iodosodalite proportion from I₂ to I₂O₅
672 experiments.

673

Table 1: Experimental conditions, temperature and time step for glass and glass ceramic syntheses, glass and matrix major element composition.

Sample	Pressure (GPa)	I ^{init.}	T _g	T _f /t _f	T _n /t _n	T _c /t _c	Composition (mol.%) ^a					
							SiO ₂	B ₂ O ₃	Al ₂ O ₃	CaO	Na ₂ O	I
Glass syntheses ^b							Glass					
NH_1b	0.0001	0	531	1300/2			39.9	19.7	10	8.6	21.8	
SoNH_1b	0.0001	0	510	1300/2			46.3	13.6	11.0	5.0	24.2	
NH_I ₂ -0	1.0	11.6		1300/3			41.5	20.7	10.5	6.9	19.7	0.7
NH_I ₂ O ₅ -0	1.0	10.6		1300/3			43.6	20.7	11.1	6.9	16.2	1.5
SoNH_I ₂ -0	1.0	9.6	510	1300/10			48.6	13.6	11.3	5.3	20.5	0.6
SoNH_I ₂ O ₅ -0	1.0	8.7	513	1300/10			50.3	13.6	11.7	5.1	18.1	1.2
Glass ceramic syntheses ^b							Matrix: Glass + nepheline					
NH_I ₂ -1	1.0	4.6		1300/1	594/24	813/24	43.4	19.7	9.4	8.6	18	0.3
NH_I ₂ O ₅ -1	1.0	4.0		1300/1	594/24	813/24	42.8	19.7	9.1	8.4	19.1	0.5
NH_I ₂ -2	1.0	10.2		1300/1	594/24	813/24	43.3	19.7	9.7	8.2	19	0.1
NH_I ₂ O ₅ -2	1.0	9.9		1300/1	594/24	813/24	45.1	19.7	10.4	7.7	16.9	0.3
SoNH_I ₂ -1	1.0	10.1		1300/2	560/24	785/24	48.9	14.4	8.1	8.1	20.3	0.8
SoNH_I ₂ O ₅ -1	1.0	11.5		1300/2	560/24	785/24	48.1	14.6	13.0	4.0	19.9	0.4
SoNH_I ₂ -3	1.5	11.1		1200/1	560/24	790/24	48.9	14.9	9.8	5.5	20.3	0.5
SoNH_I ₂ O ₅ -3	1.5	9.4		1200/1	560/24	790/24	48.6	15.3	10.0	5.4	20.4	0.4

^aThe composition of the of the matrix is reported in mol.%. The error on each oxide is on the order of ± 0.5 mol.% based on the replicated measurements from SEM EDS. For I, the error is slightly lower at ± 0.2 mol.%. It should be pointed out that the reported compositions are for pure glass and for glass+nepheline for glass and glass-ceramic syntheses, respectively. This is due to the fact that the nepheline cannot be distinguished from the glass in the glass-ceramic matrix.

^bThe experimental conditions read as follow. For glass, there is a one-step synthesis with melting at high-temperature (T_f). For glass-ceramics, there is a three-step synthesis protocol with melting (T_f), nucleation (T_n) and crystal growth (T_c). The time for T_n and T_c has been set to 24h. The whole protocol was performed under high-pressure conditions.

Table 2: X-ray Diffraction and Rietveld refinement results, cell parameters, phase proportion and iodine concentration in iodosodalite.

