Using external ion irradiations for simulating self-irradiation damage in nuclear waste glasses: State of the art, recommendations and, prospects

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Contents

1.1.	A general understanding of the problem.....	3
1.2.	Radiation sources and self-irradiation damage.....	4
1.3.	Studying the self-irradiation damage.....	5
1.4.	A brief literature review	5
1.	Experiments	7
2.1.	Materials	7
2.2.	Ion irradiations.....	8
2.3.	Characterizations	9
2.3.1.	<i>Confocal Raman spectroscopy</i>	9
2.3.2.	<i>Swelling (step-height) measurements</i>	10
2.3.3.	<i>Vickers Microhardness (H_v) and Indentation Fracture Resistance (K_{ifr})</i>	10
2.3.4.	<i>Isothermal and Isochronal annealing</i>	10
3.	Results	11
3.1.	Raman spectroscopy	11
3.2.	Vickers microhardness and indentation fracture resistance.....	19
3.3.	Step-height measurements and swelling	22
3.4.	AFM measurements of ion tracks	26
3.5.	Thermal annealing of defects (annealing of step-height)	26
4.	Discussion.....	27
4.1.	The importance of ion track threshold (Differences between BTEC and ATEC regimes)	27
4.2.	Morphology of ion tracks	29
4.3.	The similarity between the ATEC and Nuclear collisions	29
4.4.	Defect healing by BTEC (athermal defect annealing)	30
4.5.	Thermal annealing of defects (step-height annealing).....	32
4.6.	Energy deposition and damage saturation.....	34
4.7.	Global contribution of fission fragment damage.....	36
4.8.	Modifications in the glass structure and properties.	37
4.9.	Recommended ion types and ion energies.....	39
5.	A summary of the points to remember	42

31	Conclusion	43
32	References	45
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34	Terminology and symbols	
35	ATEC (Above Threshold Electronic Collisions): Electronic collisions in which electronic energy loss exceeds the	
36	ion track threshold.	
37	BTEC (Below Threshold Electronic Collisions): Electronic collisions in which electronic energy loss is below ion	
38	track threshold.	
39	NC: Nuclear collision.	
40	Dose: The SI unit of dose is J/Kg referred as gray. It is specified as keV.cm^{-3} in the current paper as is common	
41	in ion irradiation studies ($1 \text{ keV.cm}^{-3} \sim 6.4 \times 10^{-14} \text{ J/Kg} \sim 1.25 \times 10^{-20} \text{ eV/atom}$ for a glass of 2.5 g.cm^{-3} density).	
42	S_e and S_n: Electronic and nuclear energy loss of the ions respectively. The energy loss values and ion ranges	
43	were calculated using SRIM 2008.	
44	Flux and Fluence: All the flux and fluence values are reported in $\text{ions.cm}^{-2}.\text{s}^{-1}$ and ions.cm^{-2} respectively.	
45	-----	
46		

47 Abstract

48 Due to the complexities associated with handling and characterizing the radiation damage in radioactive
 49 materials such as nuclear waste forms, ion irradiation has been widely used to simulate the effects of the self-
 50 irradiation damage. This often involves ion irradiation of nuclear waste surrogate glasses using ion accelerators.
 51 Such facilities allow using a wide range of ion types ranging from H to U and energies from tens of keV to
 52 hundreds of MeV. For various reasons, the researchers often have to use ions and energies that do not
 53 necessarily match with what is expected in actual nuclear waste forms. Due to a lack of detailed and dedicated
 54 studies, there are currently no guidelines or consensus regarding the use of the ion irradiation as a means of
 55 simulating the self-irradiation damage. The purpose of this article is to delve into this subject by presenting
 56 systematic studies of a number of glasses carried out in the last decade or so. By doing so, guidelines and easy
 57 to follow ion-mass Vs ion energy contour maps are provided to best simulate the long-term radiation damage
 58 in nuclear waste forms. We also discuss how the ions of different masses and energies can be exploited for
 59 defect healing and provide a roadmap to undertake systematic studies on this subject. For the sake of brevity,
 60 a quick summary of important results and the guidelines is presented towards the end of this article and not
 61 here. Besides the nuclear waste community, the study is also of interest to a wide research community dealing
 62 with defect formation and defect healing in glasses for use in radiation environments experienced in nuclear
 63 reactors, decommissioning and space applications to name a few.

64 1. Introduction

65 1.1. A general understanding of the problem

66 Nuclear power contributes about 10 % of the world's electricity with very little or negligible CO₂ footprint.
 67 Although the emission of greenhouse gases is not an issue in this case, nuclear reactor operation results in the
 68 formation of radioactive elements. These elements emit high energy particles such as alpha, beta and gamma
 69 particles which can be fatal to living beings in high doses. The half-life time of some of these radioactive
 70 elements can be up to millions of years necessitating an appropriate long-term management strategy to avoid
 71 contaminating the environment. The various types of radioactive wastes are sorted based on their radioactivity
 72 and it is especially the high-level waste, which constitutes less than 1 % of the total radioactive waste, that
 73 requires its isolation from the biosphere for hundreds of thousands to millions of years. Based on the existing
 74 scientific knowledge and economic considerations, geological disposal of nuclear waste has internationally been
 75 accepted as the best method for its safe long-term management.

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 77 The high-level nuclear waste is generally vitrified by melting together the radioactive elements and an
 78 appropriate glass formulation and then pouring this radioactive melt into a metal canister (usually of steel) to
 79 make a solid monolith (waste form). The solidified glass monolith confined within the metal canister (waste
 80 package) is regarded as a safe package for geological disposal. The radioisotopes are chemically bonded with
 81 the glass network preventing their loss from the matrix. The glass matrix thus acts as the first barrier to the
 82 radioisotope release. The metal canister isolates the glass from the surrounding geological formation and
 83 prevents any water/moisture, which can degrade the waste form, from coming into direct contact with the
 84 glass.

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 86 Over time, the metallic canister will be lost due to its corrosion exposing the radioactive glass and
 87 making it vulnerable to leaching by the underground water. The glass and its radioactive elements will slowly
 88 dissolve by interacting with the water and these dissolved elements can potentially be carried away by the
 89 water into the water table and then distributed into the biosphere. The fundamental problem scientists are
 90 trying to understand and address is when, how and, how fast the glass dissolution will take place and what
 91 parameters will control the transport and distribution of the dissolved species. This information is essential for
 92 designing robust waste forms and incorporate the necessary mitigating measures in the design of the disposal
 93 facility. Studying the radiation damage is important because the radioisotopes will decay via alpha and beta
 94 decays and the resulting radiation will damage the glass structure. This can alter the glass structure adversely
 95 such that the radioisotopes are released earlier and at a faster rate than anticipated without considering the
 96 radiation damage. Furthermore, the radiation emitted by the radioisotopes from inside and outside (leached
 97 radioisotopes) the waste form can potentially change the water chemistry (pH and formation of free radicals)
 98 through ionization altering the reaction rates of water with the glass. Thus, studies of radiation damage play an
 99 essential role in guaranteeing the long-term chemical and physical durability of the waste forms and in building

a robust safety case for geological disposal. Keeping in mind the scientific challenges such as these, the International Atomic Energy Agency (IAEA) launched a coordinated research project in 2018 called as INWARD (Ion Beam Irradiation for High Level Nuclear Waste Form Development [1]) bringing together scientists from around the world with the aim of developing a coherent methodology and guidelines for simulating the effects of radiation damage under disposal conditions.

1.2. Radiation sources and self-irradiation damage

The main radiation sources within the waste package are short-lived beta emitters such as ^{137}Cs and ^{90}Sr and long-lived alpha emitters (actinides) [2][3]. Typical beta particle energies vary from a few hundred keV to about 2 MeV. For instance, ^{137}Cs emits beta particles of ~ 514 keV (94 %) and ~ 1.17 MeV (5.6 %) and a gamma particle of about ~ 661 keV mainly. Similarly, ^{90}Sr and ^{90}Y mainly emit beta particles of ~ 546 keV and ~ 2.3 MeV respectively. The electrons mainly interact with the electrons of the target atoms resulting in electronic excitation and ionization. The typical ionization cross-sections (σ_i) for electrons of few hundreds of keV to interact with atoms such as O, Si and B are about 10^{-19} to 10^{-20} cm^2 [4]. With a typical atomic number density of about 8×10^{22} atoms.cm^{-3} (N) for glasses, one would expect at least one ionization event per micrometer ($\sim N \cdot \sigma_i \sim 8 \times 10^{22} \times 10^{-19} \sim 8000$ cm^{-1} . The mean free path is ~ 1.2 μm). In addition to the ionization, the electrons can also cause atomic displacements by dislodging them from their equilibrium positions. Assuming average displacement energy of about 25 eV for the target atoms, minimum electron energies of about 158 and 255 keV will be needed to displace the O and Si atoms respectively (the main constituents of the glass). This shows that the typical beta particles have sufficient energy to cause the atomic displacements. For beta particles of about 550 keV, the displacement cross-section is about 10^{-23} cm^2 which can lead to about one displacement per centimeter. The ratio of ionization to displacement cross-section is about 10^3 to 10^4 highlighting that electronic ionization will be the dominant interaction mechanism and that the displacement damage due to electrons is significantly less.

In addition to the beta decays, structural damage will also occur through alpha decays. Each alpha decay will lead to the emission of an alpha particle and a heavy recoil nucleus. The energy of alpha particles varies from about 4 to 6 MeV and they will undergo dominant electronic interaction losing about 99 % of their energy in electronic collisions (electronic energy loss). The major difference between an alpha particle and an electron, (beta particle) in terms of their ionization, lies in the extent of their energy loss. Alpha particles on average lose about 0.2 keV.nm^{-1} whereas the beta particles only lose about 10^{-3} times this. Alpha particles therefore cause more intense ionization compared to electrons. A typical alpha particle will travel about 25 μm in the glass waste form causing about 200 atomic displacements (~ 8 displacements per micrometer). Recoil nuclei on the other hand, due to their large mass, only have energy in the range of 80 to 120 keV and will interact mainly through elastic interaction (nuclear collisions). They will travel up to about 40 nm causing about 1600 atomic displacements ($\sim 4 \times 10^4$ displacements per micrometer). This highlights that heavy recoil nuclei are the most significant source of the displacement damage whereas the alpha particles and electrons are a dominant source of the ionization damage.