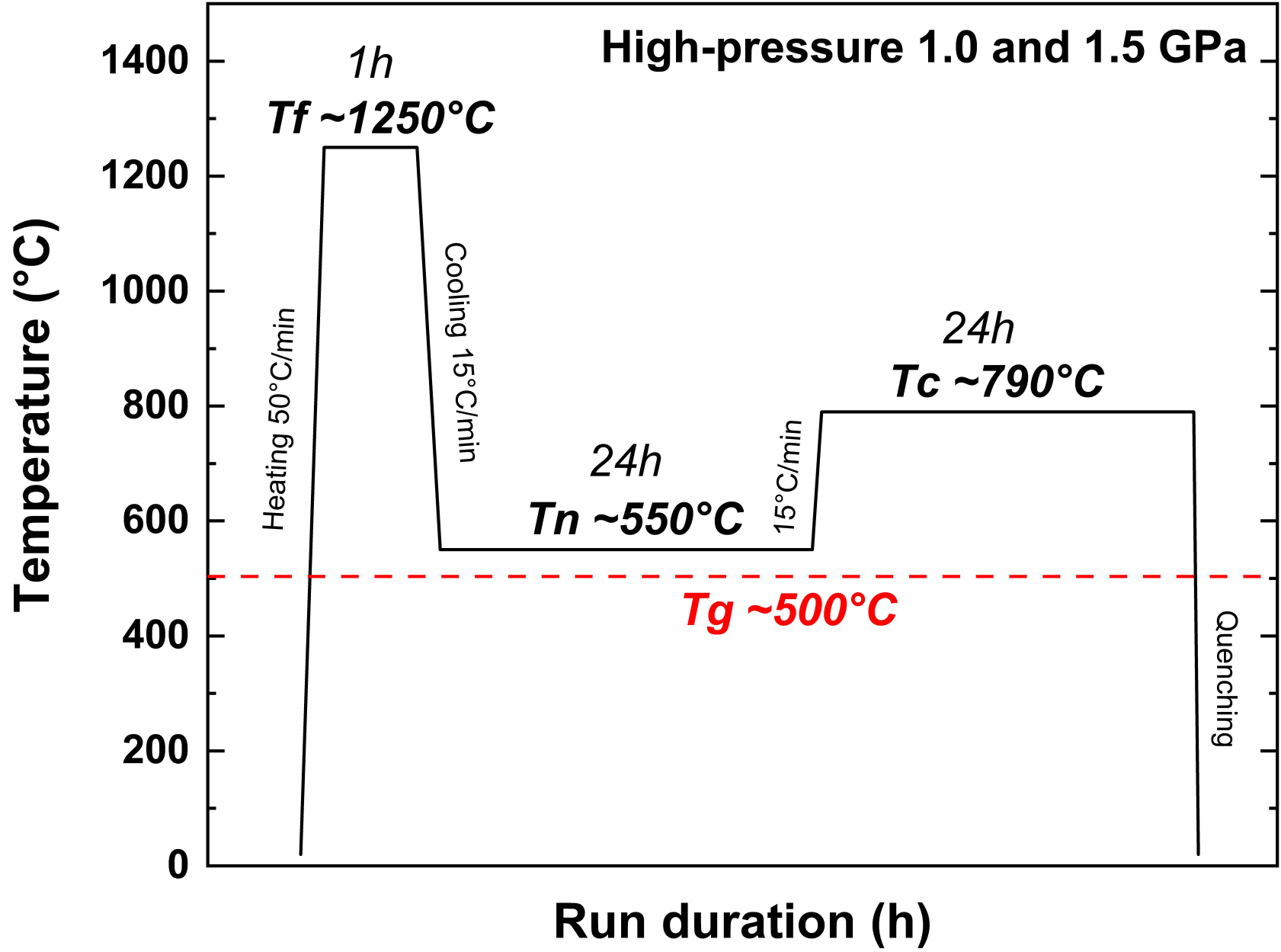
Crystalline phase	Cell parameters ^a						Cell volume (Å ³)	Space group	Proportion (wt.%)	wRp (%)	Mol.% I ^b
	a (Å)	b	c	α (°)	β	γ					
Iodo Ibar ^c											
Iodosodalite	9.0295(2)	9.0295	9.0295	90	90	90	736.2	I-43m	100	12.82	
NH I ₂ -1											
Iodosodalite	9.007(1)	9.007	9.007	90	90	90	730.8	I-43m	52.8±1.7	1.98	10.5
Nepheline	9.946(3)	9.946	8.326(4)	90	90	120	713.3	P63	47.2±1.6		
NH I ₂ -2											
Iodosodalite	9.008(2)	9.008	9.008	90	90	90	731.1	I-43m	59.1±1.4		9.3
Nepheline	9.949(3)	9.949	8.331(4)	90	90	120	714.1	P63	39.0±1.4	2.02	
NaPt ₃ O ₄	5.680(3)	5.680	5.680	90	90	90	183.3	Pm-3n	1.9±0.2		
SoNH I ₂ -1											
Nepheline	9.937(8)	9.937	8.316(9)	90	90	120	711.1	P63	73.6±1.7		
Iodosodalite	9.007(7)	9.007	9.007	90	90	90	730.7	I-43m	24.5±1.7	2.89	10.4
NaPt ₃ O ₄	5.692(4)	5.692	5.692	90	90	90	184.4	Pm-3n	1.9±0.2		
SoNH I ₂ -3											
Nepheline	9.921(6)	9.9212	8.299(6)	90	90	120	707.5	P63	91.7±0.9	4.06	
Iodosodalite	8.999(9)	8.999	8.999	90	90	90	728.9	I-43m	8.3±0.9		13.3
NH I ₂ O ₅ -1 ^d											
Iodosodalite	9.0113(5)	9.0113	9.0113	90	90	90	731.7	I-43m	54.0±0.2		14.1
Nepheline	9.947(8)	9.947	8.327(10)	90	90	120	713.6	P63	29.0±0.2	2.35	
NaPt ₃ O ₄	5.680(1)	5.680	5.680	90	90	90	183.3	Pm-3n	16.0±1.5		

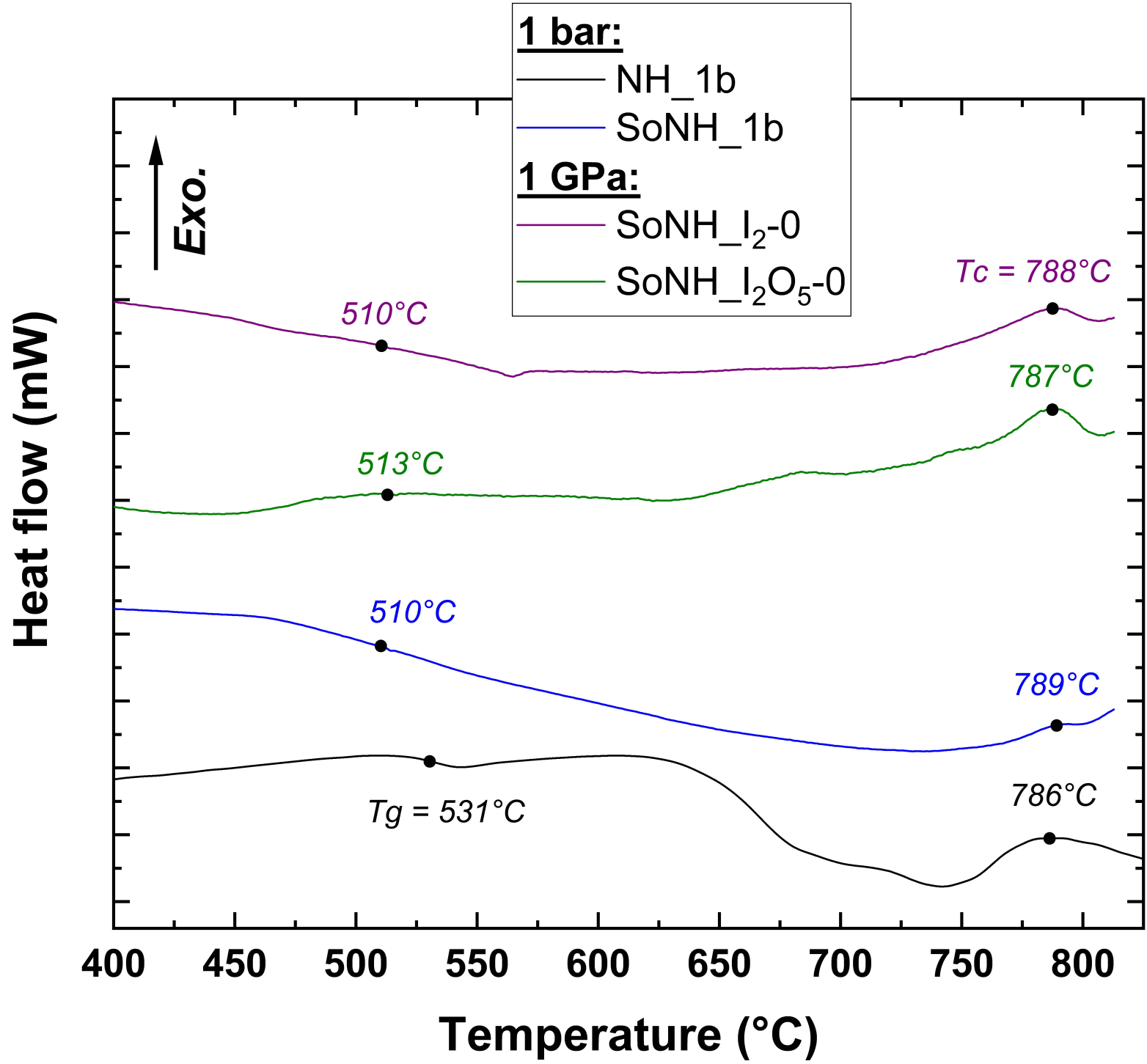
^a The lattice parameters of the different crystalline phases has been determined using Rietveld refinement of the structure with JANA2020©. The error bars on each parameter is calculated with the Berar's factor and the normalized error obtained on the fit. For the different phases, we used standard crystalline structure collected from the Crystallographic Open Database. The reliability parameter (wRp) corresponds to a satisfaction parameter.

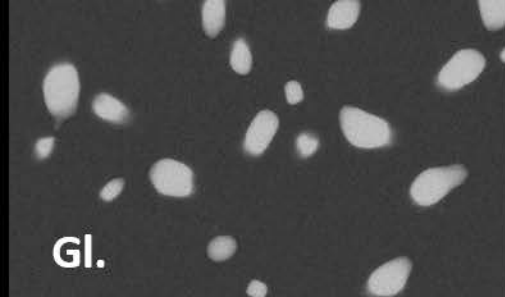
^b The mol.% I corresponds to the I concentration determined from SEM EDS measurements based on several replicated measurements.