In conjunction with alpha and beta decays, one has to consider gamma particles because the radioactive decays can leave the nuclei in an excited state which deexcite to the ground state through the emission of gamma particles. The energy of the gamma particles is mostly in the range of few hundreds of keV. For instance, ^{137}Cs is a typical radioisotope which decays to ^{137}Ba either directly by emitting an electron of about 1.17 MeV or via the metastable ^{137}Ba by the emission of an electron of 0.51 MeV and a gamma particle of 661 keV. Compton scattering, in which a gamma particle ejects an electron from the target atom, is the dominant interaction mechanism in this energy range. A gamma particle of 661 keV can transfer a maximum of about 472 keV to the electron and this Compton electron can then take part in further ionization and atomic displacements as a typical electron would. Therefore, gamma particles indirectly cause the same or similar damage as the beta particles do. However, the Compton scattering cross-sections are significantly smaller. For example, the cross-section for the production of the 472 keV Compton electron from the 661 keV gamma particle is about 10^{-26} cm^2 . To compare this with the cross-section for the electrons, it can be multiplied by the Z of the target atom, but, even then the total cross-section for this process is 10^{-5} to 10^{-6} times the electron ionization cross-section (which is $\sim 10^{-19}$ to 10^{-20} cm^2) and 10^{-2} to 10^{-3} times the electron displacement cross-sections (which is $\sim 10^{-23}$ cm^2). Therefore, the effect of the gamma particle irradiation is essentially similar to the effects of the beta

particles of few hundred keV except that the cross-section is significantly small. Furthermore, gamma particles can also cause atomic displacement, but, because the atoms are significantly heavier than electrons, the displacement cross-sections are substantially smaller than Compton scattering cross-sections. In addition, the energy transfer during such collisions is very small. For instance, Si, Na and O can receive a maximum energy of about 33, 40 and 58 eV from a 661 keV gamma particle. This is just barely more than the typical atomic displacement energies (20 to 30 eV). For all practical reasons, the direct atomic displacements from gamma particles can be completely ignored and their ionization effects can essentially be simulated using electrons of few hundreds of keV (the readers are referred to pages 88 to 91 in [5] for gamma particle interaction).

The combination of alpha, beta and gamma decays will internally damage the nuclear glass over time and this is commonly referred as the self-irradiation damage.

1.3. Studying the self-irradiation damage

In principle, one has to view and study the self-irradiation damage as a cumulative effect of alpha, beta and gamma decays. However, the focus of this article is only to deal with the effects of alpha decays because they are the longest-lived radiation source in the waste form. Actinide doping of surrogate waste forms is one of the best methods to address the self-irradiation damage arising due to alpha decays. But, besides being costly and time-consuming, handling active specimens requires dedicated research facilities and characterization tools. Also, the total damage from an alpha decay event is a cumulative effect of the alpha particle and the recoil nucleus damages. This leaves no room to identify and understand the effects of the individual particles on the pristine and the pre-damaged material. The role of the pre-existing damage on ion-matter interaction has recently been explored in more detail using double ion beam irradiations providing new insights about the long-term radiation damage in waste packages. Such studies have now shown that alpha particles can partially heal the pre-existing damage from the recoil nuclei [6][7]. Therefore, despite being the closest analogue of the long-term self-irradiation scenario of the waste packages, actinide doping has some inherent technical and fundamental shortcomings as well.

External ion irradiations of surrogate nuclear waste glasses have been explored as an alternative approach to circumvent the problems associated with actinide doping. As recoil energies are in the range of 80 to 120 keV, researchers mainly tend to use ions in the range of a few hundred keV up to a few MeV to justify simulating the low energy recoil nucleus damage. This approach is not based on any actual study of the defect types and defect kinetics as a function of the ion energy and ion mass. It is not clear whether these higher energy ions truly simulate the damage from a typical recoil nucleus. One of the main reasons to select ion energies greater than the actual energy of the decay products is that the depth resolution of several commonly used spectroscopic techniques is about a few hundreds of nanometers. If one were to use a 100 keV heavy-ion, it would only create a damage depth of about 40 nm which is far less than the typical depth resolution of many characterization tools and surface effects/contamination would be the dominant factor controlling the defect evolution. This compels one to use higher energy ions to properly characterize the irradiation-induced defects with the hope that the defect types do not change much with the ion energy. Also, at times, a large quantity of the material is needed to characterize the irradiation-induced structural changes (e.g. for NMR spectroscopy, DSC, EPR etc.) necessitating the use of higher energy ions. To date, detailed studies exploring the effect of ion mass and ion energy on the final damage state of a given glass composition have not been undertaken. A simple question one may ask is how much ion energy is too much to render the study irrelevant for simulating the self-irradiation damage in nuclear waste matrices? A similar question can then be raised about the mass of the ion. The answer is no one knows for sure. Due to a lack of sufficient studies and different glass compositions being used by researchers, it is not possible to define a contour of relevance (or irrelevance) in terms of the ion energy and ion mass (or atomic number z) with the studies currently available in the literature. This leaves a void in relating the external ion irradiation effects with the self-irradiation damage in waste packages. Therefore, a fundamental understanding of what type of ions and energies could best represent the alpha particle and recoil nucleus damage is still lacking. With these questions highlighted, a brief literature overview of the radiation damage in nuclear waste glasses is presented below.

1.4. A brief literature review

Several actinide doping studies [2,8–16] have addressed the changes occurring in the mechanical properties (hardness, elastic moduli, fracture toughness), density, stored energy and, structure as a result of the alpha decays. Maximum density changes of about $\pm 1\%$ (swelling or densification) have been observed to occur depending on the chemical composition of the glass. Similarly, studies have shown that the hardness and elastic modulus decrease and finally saturate with alpha decay accumulation. Usually, the irradiation-induced changes saturate after an accumulation of about 2×10^{18} to 5×10^{18} alpha decays per gram (nuclear dose of about 3×10^{20} to 7×10^{20} keV.cm⁻³) [3,14,17]. By varying the actinide doping concentration in the range of 0.04 to 3.25 wt. %, no dose rate effects were observed in previous studies [14]. It has been shown that the property evolution (hardness, density), when plotted against the nuclear dose, can be fitted with simple exponential models – supporting the idea that the modifications occur due to nuclear energy loss. Owing to the large number of atomic displacements induced by the recoil nuclei, it is assumed that nuclear collisions (NC) mainly control the damage formation. The role of alpha particles in damage accumulation is believed to be negligible. Furthermore, Molecular dynamics (MD) simulations of simple borosilicate glasses subjected to displacement cascades [18–23] have shown that NCs result in swelling, modulus decrease, boron coordination change (transformation of BO₄ to BO₃) and network depolymerization - all of which tend to saturation after about 4×10^{20} keV.cm⁻³ (~ 26 MGy ~ 6 eV/atom) in good agreement with actinide doping studies [15,16]. This further lends support to the inference that NCs will control the long-term evolution of waste packages. Besides these studies, which essentially deal with the effects of homogenous self-irradiation, more recent work on the effects of inhomogeneous self-irradiation (due to nonuniform radionuclide distribution) has provided some new and important insights [24]. It has been shown that electrostatic charging of waste inclusions can generate high enough fields that can lead to local discharges and fractures/cracks. While these results highlight the importance of uniform radionuclide distribution, further studies concerning typical glass waste forms and the degree of acceptable radioisotope inhomogeneity from this perspective are needed.

Similarly, from many external ion irradiation studies [10,14,25–29] the changes in various material properties have been observed to occur which usually saturate after 4×10^{20} to 4×10^{22} keV.cm⁻³ (either in nuclear or electronic energy dose). For instance, heavy-ion irradiations have been observed to: (i) decrease the hardness (by about 35 % in French Nuclear Waste Surrogates (F-NWS) and by about 13 to 36 % in Chinese-NWS (C-NWS) depending on the glass composition); (ii) decrease/increase the modulus (decrease by about 15-20 % in F-NWS, increase by about 4 % in sodium-aluminoborosilicates (C-NWS) and decrease by about 18 % in sodium borosilicates (C-NWS)); and, (iii) decrease the density (by about 1.5 % and 3 % for French SON68 and BS3 glasses respectively) [14]. Also, studies on swift heavy ion irradiation of glasses [7][30] have shown that large electronic energy loss (> 4 keV.nm⁻¹) can be as effective as NCs in modifying the material properties. In comparison to the slow and swift heavy ions, the changes due to He ions (representing alpha particles) tend to be smaller. However, the magnitude of the variation of a given property during alpha particle irradiation varies from one study to another. Studies on F-NWS show that He and heavy ions induce about 3 % and 35 % decrease in the glass hardness respectively [10][14]; suggesting that He ions play only a minor role in the modification of waste glasses. But, He and heavy-ion irradiation studies on sodium alumino-borosilicate glasses (C-NWS) show that the changes induced by He and heavy ions are quite close to each other, as indicated by the similar level of the hardness decrease by alpha particles ($\sim 15\%$) and heavy ions (~ 13 to 20%) [26–28]. Also, unlike alkali borosilicate glasses (F-NWS), a slight increase in the modulus (3.5 %) has been reported in sodium alumino-borosilicate glasses [28]. It is worth mentioning that the ion fluxes used in the studies on C-NWS are usually two to three orders of magnitude higher than the ones used by French researchers and therefore a contribution of dose rate and beam-induced specimen heating can't be ruled out in the former case. Also, MD simulations have shown that the alkali-alumino-borosilicate glasses are relatively stable to irradiation-induced modifications in comparison to the alkali-borosilicate glasses [23]. In general, it is difficult to compare the various studies when the glass compositions and irradiation conditions tend to be different – making it difficult to conclude anything for sure about the role of the ion energy, ion mass and flux on various material properties. This is exacerbated by a lack of detailed study exploring a wide mass-energy landscape and the corresponding glass response for a given glass composition. A general overview of some of the ion irradiation studies available in the literature on different nuclear waste glasses is given in contour maps of energy loss in Fig. 1. The contour maps show the electronic (S_e), nuclear (S_n) and S_e/S_n ratio from left to right respectively for various ions up to 15 MeV and atomic number (Z) up to 92. The white-filled circles indicate S_e , S_n and S_e/S_n values used by various researchers

over the years (this data and the references are compiled in supplementary Excel file named “Literature Irradiation data”). The black-filled circles indicate the values for the actual alpha particle and the recoil nucleus. The black arrows indicate the high energy ion irradiations available in the literature but not shown on these figures (this data is also added in the supplementary Excel file). These graphs indicate that most of the studies focus on ion energies less than 7 MeV whereas ion masses greatly vary from hydrogen to Bismuth.

The main aim of this article is to delve into this issue in detail by presenting ion irradiation studies conducted on F-NWS’s over the years. The idea is to reflect our current understanding of the response of the nuclear waste glasses to ion irradiations and present a road map and lay some guidelines to better simulate the effects of self-irradiation damage. This study by itself is by no means a complete and perhaps the true picture of the response of nuclear waste glasses but rather a reflection of our understanding at present. We believe that such guidelines should be helpful to a broad research community to better design their irradiation experiments and explore the scientific issues that are still either poorly understood or not explored at all.