^c The XRD acquisition for this sample was carried out with a Bragg-Brentano geometry, whereas the other samples were characterized with Debye-Scherrer geometry using capillary.

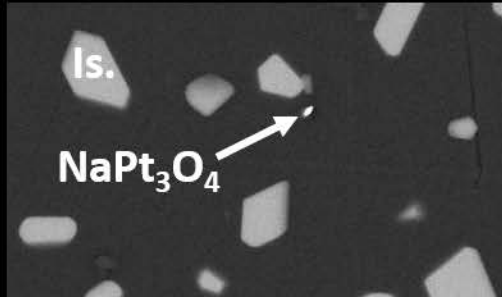
^d For NH I₂O₅-1 and for I₂O₅ glass ceramic samples, more generally, we did not manage to obtain a satisfying Rietveld refinement. Therefore, the error on the phase proportions is probably large and the cell parameters are likely to be accompanied with a large error.



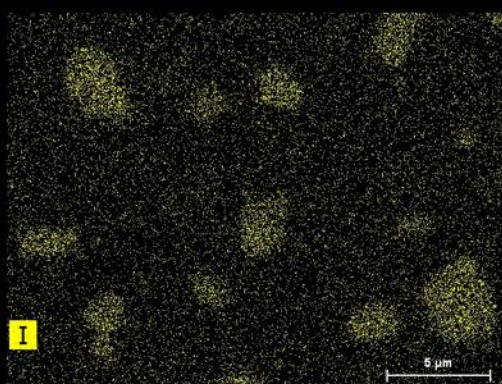
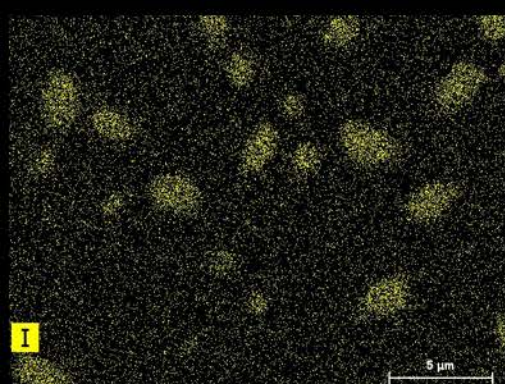
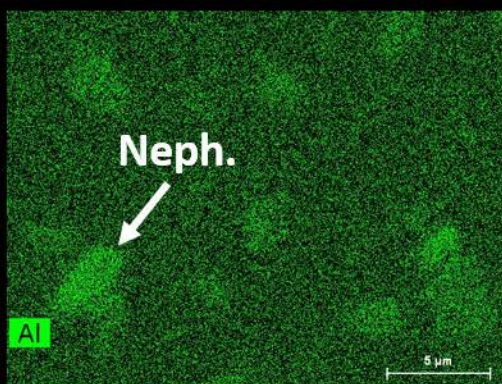
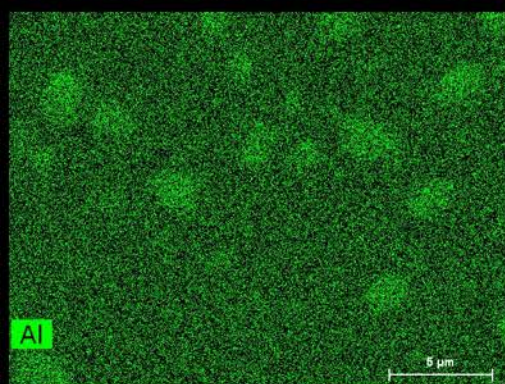
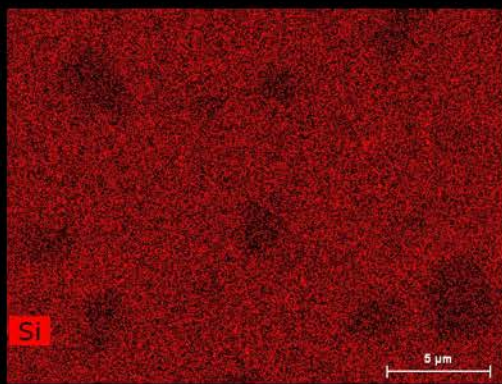
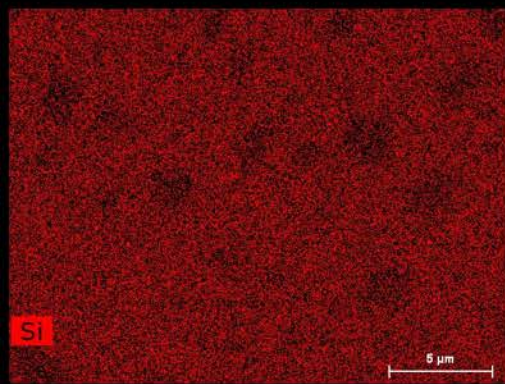