Figure 1: Energy loss contour maps showing Electronic (S_e), Nuclear (S_n) and S_e/S_n ratio for ions with Z up to 92 and energy up to 15 MeV. The circles show data points from various earlier works [10,26,29–41] (also see the “literature Irradiation data” excel sheet included as supplementary material for the irradiation conditions in these earlier works).

1. Experiments

2.1. Materials

Three different glass compositions with same R ($[\text{Na}_2\text{O}]/[\text{B}_2\text{O}_3]$) and K ($[\text{SiO}_2]/[\text{B}_2\text{O}_3]$), but with increasing complexity were studied. They are referred as BS3 (three oxide sodium borosilicate), BS6/ISG (six oxide borosilicate, commonly known as international simplified glass-ISG) and SON68 (complex thirty oxide borosilicate glass that acts as a surrogate of R7T7 glass - which is used for the conditioning of high-level nuclear waste in France). The composition of the glasses is given in Table-I. The glasses were prepared by melting the powders in a Platinum crucible with stirring for three hours (the melting temperatures are shown in the table). The molten glass was poured into graphite crucibles pre-heated up to T_g (300-gram capacity per crucible) and then the crucibles were cooled to room temperature with a cooling rate of about 60 K per hour. The glass bars were cut and polished on all the six faces into desired specimen dimensions ($3 \times 3 \times 0.5$ mm used during He and Au ion irradiations and $6 \times 6 \times 0.5$ mm for rest of the cases). After polishing (roughness ~ 1 -3 nm, measured using AFM), the specimens were annealed at $T_g + 10$ K for about 15 minutes to remove any residual stresses as a result of the polishing and to further reduce the surface roughness to less than 1 nm.

Table-I: Composition of BS3, ISG and SON68 glasses (wt. %). T_m and T_g are glass fabrication and glass transition temperatures respectively.

SON68 ($T_m = 1473$ K, $T_g = 765$ K)								
SiO ₂	45.28	Ag ₂ O	0.03	Cs ₂ O	1.1			
B ₂ O ₃	13.97	CdO	0.03	TeO ₂	0.23	SiO ₂	56.18	65.56
Na ₂ O	10.1	Cr ₂ O ₃	0.52	SnO ₂	0.02	B ₂ O ₃	17.33	20.23
Al ₂ O ₃	4.94	ZnO	2.5	Y ₂ O ₃	0.2	Na ₂ O	12.17	14.21

CaO	4.02	P ₂ O ₅	0.29	La ₂ O ₃	0.92	Al ₂ O ₃	6.06	
Li ₂ O	1.97	SrO	0.34	Ce ₂ O ₃	0.95	CaO	4.98	
Fe ₂ O	2.99	ZrO ₂	2.72	Nd ₂ O ₃	1.64	ZrO ₂	3.28	
NiO	0.42	MoO ₃	1.76	Pr ₂ O ₃	0.45	ISG: T _m =1673, T _g = 865		
BaO	0.61	MnO ₂	0.38	BS3: T _m = 1623 K, T _g =865 K				

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2.2. Ion irradiations

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The ion irradiations were performed in single-beam and double-beam/sequential irradiation mode. In the single-beam irradiation mode, the specimens were irradiated with only one type of the ion for various fluences. In the sequential beam irradiation mode, the specimens were first irradiated with one type of the ion (usually a heavy-ion) to a certain fluence and then by a different light ion. The purpose of the sequential ion irradiations is to study the effects of the pre-existing defects on the irradiation response and to better simulate the effects of alpha decays, where a combination of recoil nucleus and alpha damage take place. In the case of the single-beam irradiations, ion irradiations were performed with light and heavy ions covering a total stopping power range of about 0.3 keV.nm⁻¹ to 15 keV.nm⁻¹. Detailed irradiation conditions are specified in Table-II and the corresponding legend. Aluminium (99.9 %) degraders were used during ¹²⁹Xe, ¹³⁶Xe and ⁸⁴Kr irradiations to obtain various energy loss values at the specimen surface. The specimens were irradiated to various ion fluences (except in the case of 1.3 MeV ⁸⁴Kr where only a single high fluence of 2x10¹⁴ ions.cm⁻² was used) to track the damage formation as a function of the fluence. In all the cases, irradiations were carried out for long enough time to reach the saturation damage state. For the sequential beam irradiations, four different sequential ion irradiations as shown in Table-II were performed. The specimens were first irradiated with one type of the ion followed by irradiation with the second ion type.

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Table-II: Irradiation conditions: All the ion irradiations except Au and He were performed at GANIL, Caen, France at normal incidence and room temperature. In the case of the ¹²⁹Xe (91.6 MeV) and ¹³⁶Xe (96.6 MeV), Aluminium degraders were used to reduce the beam energy to obtain various energy loss values on the specimen surface. The thickness of Al stoppers was determined by measuring the surface area and mass of the foils - which yielded thickness values with an uncertainty of ± 2 %. The numbers in the brackets in column-2 are the specific ion energies (energy per unit mass). S_e and S_n are the electronic and nuclear energy losses on the specimen surface respectively. S_{ave} is the average total stopping power of the ion (kinetic energy divided by the projected ion range). Its significance will be discussed later in the context of the specimen swelling. Au and He ion irradiations were performed at JANNUS Saclay, France. Ion beams were incident at an angle of 15° to the surface normal. The pressure in the chamber was maintained at 2x10⁻⁷ torr. All the stopping power data is given for the BS3 glass (density = 2.45 g.cm⁻³ ~ 7x10²² atoms.cm⁻³). The values remain the same for the ISG glass. SON68 glass is about 10 % denser than the BS3 glass and the range of ions is smaller by about 8 %. Consequently, the stopping power is slightly higher. The numerals (i) and (ii) in column-1 will be referred to later when presenting the results which are divided into cases (i) and (ii).

Ion	Energy (MeV)	Range (μm)	S _e (keV/nm)	S _n (keV/nm)	S _e /S _n	S _{ave}	Flux (ions.cm ⁻² .s ⁻¹)	Fluence range (ions.cm ⁻²)
Single-beam ion irradiations								
⁴ He ⁺ (ii)	2 (0.5)	6	0.3	3x10 ⁻⁴	1000	0.33	1x10 ¹³	4x10 ¹⁵ - 10 ¹⁷
¹² C (ii)	12 (1)	9.5	1.2	1x10 ⁻³	960	1.3		8x10 ¹³
¹⁸ O (ii)	135 (7.5)	124	0.7	4x10 ⁻⁴	1892	1	2.5x10 ⁸	5x10 ¹¹ - 4x10 ¹³
⁵⁸ Ni ⁺ (i)	17.4 (0.3)	6.7	6	6x10 ⁻²	97	2.6	<10 ⁹	3x10 ¹³
⁸³ Kr (i)	0.4 (4.8x10 ⁻³)	0.2	0.4	1.2	0.3	2.0		10 ¹³ - 5x10 ¹⁴

⁸⁴ Kr (i)	1.3 (0.015)	0.7	0.8	0.7	1	1.7	6x10 ⁹	2x10 ¹⁴ only
⁸⁴ Kr (i)	25.2 (0.3)	7	7	0.1	72	3.6		10 ¹¹ - 10 ¹⁴
⁸⁶ Kr ⁺⁸ (i)	74 (0.86)	12.2	10	4x10 ⁻²	250	6	5x10 ⁹	1x10 ¹² - 3x10 ¹³
¹²⁹ Xe (i)	91.6 (0.71)	11.8	13.6	0.1	136	7.8	2x10 ⁹	10 ¹¹ - 2x10 ¹⁴
	65.8 (0.51)	9.8	12	0.1	92	6.7		
	43.9 (0.34)	7.9	10	0.2	56	5.5		
	25.8 (0.2)	5.8	7.2	0.3	27	4.3		
	12.9 (0.1)	3.7	4.4	0.4	10	3		
¹³⁶ Xe (i)	96.6 (0.71)	12.3	13.6	0.1	136	7.7	6x10 ⁹	2x10 ¹² - 4x10 ¹³
	59.8 (0.44)	9.6	11.2	0.1	112	6.3		
	32.6 (0.24)	6.8	8.1	0.2	41	5.3		
	13.6 (0.1)	3.8	4.6	0.4	12			
¹⁹⁷ Au ⁺⁶ (i)	14 (0.071)	3	3.3	1	3	4.66	2x10 ¹⁰	8x10 ¹³
²³⁸ U ⁺³² (i)	109.5	12.3	15.5	0.4	42	8.9	1.5x10 ⁸	10 ¹¹ – 3.8x10 ¹³
¹³² Xe	343	Note ^a						
¹³² Xe	92.4							
⁷⁸ Kr	780							
Double-beam ion irradiations								
¹⁹⁷ Au (14 MeV) + ⁴ He (2 MeV) ⁴ He (2 MeV) + ¹⁹⁷ Au (14 MeV) ¹³⁶ Xe (96.6 MeV) + ¹² C (12 MeV) ¹³⁶ Xe (96.6 MeV) + ⁵⁸ Ni (17.4 MeV)				The ion irradiation conditions (temperature, flux) are the same as during single-beam ion irradiations				

Note^a: These cases were studied for SAXS measurements of ion tracks which are not presented in this article. The specimens were thin enough for the ions to traverse the specimen. The specimens were irradiated to a single low fluence only ($< 10^{11}$ ions.cm⁻²).

2.3. Characterizations

2.3.1. Confocal Raman spectroscopy

Raman spectroscopy was performed at room temperature (295 K) using a 532 nm laser (green) and LabRam HR800 micro-spectrometer from Jobin Yvon. By adjusting the confocal hole and grating, depth, lateral and, spectral resolutions of 1.6 μm , 0.8 to 1 μm and 1.7 cm⁻¹ were obtained respectively. Each spectrum was acquired for a total time period of 300 s. The Raman spectra, therefore, represent an average change occurring in a depth of about 1.6 μm and lateral diameter of about 1 μm (a cylindrical analysis volume of about 1.2 μm^3). At each ion fluence, non-polarized Raman spectra were acquired on the irradiated surface referred to as surface Raman spectroscopy (shown in Fig. 2 (a)). The spectra were obtained at different positions to confirm the damage homogeneity. In a few cases, cross-sectional Raman spectroscopy was performed from the specimen surface to beyond the ion range along one of the edges (as indicated in Fig. 2(a, b). Fig. 2 (b) shows a dark-field optical microscopy image of a specimen irradiated with 96.6 MeV Xe ions). The bright layer is the radiation-damaged region (~ 12 μm thick layer). This methodology allowed characterizing the damage along the ion path as a function of the energy loss of the ions. In this case, the Raman spectra were acquired at a spatial interval of 0.5 μm .

Figure 2: A schematic of the cross-sectional and surface Raman spectroscopy. (a) Shows a schematic of the surface and cross-sectional Raman spectroscopy; (b) a dark-field optical micrograph of a BS3 specimen irradiated with 96.6 MeV ^{136}Xe ions. The bright region is the irradiated layer of the specimen ($\sim 12\ \mu\text{m}$).

2.3.2. Swelling (step-height) measurements

To measure the irradiation-induced swelling, aluminium masks thick enough to stop the ion beam were used to cover a small region of the specimens. Due to the swelling upon irradiation, a step was formed between the irradiated and the non-irradiated part of the specimens. Step-height was measured at various fluences using a Dektak150 surface profiler by scanning across the step between the irradiated and the non-irradiated regions. At least three measurements at different locations were performed on each specimen. In a few cases, the step-height measurements were also performed by 2D-laser interferometry and AFM to obtain two-dimensional maps. All the three techniques yielded the same results and the results presented in this article are mostly based on the Dektak surface profiler measurements. The step-height was converted to swelling by dividing the step-height by the projected ion range as given in Table-II.

2.3.3. Vickers Microhardness (H_v) and Indentation Fracture Resistance (K_{ifr})

The Vickers hardness was measured at various fluences using Anton Paar MHT10 system. The load was varied from 10 gf (0.098 N) to 400 gf (3.92 N) using a 15 s dwell time to successively probe the damage layers from the specimen surface to beyond the ion range. The indents were observed using an Olympus BX51 optical microscope with a 100 $\times$ magnification objective. The value of the hardness was obtained from an average of 25 images (five indents and 5 images per indent) for each indentation load and the irradiation fluence. Since each load probed a specific depth of the specimen, it allowed studying the depth variation of the hardness. Whenever cracks were observed (usually at high loads), such indents were further analyzed to measure the length of the cracks and estimate the indentation fracture resistance. The indents in all the cases were observed with the optical microscope within 1 – 2 minutes of the indentation.

2.3.4. Isothermal and Isochronal annealing

The effect of annealing was studied using step-height measurements. Specimens of the BS3 glass irradiated with ^{129}Xe (91.6 MeV) up to 10^{13} and 10^{14} ions. cm^{-2} were annealed under isothermal ($T = 300\ ^\circ\text{C}$, $t =$ up to 6 hours) and isochronal ($t = 40$ minutes, $T = 200, 300$ and $590\ ^\circ\text{C}$) conditions in air. For isothermal annealing, the step-heights were measured after 40 minutes and 6 hours of annealing. For isochronal annealing, step-height measurements were performed after 40 minutes of annealing at 200, 300 and $590\ ^\circ\text{C}$.

3. Results

3.1. Raman spectroscopy

3.1.1. BS3 glass

All the ion irradiations followed by numeral (i) in column-1 of Table-II (referred to as scenario-(i) henceforth) resulted in the formation of the same saturation damage state as indicated by the similarity of various peaks in the Raman spectra (in terms of the peak shifts and intensities). As a representative case, the result of ^{129}Xe (91.6 MeV) ion irradiation on the BS3 glass is shown in Fig. 3 (a) (the spectra were acquired on the irradiated surface of the specimen). For the sake of brevity, Raman spectra of the BS3 glass for some other ion irradiations in scenario (i) are shown in Fig. S1 in the SI.

Figure 3: Non-polarized Raman spectra of the BS3 glass specimen irradiated with 91.6 MeV Xe ions. **(a)** Raman spectra at various fluences. The spectra are vertically shifted for clarity; **(b)** Shift of the R-band position as a function of the irradiation fluence. The vertical dotted line indicates the saturation fluence (95 % change in the R-band position).

Some of the well-known bands/peaks are indicated in Fig. 3 (a). Figure 3 (b) shows the variation of the R-band position as a function of the irradiation fluence. The solid line represents the evolution as per the direct impact damage model [42]. The vertical dotted line indicates a 95 % change in the R-band position and the fluence (and dose) corresponding to this value are also shown on the figure (referred to as saturation fluence and saturation dose). The electronic dose was calculated by taking the average electronic energy loss value in a depth of about 1.6 μm from the specimen surface (Raman depth resolution $\sim 1.6 \mu\text{m}$) and multiplying it by the saturation ion fluence. The saturation dose is about $4 \times 10^{20} \text{ keV.cm}^{-3}$ ($\sim 26 \text{ MGy} \sim 6 \text{ eV/atom}$). Some of the clearly visible modifications in various features of the spectra as a function of the irradiation fluence are listed below. The interpretation regarding the origin of various bands and the information they provide about the structural modifications induced by the ion irradiation are discussed in some of our earlier publications [30][43] and briefly here.

- I. The position of the R-band, assigned to the mixing bending and rocking vibrations of the Si-O-Si bonds, increased from about 494 cm^{-1} (pristine value) to about 506 cm^{-1} (saturation value) with increasing fluence as shown in Fig. 3 (b) (shift by 12 cm^{-1}). The damage saturation was attained after about $2.8 \times 10^{12} \text{ ions.cm}^{-2}$ ($\sim 4 \times 10^{20} \text{ keV.cm}^{-3}$). Its shift indicates a change in the distributions of the Si-O-Si angle and of the various rings.
- II. The Raman bands in the region from 590 cm^{-1} to 630 cm^{-1} with a prominent peak at 630 cm^{-1} in the pristine glass specimen were modified. The intensity of the peak near 600 cm^{-1} relative to the peak at 630 cm^{-1} increased. The peak at 630 cm^{-1} corresponds to the breathing vibration of danburite type rings whereas the one at 600 cm^{-1} is assigned to the vibration of 4-membered silica rings called D2 band.
- III. The shape of the Q_n region, assigned to the Si-O stretching vibrations, significantly changed (Q_n represents a silica tetrahedron connected to 'n' bridging oxygen atoms, where n varies from 0 to 4). This band is usually de-convoluted into three to five peaks representing different Q_n units. The two distinctly visible humps in the pristine spectrum seem to have merged leading to a prominent peak near 1080 cm^{-1} (usually assigned to a Q_3 unit).

- IV. The area of the band from 1300 cm^{-1} to 1600 cm^{-1} (labelled as BO_3 -region), assigned to the B-O stretching vibration in BO_3 units, increased with an increase in the fluence (BO_3 represents a boron atom connected to three oxygen atoms. The oxygen atoms may or may not be bridged to the rest of the network).
- V. Molecular oxygen (peak at 1552 cm^{-1}) was formed upon ion irradiation (a small peak at 1558 cm^{-1} represents the atmospheric oxygen).

For all the other irradiations in scenario-(i) (Table-II), the saturation was obtained at a similar value (from about 3×10^{20} to $6 \times 10^{20}\text{ keV.cm}^{-3} \sim 4$ to 7 eV/atom). The evolution of the R-band for various other ion types/energies shown in Table-II is shown in Fig. S2 in the SI. When fitted with the direct impact damage model, one can obtain information about the damage cross-section (ion track cross-section) of the ion. These ion track cross-sections are shown in Table-S1 in the SI.

Raman spectra were also acquired along the cross-section of some of the irradiated specimens. One such example is shown in Fig. 4 (a) for the case of the BS3 specimen irradiated with $96.6\text{ MeV }^{136}\text{Xe}$ ions up to $4 \times 10^{13}\text{ ions.cm}^{-2}$. The Raman spectra in Fig. 4 (a) are shown at a spatial interval of $2\text{ }\mu\text{m}$ and there are no relative changes between the spectra from the surface up to a depth of about $11\text{ }\mu\text{m}$. The next spectrum shown at a depth of about $13\text{ }\mu\text{m}$ from the surface shows a lower damage level (because it is near the end of the ion path and has a slight contribution from the undamaged region) and the spectrum at $15\text{ }\mu\text{m}$ shows an undamaged state. Figure 4 (b) shows the evolution of the R-band position for three different fluences as a function of the irradiation depth (at a spatial interval of $0.5\text{ }\mu\text{m}$). The damage cross-sections extracted at each sample depth using direct impact model are shown in Fig. 4 (c). The data clearly shows a depth dependence of the ion track cross-section. This is due to a continuous decrease in the energy loss of the ions as a function of the depth. The energy loss curves are also shown in Fig. 4 (c). In fact, the cross-sections very well follow the stopping power curve. The depth-dependent cross-sections shown in Fig. 4 (c) and the cross-sections extracted from Fig. S2 in the SI (which are listed in Table S1 in the SI) are plotted in Fig. 4 (d) as a function of the average electronic energy loss. A linear fit to the data yields an ion track threshold of $2 \pm 0.7\text{ keV.nm}^{-1}$. This shows that for electronic energy losses greater than 2 keV.nm^{-1} , ion tracks are formed and the extent of structural modifications induced by the ions becomes independent of the ion type.

Figure 4: Results of the cross-sectional Raman spectroscopy on the BS3 specimen irradiated with 96.6 MeV Xe ions. (a) Raman spectra taken at various depths along the irradiated cross-section of the BS3 specimen irradiated with 4×10^{13} ions. cm^{-2} ; (b) R-band position as a function of the irradiation depth for three different fluences, (c) damage-cross-sections obtained from the data in Fig. 4 (b) using direct impact damage model (square symbols). Electronic, nuclear and total energy loss of the ions as a function of the depth (results from SRIM simulation) are also shown and, (d) linear fit to the damage-cross-sections to evaluate the ion track threshold.