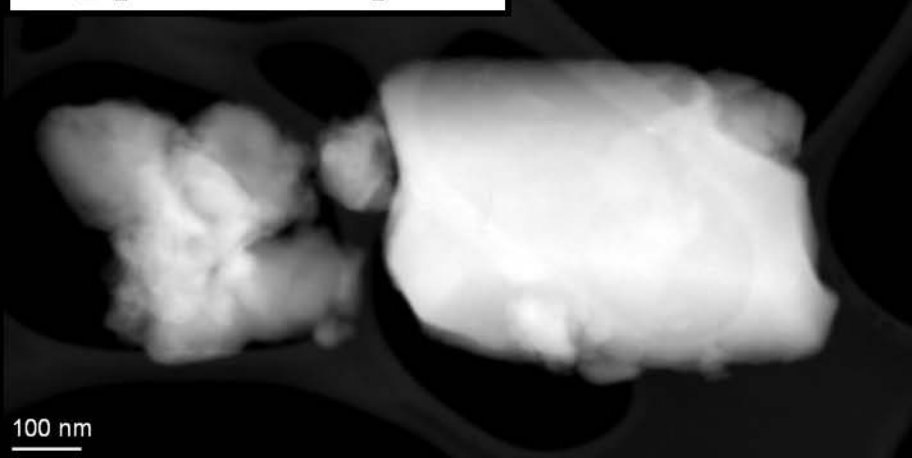
NH_I₂-2: 1.0 GPa + I₂



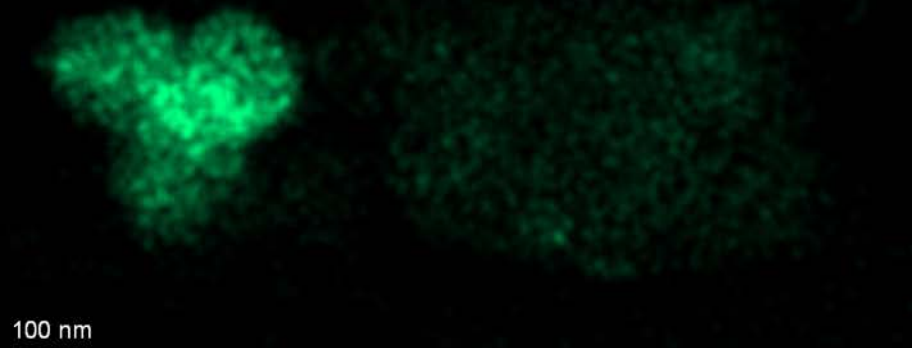
NH_I₂O₅-2: 1.0 GPa + I₂O₅



NH_I-2: 1.0 GPa + I₂



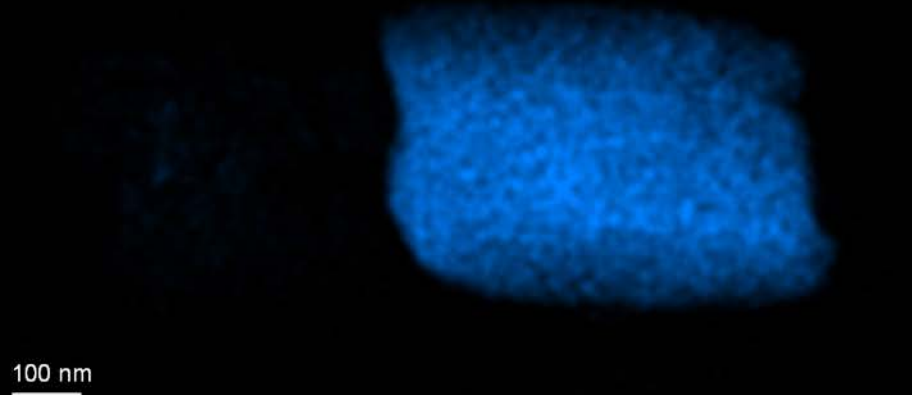
Glass



Neph.