We will now discuss some cases where electronic energy loss of the ions is less than the ion track threshold (scenario (ii) in Table-II). Figure 5 (a) shows the impact of 2 MeV He irradiation on the BS3 glass structure for fluences ranging from 4×10^{15} to 1×10^{17} ions. cm^{-2} . Raman spectrum of the BS3 glass irradiated with 91.6 MeV ^{129}Xe ions up to 10^{14} ions. cm^{-2} is also shown for comparison. A visual comparison with the Xe irradiated specimen clearly shows that the structural modifications due to He ions are much smaller (a comparison of Fig. 5 (a) with the Raman spectra in Fig. 3 (a) indicates that the Raman spectrum after irradiation with 10^{17} He. cm^{-2} resembles closely with the Raman spectrum after irradiation with about 10^{12} Xe. cm^{-2}). The R-band position was observed to increase by about 5 cm^{-1} only. Similarly, the modifications in the Q_n and BO_3 regions were also relatively smaller. The first visible structural modifications were observed after a fluence of about 2×10^{15} He. cm^{-2} (not shown). This corresponds to an energy deposition of about $6 \times 10^{21} \text{ keV.cm}^{-3}$ ($\sim 380 \text{ MGy} \sim 86 \text{ eV/atom}$). For fluences between 4×10^{15} to 2×10^{16} He. cm^{-2} only mild changes were observed and no further changes beyond 2×10^{16} to 1×10^{17} He. cm^{-2} were observed. Therefore, we assume that the structural modifications at most saturated by 2×10^{16} ions cm^{-2} . This corresponds to an electronic energy deposition of about $6 \times 10^{22} \text{ keV cm}^{-3}$ ($\sim 3.8 \text{ GGy} \sim 860 \text{ eV/atom}$). This dose level is about 100 to 150 times greater than what was needed for damage saturation during the heavy ion irradiation (scenario (i)).

BS3 glass specimens were also irradiated with 135 MeV ^{18}O ions up to a fluence of 4×10^{13} ions cm^{-2} ($\sim 2.5 \times 10^{20} \text{ keV.cm}^{-3} \sim 16 \text{ MGy} \sim 3.6 \text{ eV/atom}$). No visible structural modifications and no changes in the mechanical properties were observed [44]. Similarly, irradiation with 12 MeV ^{12}C up to a fluence of 8×10^{13}

ions.cm⁻² ($\sim 1 \times 10^{21}$ keV.cm⁻³ ~ 64 MGy ~ 14.3 eV/atom) resulted in only mild structural changes. It is important to bear in mind that at dose levels much smaller than this, a complete saturation was observed when electronic energy loss was greater than 2 keV.nm⁻¹ during heavy ion irradiations. Therefore, it is plausible to assume that the BS3 glass responded similarly to ⁴He, ¹⁸O and ¹²C irradiations.

Figure 5: Raman spectra of the pristine and irradiated BS3 glass. **(a)** Raman spectra after irradiation with 2 MeV He ions to various fluences (ions.cm⁻²). A spectrum of Xe irradiated specimen is also shown for comparison (91.6 MeV Xe), **(b)** a comparison of the Raman spectra of the pristine and irradiated BS3 glass irradiated with either 2 MeV He ions or with 2.3 MeV electrons.

Also, a comparison of the He irradiation with 2.3 MeV electron irradiation of the BS3 glass is presented in Fig. 5 (b). The case of 2×10^{16} He.cm⁻² at which the electronic dose level is about 4 GGy is compared with electron irradiation doses of 3.14 GGy and 4.55 GGy (the detailed results of the electron irradiation have already been presented elsewhere [4][43]). Interestingly, the He irradiation effects at a similar dose level are similar to the effects of the 2.3 MeV electron irradiation when comparing the Raman spectra. This indicates that when electronic energy loss of the ions is below the ion track threshold, the structural changes are dictated by electronic excitation and ionization effects — as in the case of the electrons. However, the modifications strongly differ when the electronic energy loss exceeds the ion track threshold. Therefore, despite the fundamental mechanism of energy loss being the same in both the cases (electronic energy loss), the magnitude of the energy loss plays an important role in defining the final damage state. Henceforth we will refer to the electronic collisions in which the electronic energy loss exceeds the ion track threshold as **Above Threshold Electronic Collisions (ATEC)** and as **Below Threshold Electronic Collisions (BTEC)** when the electronic energy loss is less than the ion track threshold.

3.1.2. ISG Glass

Some Raman spectra of the pristine and irradiated ISG glass are shown in Fig. 6. Figures 6 (a) and (c) show the evolution of the Raman spectra as a function of the fluence for 91.6 MeV Xe and 109.5 MeV U ions respectively. The evolution of the R-band (473 cm⁻¹ in the pristine) for both these cases is shown in Fig. 6 (b) and (d) for Xe and U ions respectively. The R-band position increased by about 25 to 27 cm⁻¹ and damage saturation was obtained after about 9×10^{20} (7×10^{12} ions.cm⁻²) and 5×10^{20} (3.7×10^{12} ions.cm⁻²) keV.cm⁻³ respectively (in electronic dose). Besides single beam irradiation experiments, sequential beam irradiation experiments using 2 MeV He and 14 MeV Au ions were also performed. The results of the sequential beam irradiation on the BS3 glass have already been published in our earlier works [6][7] and some results are shown in Figure 6 (e-g) for the ISG glass. Like the studies on amorphous SiO₂ [45] and the BS3 glass, the evolution of the Raman spectra was studied as a function of the He fluence from 2×10^{15} to 1×10^{17} ions.cm⁻² and as a function of Au fluence from 4×10^{12} to 8×10^{13} ions.cm⁻². Also, many cases of sequential irradiation with He followed by Au irradiation (He+Au) and vice versa (Au+He) and, simultaneous irradiation with He and Au ions (dual) were studied. The results in Fig. 6 (e) are shown only for the cases where saturation damage state (or near saturation in the case of the Au irradiation) was obtained to highlight the differences between various irradiation scenarios. Unlike Xe and U,

He irradiation only induced mild changes (for instance, R-band shifted by about 14 cm^{-1} only) whereas Au irradiation, as in the case of Xe and U, induced the maximum evolution in the Raman spectra (R-band shifted by about 22 cm^{-1}). The changes in the Q_n bands due to He and Au ion irradiations are highlighted in Fig. 6 (f). These spectra show a large increase in the intensity on the higher frequency side of the Q_n region after Au irradiation (similar to what was observed in the case of the BS3 glass). Also, after Au irradiation, the BO_3 -region showed a more pronounced rightward shift and a large molecular oxygen peak (1552 cm^{-2}) was observed when compared to He irradiation. A comparison of the sequential and dual beam irradiation scenarios is given in Fig. 6 (g) showing visible intensity changes in the Q_n regions between the three scenarios. When comparing the case of $2 \times 10^{16}\text{He} + 4 \times 10^{13}\text{Au}$, the Raman spectra were shifted towards the case of Au irradiation (compare spectra 3 and 5 in Fig. 6 (e)) whereas an opposite trend was observed in the case of $4 \times 10^{13}\text{Au} + 2 \times 10^{16}\text{He}$ (compare spectra 2 and 4 in Fig. 6 (e)). Therefore, as observed in the case of the SiO_2 and BS3 glass in our earlier studies, the last irradiating ion essentially controls the nature of the final damage state. A comparison of these two sequential irradiations with simultaneous irradiation with He and Au ions (dual) shows that the dual-beam irradiation resulted in an intermediate damage state. These aspects of the sequential and simultaneous beam irradiation have been addressed in more detail in our earlier publication [45].

Irrespective of the magnitude of the change, some of the general irradiation-induced changes in the Raman spectra of ISG glass are listed below (the peak assignments/interpretations are the same as for the BS3 glass):

- I. The position of the R-band increased from about 473 cm^{-1} (pristine value) to about 500 cm^{-1} (saturation value) with increasing fluence of U, Xe and Au ions (shift by about 27 cm^{-1}). A maximum shift of 14 cm^{-1} only was observed during He irradiation.
- II. The Raman bands in the region from 590 cm^{-1} to 630 cm^{-1} with a prominent peak at 630 cm^{-1} in the pristine glass specimen were modified. The intensity of the peak near 595 cm^{-1} relative to the peak at 630 cm^{-1} increased as in the case of the BS3 glass.
- III. The shape of the Q_n region significantly changed. The intensity on the low-frequency side (990 cm^{-1}) of the band decreased whereas the intensity on the high-frequency side of the band (1060 cm^{-1}) increased.
- IV. The area/intensity of the band from 1300 cm^{-1} to 1600 cm^{-1} (BO_3 region) and its peak position increased with an increase in the fluence.
- V. Molecular oxygen (peak at 1552 cm^{-1}) was formed upon irradiation with heavy ions but no molecular oxygen was observed during He irradiation. Also, the molecular oxygen was destroyed during Au + He sequential irradiation and relatively smaller molecular oxygen peak was seen during the simultaneous ion beam irradiation (Fig. 6 (g)). The reasons behind the formation and disappearance of molecular oxygen during various irradiation scenarios are discussed elsewhere [45].

To conclude this section, the results of the single, sequential and simultaneous beam ion irradiation of the ISG glass essentially showed the same trends as observed in the case of the BS3 glass.

Figure 6: Raman spectra of the pristine and ion irradiated ISG glass. **(a)** Evolution of the Raman spectra as a function of the fluence (ions.cm⁻²) for 91.6 MeV Xe ion irradiation; **(b)** evolution of R-band position as a function of the fluence for 91.6 MeV Xe. The solid line shows direct impact damage model fitting; **(c)** evolution of the Raman spectra as a function of the fluence (ions.cm⁻²) for 109.5 MeV U ion irradiation; **(d)** evolution of the R-band position as a function of the fluence for 109.5 MeV U; **(e)** Raman spectra showing the effect of He, Au, He followed by Au (He + Au) and Au followed by He (Au + He) sequential ion irradiations; **(f)** Raman spectra to highlight the changes in the Q_n and BO₃ regions for He and Au ion irradiations and, **(g)** Raman spectra comparing the sequential and simultaneous beam irradiation scenarios.

3.1.3. SON68 glass

Unlike the BS3 and ISG glasses, where the various Raman peaks have been assigned based on the experimental studies of several simple glass compositions, the complexity of the SON68 glass does not allow a clear identification and assignment of the various peaks. Ion irradiation at best leads to some minor intensity changes in various regions of the non-polarized spectra and usually very little peak shifts are seen in the non-polarized spectra. Therefore, the common approach of following the peak shifts or intensities of some reasonably well-identified peaks as a function of the fluence is not as simple as it is for the simple glasses. Nonetheless, to explore the feasibility of using Raman spectroscopy to “at least” follow the irradiation induced-modifications in the SON68 glass, polarized Raman spectra (HH and HV) were also acquired. The irradiation-induced modifications could be more easily seen in the polarized spectra as compared to the non-polarized spectra. Therefore, we will first go into some of the details of the polarized spectra and then compare the irradiation-induced changes as seen in the polarized and non-polarized spectra.

The polarized and non-polarized spectra of the pristine SON68 glass are shown in Fig. 7 (a). The spectra in this figure are normalized to 1 using the maximum intensity in the spectrum and are vertically shifted for easier relative comparison. Note that the actual intensity in the HV spectra is significantly lower as compared to the HH and non-polarized spectra. The depolarization ratio, obtained by dividing the HV spectra by HH spectra, is shown in Fig. S3 in the SI. Some of the clearly visible peaks in the HH and HV spectra are labelled in Fig. 7 (a). A comparison with the simple glasses (BS3 and ISG) shows that the peaks such as 630 and 770 cm^{-1} seen in the HH spectrum (and very faint in the non-polarized spectra) are common in all the three glasses. Also, regions similar to the Q_n and BO_3 can be identified in the HH and non-polarized Raman spectra although the assignment of the various peaks to different Q_n units would be premature at this stage (they will be referred as Q_n -like and BO_3 -like hereafter). The HV spectra show a broad peak (950 cm^{-1}) in the Q_n -like region resulting in a convolution such that the two distinct humps seen in the HH spectra at 910 and 1060 cm^{-1} are no more clearly distinguishable in the non-polarized spectra (this peak from HV spectrum essentially fills the valley between the two humps in the HH spectra leading to a smoothening of the non-polarized spectrum). Similar merging of the peaks from the HH and HV spectra in the range from 320 to 480 cm^{-1} lead to only two major humps in the non-polarized spectrum with lower intensity for the second hump because of the very little contribution from the HV spectrum in this region.

The effect of 96.6 MeV Xe ion irradiation on the HV and HH Raman spectra are shown in Fig. 7 (b, c) respectively. In Fig. 7 (b), the intensity of the peaks at 320 and 950 cm^{-1} decreased with an increase in the fluence (the spectra are shown in the order of increasing fluence from 1 to 4). No major intensity changes were seen after around 8×10^{12} ions. cm^{-2} . On the other hand, the intensity of the peak at 710 cm^{-1} increased with fluence. Out of all the peaks, the peak at 320 cm^{-1} was affected the most; to the extent that it is visible only as a very weak feature at the end of the ion irradiation. Its area (with a linear or non-linear background fitting) could be potentially used to follow the irradiation-induced modifications. The inset-(I) in Fig. 7 (b) shows the ratio of the intensity of the peaks at 950 and 710 cm^{-1} as a function of the fluence. It changed from an initial value of about 13 to a saturation value of about 4 (saturation fluence = $2.6 \times 10^{12} \sim 3.5 \times 10^{20}$ keV. cm^{-3}) following a typical direct impact damage model (shown by the solid line). Figure 7 (c) shows the changes in the HV spectra as a function of the fluence. The intensity of the various peaks decreased and no changes were seen after around 8×10^{12} ions. cm^{-2} . The peak at 770 cm^{-1} was not observed after the irradiation. The inset-(I) shows the ratio of the intensity of the peaks at 910 and 1060 cm^{-1} which showed the same saturation behaviour as observed in the HV spectra. The intensity ratio changed from an initial value of about 2.86 to 1.88 at the end of the ion irradiation (saturation fluence = $3.8 \times 10^{12} \sim 5 \times 10^{20}$ keV. cm^{-3}). Therefore, the polarized spectra offer a viable way of following the irradiation-induced changes in the SON68 glass. A comparison of the He (2 MeV) and Xe ion irradiations (96.6 MeV) is given in Fig. 7 (d) (HV spectra) to highlight that these two ions lead to different damage states in excellent agreement with what was observed in the case of the BS3 and ISG glasses (lower intensity decrease in the case of the He irradiation). Finally, the irradiation-induced modifications as seen in the non-polarized Raman spectra are shown in Fig. 7 (e). Intensity modifications in agreement with the results of the HH and HV spectra can be seen although the changes are lesser. Note that the peaks in the 710 to 770 cm^{-1} were not seen after irradiation as also observed in the HH spectra. The inset-(I) shows the intensity ratio of the peaks at around 320 cm^{-1} and around 910 cm^{-1} which changed from an initial value of 1.33 to a saturation value of about 1.46. A magnified graph of the Q_n -like region is shown in Fig. 7 (f) to better visualize the irradiation-induced change in the intensity

of the peaks. The inset-(I) shows the change in the intensity ratio of the peaks as in Fig. 7 (c). However, the intensity ratio in this case only changed from an initial value of about 2.85 to 2.59 at the end of the ion irradiation (saturation fluence = 6×10^{12}). Also, note that the valley between the two humps as indicated by the arrow became more visible due to ion irradiation. This is potentially because of a significant decrease in the intensity of the peak at 950 cm^{-1} as seen in the HV spectra in Fig. 7 (b). These results highlight that polarized spectra show larger and more visible changes in the various peaks compared to the non-polarized spectra. Nonetheless, these results show that the intensity ratio of the peaks in the Q_n -like region or the low-frequency region of the non-polarized Raman spectra can be used to follow the irradiation-induced modifications. As discussed later, the saturation behaviour observed in the Raman spectra was also confirmed by the microhardness and the swelling data.

607

Figure 7: Polarized and non-polarized Raman spectra of the pristine and irradiated SON68 glass. (a) Polarized (HH and HV) and non-polarized Raman spectra of the SON68 glass. The various peaks are indicated in the figure and the spectra are vertically shifted to better see the various peaks; (b) the evolution of the HV spectra as a function of the Xe irradiation fluence (96.6 MeV). Inset-(I) shows the ratio of the intensity of the peaks at 950 and 710 cm^{-1} at various fluences; (c) the evolution of the HV spectra as a function of the fluence. The inset-(I) shows the ratio of the intensity of the peaks at 910 and 1060 cm^{-1} at various fluences; (d) a comparison of the HV spectra after irradiation with 2 MeV He and 96.6 MeV Xe; (e) non-polarized Raman spectra of the SON68 glass irradiated with 91.6 MeV Xe ions up to various fluences. The inset shows the intensity ratio of the peaks at around 320 and 910 cm^{-1} ; (f) a magnified graph showing the Q_n -like region from (e) to better see the intensity changes. The inset-(I) shows the ratio of the intensity of the peaks at 910 and 1060 cm^{-1} . The arrow indicates the valley between the two humps.

3.2. Vickers microhardness and indentation fracture resistance

The Vickers microhardness of the pristine and irradiated BS3, ISG and SON68 glasses was measured. The different ion irradiations and the loads which were used for this analysis are shown in Table-III. The data is aimed to cover various stopping power values such that we have a dominant electronic energy loss ($S_e \sim 15 \text{ keV.nm}^{-1}$ for 109.5 MeV U), medium electronic energy loss ($S_e \sim 7 \text{ keV.nm}^{-1}$ for 25.2 MeV ^{84}Kr), similar electronic and nuclear energy losses ($S_e \sim 3$, $S_n \sim 1 \text{ keV.nm}^{-1}$ for ^{197}Au), low electronic and nuclear energy losses ($S_e \sim 0.3$, $S_n \sim 3 \times 10^{-4} \text{ keV.nm}^{-1}$ for ^4He) and, dominant nuclear energy loss ($S_e \sim 0.4$, $S_n \sim 1.2 \text{ keV.nm}^{-1}$ for 400 keV ^{83}Kr). For the case of the 400 keV Kr irradiation, nanoindentation was employed. The results of the 25.2 MeV ^{84}Kr , 109.5 MeV U, 14 MeV Au and 2 MeV He irradiation on the hardness of the BS3 glass have already been published in our earlier work [7]. Similarly, the results of 25.2 MeV ^{84}Kr , 109.5 MeV U and 400 keV Kr irradiation on the hardness of the SON68 glass have also been published in our previous work [7]. The rest of the cases for these glasses and the data on the ISG are the new results presented here.

The microhardness was plotted as a function of the irradiation fluence and the results are shown in Fig. 8-10 for the BS3, SON68 and ISG glasses respectively. The lines show the fits of the direct impact damage model. In the case of the He irradiation, the hardness of the BS3, ISG and SON68 glasses decreased by about 18, 20 and 14 % respectively; indicating a slight composition dependence (as seen during electron irradiation [4]). For the rest of the cases, the hardness of all the three glass compositions decreased by about 35 % ($\pm 1 \%$) (by 30% in the case of 400 keV Kr irradiation).

Table-III: Ion irradiations and indentation loads used for BS3, ISG and SON68.

Glass type	Ion type	Indentation loads (gf)
BS3	^{84}Kr (25.2 MeV)	20, 50, 100, 200, 400
	^{238}U (109.5 MeV)	20, 200, 400
	^{136}Xe (96.6 MeV)	20
	^{197}Au (14 MeV)	20
	^4He (2 MeV/u)	20
SON68	^{84}Kr (0.3 MeV/u)	10, 20, 50, 70, 100, 200, 400
	^{238}U (109.5 MeV)	20, 200, 400
	^{136}Xe (60 MeV)	20
	^{197}Au (14 MeV)	20
	^4He (2 MeV)	20
	400 keV ^{83}Kr	Nanoindentation
ISG	^{84}Kr (25.2 MeV)	20
	^{238}U (109.5 MeV)	20
	^{136}Xe (60 MeV)	20

640 **Figure 8:** Effect of ion irradiation on the hardness of the BS3 glass. For the case of the U (109.5 MeV) and Kr (25.2 MeV), the indentation was performed with different loads to probe various depths. The insets in these two
 641 (25.2 MeV), the indentation was performed with different loads to probe various depths. The insets in these two
 642 cases highlight the behaviour at low fluences. For the rest of the cases, the indentation was performed with 20
 643 gf load only. The lines show the fits of direct impact damage model (in Hv-xx, xx shows the values of load in gf).

644 **Figure 9:** Effect of ion irradiation on the hardness of the SON68 glass. For the case of U (109.5MeV) and Kr (25.2
 645 MeV), the indentation was performed with different loads to probe various depths. For the rest of the cases, the
 646 indentation was performed with 20 gf load only. For Au (14 MeV), the indentation was only performed for the
 647 pristine and the specimen irradiated with 4×10^{13} Au.cm⁻². The lines show the fits of direct impact model except
 648 for the case of the Au (no line) and He (2 MeV, straight-line connects).
 649

650 **Figure 10:** Effect of ion irradiation on the hardness of the ISG glass. All the indentations were performed with a
 651 20 gf load. The lines show the fits of the direct impact damage model.
 652

653 By fitting the evolution of the hardness as a function of the fluence using direct impact damage model, ion track
 654 cross-sections were evaluated (for 20 gf data only). The ion track cross-sections are plotted as a function of the
 655 electronic energy loss in Fig. 11 (the average electronic energy loss values were calculated in a depth equal to
 656 twice the penetration depth of 20 gf indenter $\sim 2 \mu\text{m}$). The ion track thresholds were calculated by taking linear
 657 fits of the data in Fig. 9. Thresholds of 2.5, 3 and 2.4 keV.nm⁻¹ ($\pm 20\%$) for BS3, ISG and SON68 glasses were
 658 obtained. The results for the BS3 glass are in good agreement with the threshold derived from the Raman
 659 spectroscopy.