Iodosodalite

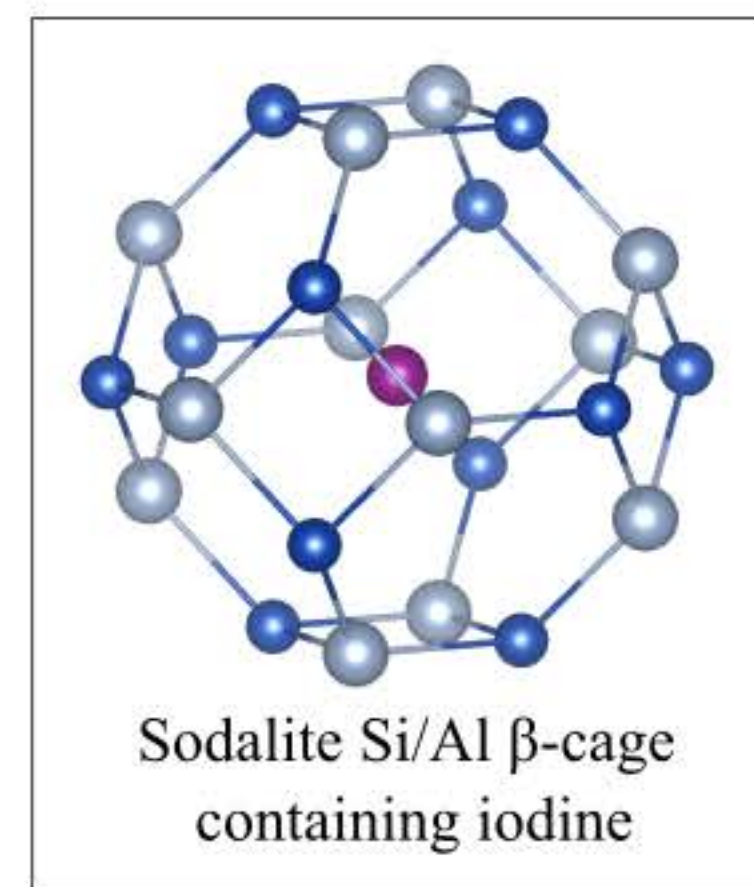


NH_2I_2 - 2 1 GPa - 24h nucleation + 24h growth

- Observed
- Simulated
- Residual
- | Iodosodalite
- | Nepheline
- | NaPt_3O_4

Intensity (a.u.)

Amorphous bump



20

30

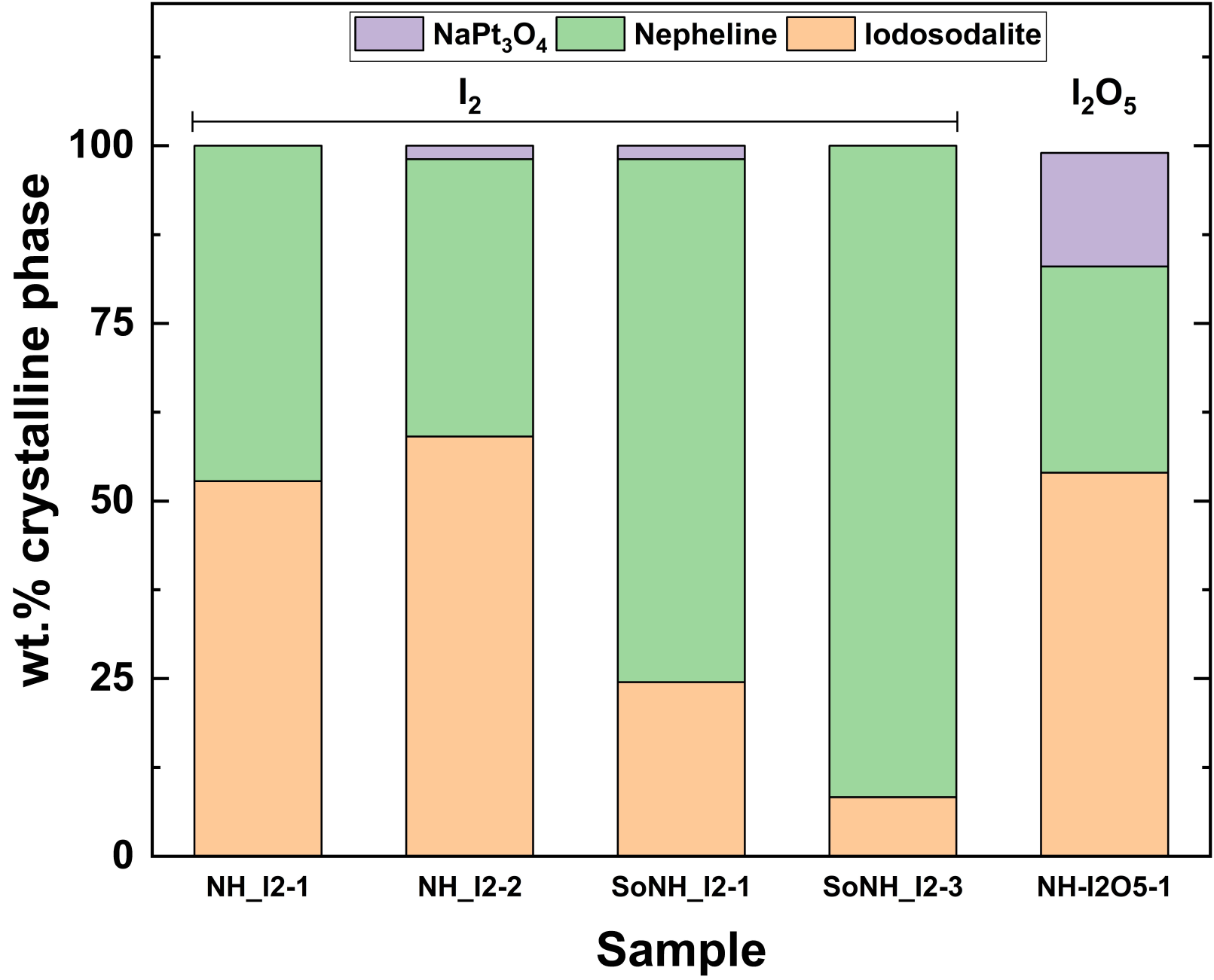
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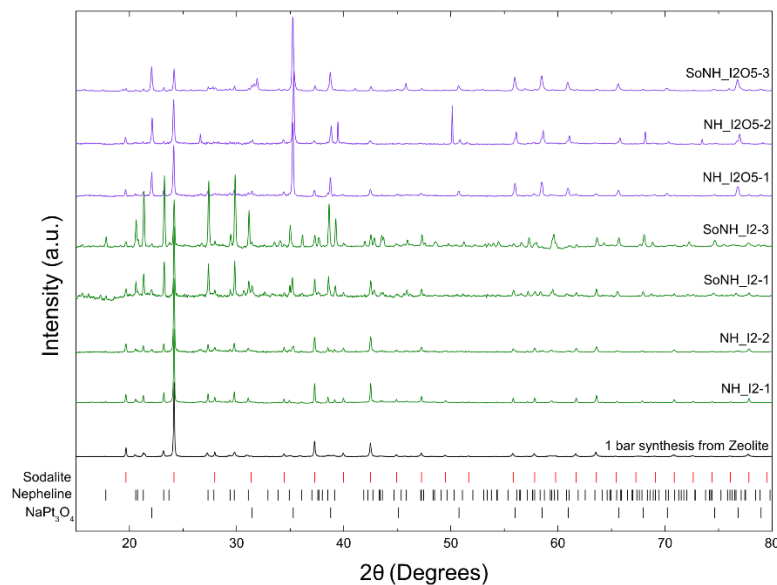
2θ (Degrees)