Figure 11: Determination of ion track threshold from micro-hardness. The thresholds are shown for the BS3, ISG and SON68 glasses. The x-axis shows a 10 % error on the stopping power values and the y-axis shows the errors on the cross-section obtained from least-square fitting of the data in Fig. 8 to 10.

In addition to the changes in the hardness, ion irradiation also had a significant effect on the fracture toughness of all the irradiated glasses as indicated by the Vickers indentation fracture method. The actual fracture toughness was not measured but rather the cracks generated after the Vickers indentation. This allows to calculate what is referred as indentation fracture resistance (K_{ifr}), which can be very close to the actual fracture toughness of the material but not necessarily always [46][47] (see Ref [46] for a critical evaluation of the various formulations used for the calculation of the fracture toughness (K_{Ic})/fracture resistance (K_{ifr}) and Ref [47] for the compatibility between the K_{Ic} and K_{ifr}). Furthermore, the irradiated specimens in our case are at least a bilayer system in terms of their mechanical properties because of the presence of shallow irradiated depth ($< 13 \mu\text{m}$ in most of the cases, constituting Layer-1) and the thick non-irradiated specimen lying underneath the irradiated region (layer-2). To avoid a strong influence of the non-irradiated region on the fracture properties, we will restrict our discussion to the case of the 109.5 MeV U ion irradiation where the irradiated depth is about $12.3 \mu\text{m}$ (BS3 glass). Also, we will limit our analysis to the case of $1.8 \times 10^{13} \text{ ions.cm}^{-2}$ where we know that the entire irradiated depth is fully damaged and therefore has uniform mechanical properties. The penetration depth of the indent in the pristine BS3 glass is about 1, 1.7, 2.4, 3.4, 4.2 and $4.9 \mu\text{m}$ for indentation loads of 0.196, 0.49, 0.98, 1.96, 2.94 and 3.92 N respectively, which in most of the cases (except the 3.92 N load) is at least one-third of the ion range. It is clear that although the indents and their plastic interaction zone remain confined to the irradiated layer, any cracks larger than the ion range (i.e. $> 12.3 \mu\text{m}$) will extend into the un-irradiated region thereby influencing their propagation and consequently the fracture behaviour we observe. Also, note that the c/a values (" c " is the length of the crack measured from the centre of the indent and " a " is half of the indent diagonal) listed in the table in Fig. 12 show that the cracks for loads $\geq 0.49 \text{ N}$ in the pristine BS3 glass are half-penny type ($c/a \geq 2$ for half-penny cracks) whereas the cracks in the irradiated BS3 glass have $c/a < 2$ for most of the loads (except for the 3.92 N) showing they are Palmqvist type ($c/a < 2$ for the Palmqvist type cracks). With these issues highlighted, we will now present the results on indentation induced fracture.

The images of the indents on the BS3 glass before and after irradiation with $1.8 \times 10^{13} \text{ U ions.cm}^{-2}$ (109.5 MeV) are shown in Fig. 12 (a) for the various indentation loads listed above. By just looking at the size of the cracks and the loads at which the cracks were first formed, one can readily confirm that ion irradiation suppressed the crack formation and increased the fracture resistance of the BS3 glass. In Fig. 12 (a), the first crack in the pristine glass was seen after an indentation load of about 0.196 N whereas for the irradiated glass the first crack was seen after an indentation load of about 1.96 N. To better present the formation of cracks, the average total crack length, obtained by summing the lengths of all the cracks measured from the outermost edge of the indent, is plotted in Fig. 12 (b). The inset highlights the crack sizes at low loads (up to 0.98 N). This figure clearly shows that the average total length of the cracks in the pristine BS3 is always larger and follows a near-linear dependence on the load. For the irradiated BS3, very small cracks were observed only after 0.98 N and with further increasing the load, the size of the cracks increased as in the case of the pristine BS3 but rather slowly. At 0.98 N, the ratio of the total crack length in the irradiated and the pristine BS3 was only about 0.11

which then increased to 0.55 for an indentation load of 3.92 N. This shows that at higher loads, the cracks in the pristine and in the irradiated BS3 tend to approach each other because of the diminishing role of the thin irradiated layer at high loads. The fraction of the indents in which 1 and 4 cracks were observed in the pristine and the irradiated BS3 are shown in Fig. 12 (c). It shows that at 0.98 N, about 25 % of the indents showed at least 1 crack whereas no indent showed four cracks in the irradiated BS3. On the other hand, 75 % of the indents showed at least 1 crack and no indent showed four cracks at this load in the pristine material. Figures 12 (b) and (c) together show that the total crack length increased firstly because the average number of the cracks increased and secondly because the size of each crack increased with the indentation load (as can be visually seen in Fig. 12 (a)). The indentation fracture resistance was calculated using Miyoshi's equation shown below (equation 10 in [46])

$$K_{ifr} = 0.018 \left(E/H_v \right)^{0.5} \left(P/c^{1.5} \right) \quad (1)$$

Where, K_{ifr} is the indentation fracture resistance (in Pa. $\sqrt{m}$), E is the Youngs modulus (in GPa ~ 82 GPa), H_v is the Vickers hardness (in GPa ~ 6.5), P is the indentation load (in N) and c is the crack length measured from the centre of the indent to the tip of the crack (in m). Taking the E and H_v of the pristine BS3 glass as 82 GPa [48] and 6.5 GPa [7] respectively and, considering 15 to 30 % drop in the Youngs modulus [11,14,49,50] and about 35 % drop in the hardness [7] due to heavy ion irradiation as shown by earlier studies, the fracture resistance of the pristine and irradiated BS3 glass is about 1.1 and, 2.8 to 3.1 MPa. $\sqrt{m}$ respectively (at 3.92 N). Using Anistis equation [47][46], the K_{ifr} values were about 3 % smaller compared to Miyoshi's equation but the relative changes between the pristine and the irradiated were the same. In any case, these results show that ion irradiation increased the fracture resistance of the BS3 glass by about 140 to 166 %. Taking the ratio H_v/K_{ifr} as a measure of the brittleness [11], the brittleness dropped from around 6 to 1.8 $\mu\text{m}^{-0.5}$. Thus, heavy-ion irradiated glasses have a lower hardness (by about 35 %), higher fracture toughness (by about 166 %) and lower brittleness (by about 70 %). All these changes represent some of the positive aspects of radiation damage.

Figure 12: Optical microscopy images and analysis of the indents at various loads on a BS3 glass before and after irradiation with 1.8×10^{13} U ions. (a) Optical microscopy images of the indents at various loads for the pristine (top row) and irradiated glass (bottom row); (b) average total crack length vs indentation load and, (c) the fraction of the indents with 1 and 4 cracks at various loads for the pristine and the irradiated glass. The table shows the c/a ratio; where c is the crack length and a is the indent half diagonal.

3.3. Step-height measurements and swelling

Prior to ion irradiation, all the specimens had been polished and annealed to obtain a high surface finish (surface roughness $\leq 1\text{ nm}$) thereby allowing step-height measurements as small as 10 -15 nm. Typical line scans on a BS3 specimen irradiated with 109.5 MeV U ions to various fluences are shown in Fig. 13. The step-height measurements on the BS3 glass irradiated with various ions are shown in Fig.14 (a). The inset highlights the low fluence region to better visualize the tendency to saturation. The lines are fits of the direct impact damage model. The step-height grew linearly with the ion fluence and then tended to saturate at higher fluences. Since the step-height (swelling) is a result of the cumulative damage along the ion path, the maximum step-height is proportional to the projected ion range (or energy of the ions) as evident from Fig. 14 (a) (the higher the ion range, the larger the step-height). The swelling was calculated by dividing the step-height by the projected ion range (swelling = $\frac{h_{max}}{R}$, where h_{max} is the maximum step-height and R is the projected ion range as shown in Table II). The swelling is shown in Fig. 14 (b-d) for the BS3, ISG and SON68 glasses respectively. No swelling was observed in the case of 135 MeV O and 12 MeV carbon ion irradiations within the studied fluence range. This is consistent with the results of the Raman spectroscopy where no measurable changes were seen in the Raman spectra in these two cases.

Figure 13: Surface profilometry scans on the BS3 glass specimen irradiated with 109.5 MeV U ions up to 2×10^{12} (blue), 7×10^{12} (black) and 1.7×10^{13} (red) ions.cm⁻².

Figure 14: Step-height measurements and swelling of the BS3, ISG and SON68 glasses irradiated with various ions. **(a)** Step-height measurements on the BS3 glass irradiated with various ions to different fluences. The inset shows the low fluence data to highlight the saturation behavior. The error bars show a standard deviation of three measurements. The numerals in the brackets in the figure legend are specific ion energies in MeV/u (also shown in column-II in Table-I), **(b)** swelling of the BS3 glass calculated by dividing the step-height by the projected ion range, **(c, d)** swelling of the ISG and SON68 glasses respectively calculated by the same way as for the BS3 glass. The insets highlight the low fluence data to show the saturation behavior.

The swelling obtained for various ion irradiations is shown in Fig.15 for all the three glasses. Taking into consideration all the ion irradiations, an average saturation swelling of 2.8 ± 0.07 %, 1.3 ± 0.05 % and 1.5 ± 0.07 % was obtained for the BS3, ISG and SON68 respectively (the errors are standard errors of the mean). These results show that the ISG glass is a good simulant for the SON68 glass swelling and that the overall swelling of the waste glass should not exceed 1.5 %.

Figure 15: Saturation swelling values for the BS3, ISG and SON68 glasses. The swelling was calculated by dividing the saturation step-height by the projected ion range.

It is important to highlight that the confocal Raman spectroscopy and microhardness measurements at low loads essentially probe the changes occurring near the surface region whereas swelling is a global phenomenon with contribution coming from the entire ion path. Therefore, nuclear collisions form an integral part of the swelling. The contribution of nuclear collisions for high energy ions is however relatively small because a majority of the ion path is dominated by electronic collisions. Nonetheless, because the swelling is a cumulative effect of the ion damage along the entire ion path with inherent contribution from nuclear collisions, a precise determination of ion track threshold from swelling is complex involving deconvolution of these two energy loss contributions. For the sake of brevity, these issues are discussed in full detail elsewhere [44] and briefly in the current article.