1 **SUPPLEMENTARY MATERIAL: HIGH-PRESSURE REAL GLASS-CERAMICS**
2 **FOR IODINE NUCLEAR WASTE IMMOBILIZATION: PRELIMINARY**
3 **EXPERIMENTAL RESULTS**

4
5 1. X-ray Diffraction patterns

6 We acquired X-ray diffraction patterns for each of the glass ceramics sample and the
7 iodosodalite synthesized at 1 bar pressure. The diffractograms are shown in the Figure S1.
8 The peaks for each crystalline phase are also shown. We do not show the Rietveld refinement;
9 however, refinements are available on demand for I₂ loaded samples.

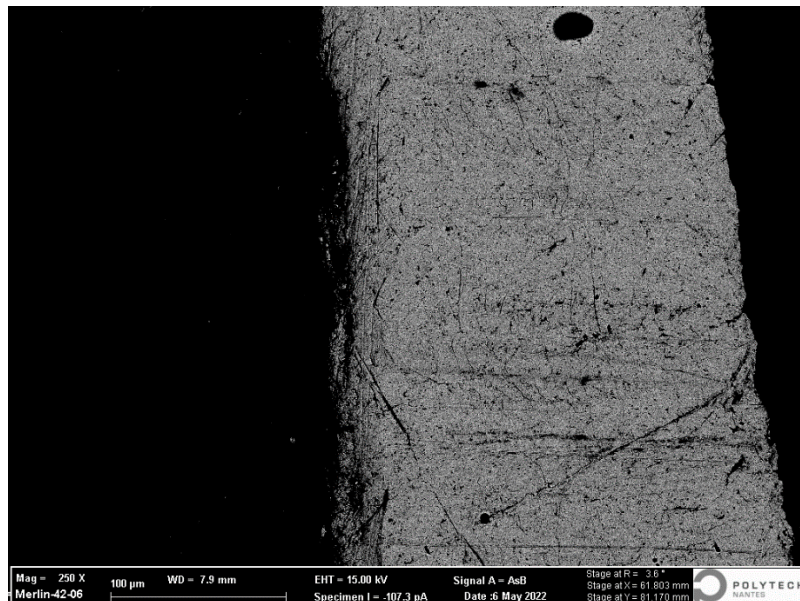
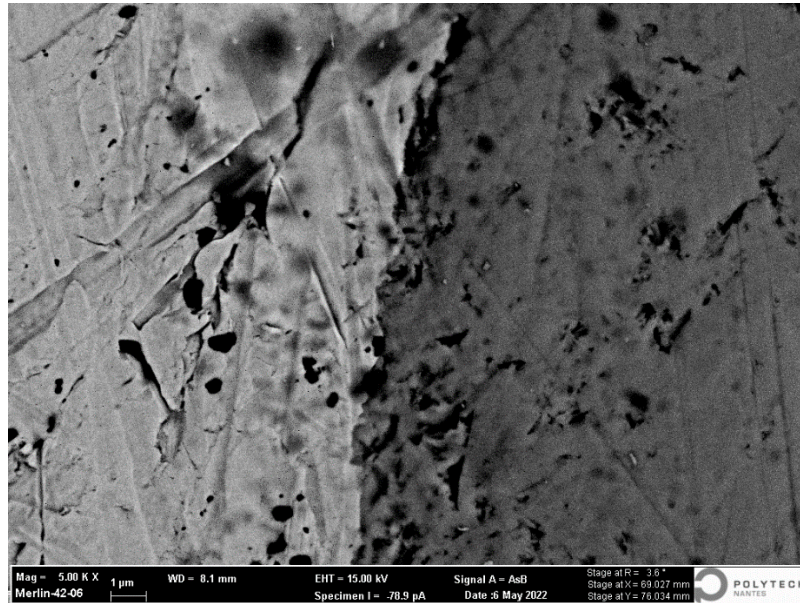


11 Figure S1: X-ray Diffraction patterns obtained on the glass ceramics in the present study.

12 2. Evidence for Pt capsule walls and inside experimental charge chemical reaction

13 For the SoNH_I₂O₅-0 and SoNH_I₂-0 glass syntheses (see Table 1) conducted at 1.0 GPa and
14 1300°C for 10h, we have analyzed the Pt container walls to evaluate the potential reaction
15 between the inside experimental charge and the walls. The measurements were performed on
16 a Wavelength Dispersive Spectroscopy Scanning Electron Microscope (WDS SEM) at the

17 IMN Jean Rouxel Polytech Nantes. The acquisitions are carried out on a Zeiss Merlin
18 equipped with a WDS probe. We used a 15 kV acceleration current and the samples were
19 mounted in an epoxy plug and analyzed without carbon coating.



22 Figure S2: Backscattered Electron Microscope image obtained on the Pt capsule walls for
23 SoNH₂-0 (Bottom) and SoNH₂O₅-0 (Top) samples. The images are shown at different
24 magnification. We observe a contrast in color for SoNH₂O₅-0 in the Pt walls indicating a
25 change in the composition of the walls. The element concentration (see Table S1) shows an
26 increase in the O concentration in the inside of the Pt capsule wall.

27

28 The images are shown in Figure S2 for SoNH_I₂O₅-0 and SoNH_I₂-0 at different
 29 magnifications and showing a portion of the Pt capsule walls. For SoNH_I₂O₅-0, we clearly
 30 observe that there is a contrast in the Pt wall between a brighter color on the left and a darker
 31 color on the right hand side. This is explained by a difference in the chemical composition.
 32 This difference in chemical composition within the capsule wall is not visible for the
 33 SoNH_I₂-0 sample suggesting a homogeneous composition of the Pt walls. We have
 34 quantified the element in each part of both SoNH_I₂-0 and SoNH_I₂O₅-0 samples. The results
 35 are provided in the following Table S1.

	Na (mol.%)	Ca	O	Pt
SoNH_I ₂ O ₅ -0				
Outer Pt wall	0	0	11.2	88.8
Inner Pt wall	6.5	1.9	37.7	53.9
SoNH_I ₂ -0				
Pt wall	0	0	6.3	93.7

36 Table S1: Element concentrations in mol.% determined from WDS analyses in the Pt walls
 37 for SoNH_I₂-0 and SoNH_I₂O₅-0. The error on the reported concentrations is on the order of
 38 ±10% in relative to the value.

39 For SoNH_I₂-0, the capsule wall is mostly represented by Pt at 94 mol.% and is slightly
 40 enriched in O at 6 mol.%. We find roughly the same composition for the outer Pt wall for
 41 SoNH_I₂O₅-0 sample. For the inner Pt wall of SoNH_I₂O₅-0 we clearly observe that there is a
 42 strong chemical reaction with the Pt alloying with the available O in the experimental charge
 43 but also Ca and Na. the O concentration measured is as high as 38 mol.%. Such a high O
 44 concentration is explained by the presence of excess O in the experimental charge coming
 45 from the dissociation of I₂O₅ into I₂ and O₂ above 350°C. The Pt-O alloying in the I₂O₅
 46 experiments could explain the presence of identified NaPt₃O₄ observed from XRD (see Table
 47 2).