The cross-sections obtained by fitting the swelling data (Fig. 14) with direct impact damage model reflects the average ion track cross-section along the ion path. Also, the rate of increase in the step-height as a function of the ion fluence (slope of the curves in Fig. 14) and the maximum step-height step are both proportional to ion range. The maximum step height is however independent of the ion track cross-section but it affects the rate with which the saturation is attained. Thus, when comparing the step-height data from different ions, the relevant quantity to compare is the product of the normalized step-height (swelling), and the damage cross-section (σ). A detailed mathematical description leading to this conclusion is given elsewhere [44]. Figure 16 shows this plot as a function of the average energy loss along the ion path for all the three glasses. Ion track thresholds of 2.4 ± 1 , 2 ± 0.8 and 1.4 ± 0.5 keV.nm⁻¹ were obtained. Note that $\frac{h_{max}}{R}$ is the swelling and σ is the ion track cross-section.

Figure 16: Ion track thresholds of the BS3, ISG and SON68 glasses from step-height measurements. The y-axis shows the product of swelling ($\frac{h_{max}}{R}$) and damage cross-section (σ) and the x-axis shows the average stopping power. The lines are linear fits to the data.

The fraction of the ion path along the specimen depth that experiences energy loss less than the ion track threshold does not have a significant contribution towards the swelling through electronic collisions. Therefore, the actual ion range (R_a ; which is the range up to $S_e < \text{ion track threshold}$) that contributes towards swelling through ATEC is less than the projected ion range R . Without any other information about the threshold, this leads to an iterative procedure wherein the value of R on the Y-axis in Fig. 16 needs to be updated to R_a to estimate the ion track threshold. Furthermore, the fraction of the ion path experiencing BTEC will contribute to swelling mainly through nuclear collisions. The swelling contribution (step-height contribution) from this region, therefore, needs to be deconvoluted from the total step-height. A detailed mathematical description of both these corrections is beyond the scope and the aim of this article and is presented elsewhere [44]. The final ion track thresholds obtained after these two corrections are $3.5 \pm 0.7 \text{ keV.nm}^{-1}$ for the BS3 and ISG glasses and $2.8 \pm 0.5 \text{ keV.nm}^{-1}$ for the SON68 glass.

3.4. AFM measurements of ion tracks

The specimens of the BS3 glass were irradiated with 109.5 MeV U ions and the irradiated surfaces were analyzed using AFM to probe the ion tracks on the specimen surface. The AFM revealed the formation of surface hillocks at the location of the ion impacts as shown in Fig. 17 (a). The height of the hillocks was usually less than 2 nm and the diameter of the hillocks was in reasonable agreement with the damage cross-section obtained from Raman spectroscopy. This has been discussed in more detail in our earlier work [7]. AFM was also performed on specimens irradiated with 14 MeV Au ions but no ion impacts were detected in this case.

To probe the individual ion tracks formed due to swift heavy ion irradiation, thin specimens were irradiated with low ion fluences to only have isolated ion tracks for the small-angle x-ray scattering (SAXS) measurements. The SAXS measurements were performed on the BS3 specimens irradiated with ^{132}Xe ions (343 and 92.4 MeV) and 780 MeV ^{78}Kr ions. Experiments were also performed on the SON68 and ISG specimens irradiated with 780 MeV Kr ions. Ion tracks were observed in all these cases. This is an ongoing work currently looking into the morphology of the individual ion tracks and will be published separately.

Figure 17: AFM image of ion tracks on the surface of the BS3 glass irradiated with 109 MeV U ions up to $7 \times 10^{10} \text{ ions.cm}^{-2}$.

3.5. Thermal annealing of defects (annealing of step-height)

There is essentially no data published on the annealing of ion irradiation-induced defects in surrogate French nuclear waste glasses. However, several studies on defect annealing in a-SiO₂ indicate that temperatures at least in the range of 200 to 300 °C are usually required to observe defect annealing (e.g. a decrease in E' and ODC defect centres [51], stress relaxation [52], changes in IR spectra [53]) in a reasonable time (~hours)). Studies on He irradiated borosilicate glasses indicate that temperatures greater than 200 °C are required for the annealing of peroxy radicals [40]. Similarly, some limited annealing studies on actinide doped nuclear waste glasses [54] show that temperatures higher than 180 °C are needed to observe defect annealing effects in a reasonable time (e.g. studies reported in ref [54] show a density recovery of about 20 % after 100 hours of annealing at 180 °C).

With these results in mind, some preliminary annealing tests as reported below were conducted on the BS3 glass specimens to gauge the time and temperature scales necessary to observe measurable annealing effects. Two specimens of the BS3 glass irradiated with 96.6 MeV Xe ions up to 10^{13} (specimen-1; initial step-height ~ 167 nm) and 10^{14} Xe.cm $^{-2}$ (specimen-2; initial step-height ~ 325 nm) were annealed under isochronal and isothermal annealing conditions as shown in Fig. 18 (a)-(b) respectively. The isochronal experiments were performed for a time period of 40 minutes and the isothermal experiments were performed at a temperature of 300 °C. After annealing for 40 minutes at 200 °C, the step-height decreased by about 2 % only (~ 6 nm decrease in the step-height) for specimen-2. No measurable change was observed in specimen-1. This is plausible because a 2 % decrease as indicated by specimen-2 would correspond to only 3 nm step-height decrease for specimen-1, which is difficult to measure. At 300 °C, the step-height decreased by about 14 % and 20 % for the specimen-1 and specimen-2 respectively after 40 minutes of annealing (Fig. 18 (a)). At 590 °C ($T_g = 595$ °C), the step-height on the specimen-2 was reduced to less than 5 nm after 40 minutes which we assume to be a complete recovery (specimen-1 was lost). On the other hand, isothermal annealing for up to 6 hours at 300 °C resulted in a step-height recovery of about 33 % only (Fig. 18 (b)) (the lines are exponential fits to the data).

Figure 18: Annealing of the BS3 glass specimens irradiated with 96.6 MeV Xe ions up to 10^{13} and 10^{14} ions.cm $^{-2}$. **(a)** Effect of isochronal annealing on the step-height as a function of the annealing temperature ($t_{\text{isochronal}} = 40$ minutes), **(b)** effect of isothermal annealing on the step-height ($T_{\text{isothermal}} = 300$ °C).

4. Discussion

4.1. The importance of ion track threshold (Differences between BTEC and ATEC regimes)

The ion track thresholds of the BS3, ISG and SON68 glasses were obtained from the Raman spectroscopy, swelling and microhardness. The thresholds obtained from all the three characterizations are shown in Table IV and are in good agreement with each other. The values range from 2 to 3 keV.nm $^{-1}$ and do not show a significant compositional dependence. The ion track threshold of a-SiO $_2$ is known to be between 2 to 2.5 keV.nm $^{-1}$ [55][56]. Therefore, it is plausible to propose that the ion track thresholds of simple and complex inorganic oxide glasses are expected to be in this range and nuclear waste glasses and their surrogates used around the world should have ion track thresholds in the range of 2 to 3 keV.nm $^{-1}$.

The electronic energy loss of 4 MeV alpha particles is less than 0.2 keV.nm $^{-1}$ and are therefore unable to form any ion tracks by themselves in nuclear waste glasses. The maximum energy these alpha particles can transfer to the target atoms ranges from 2.5 MeV for O to 1.8 MeV for Si (and lesser for other heavier target atoms). The maximum electronic energy loss of O and Si knock-on's is mostly < 2 keV.nm $^{-1}$ which is just below the ion track threshold. On the other hand, the electronic energy loss of heavy alpha recoils is less than 0.6 keV.nm $^{-1}$ (for 120 keV U recoil) and the target knock-on's (O and Si) have electronic energy loss less than 0.2 keV.nm $^{-1}$. Therefore, alpha particles, heavy recoils and, any target knock-on's resulting from the collisions of alpha particles and recoil nuclei cannot create any ion tracks in nuclear waste glasses through their electronic energy loss. The case of fission fragments resulting from spontaneous fissions of elements such as ^{252}Cf will be discussed in section 4.6.

As above threshold electronic collisions (ATEC) and nuclear collisions induced the highest damage state (and same), external single beam swift heavy ion irradiations provide the maximum limit of the damage that can be expected in nuclear waste matrices (the alpha-induced healing effects are ignored in this case). As far as the study of structural and mechanical aspects of waste matrices are concerned, swift heavy ions provide a convenient way to reproduce the maximum possible damage from nuclear collisions and therefore offer a way of simulating the safety case for the most damaging scenario of the waste matrices. However, for studying the chemical aspects such as leaching, one must be very careful in choosing the external ion energy. Formation of ion tracks due to swift heavy ions can potentially lead to a preferential release of radioelements from the ion tracks. Leaching experiments on such specimens may thus overestimate the radioisotope release. Nonetheless, from a safety perspective, leaching experiments on swift heavy ion irradiated specimens may be regarded as an upper limit to radioisotope release from nuclear waste matrices and are thus very relevant for such type of studies.

Also, the results showed that ion track threshold acts as a very robust indicator of differentiating the ion irradiation effects into at least two categories in terms of the maximum property change and the amount of the energy deposition it takes to induce these property changes. ATEC on average required doses in the range of 3×10^{20} (4.3 eV/atom) to 5×10^{20} keV.cm⁻³ (7 eV/atom) to induce saturation in the measured modifications (more discussion on the saturation dose is given in section 4.5). The maximum modifications induced by the below threshold electronic collisions (BTEC) on the other hand were only about 30 to 50 % of the modifications due to ATEC. These results clearly show that ion track threshold demarcates the strength of electronic energy loss effects and provides a quantitative way of referring to “high” (ATEC) and “low” (BTEC) electronic energy loss. Although the mechanism of energy loss in both cases involves electronic excitation and ionization, the end result is significantly different depending on the magnitude of the electronic energy deposition. Furthermore, in light of the results available so far, the study showed that the changes due to ATEC and nuclear collisions are the same, both, in terms of the maximum property changes and the energy deposition needed to induce such changes.

In stark contrast to the ATEC, an interesting and important aspect of the BTEC is their ability to induce partial defect healing and reversal of some of the changes induced by the ATEC/nuclear collisions during sequential ion irradiations. Thus, the response of the glasses not only depends on the magnitude of the electronic energy loss but also on the pre-existing defect concentration. Furthermore, a comparison of the BTEC and high-energy electron irradiations showed a very close agreement between these two in terms of the structural modifications and the changes in the mechanical properties. This is despite the difference of 3 to 4 orders of magnitude in the electronic energy losses during these two processes ($\sim 10^{-3}$ to 10^{-4} keV.nm⁻¹ by electrons and < 2 keV.nm⁻¹ during BTEC).

The major difference between the ATEC and BTEC lies in the fact that local melting in ion tracks to high temperatures (e.g. temperatures > 3000 K are reached during 14 MeV Au ion irradiation of SiO₂ [45]) and subsequent fast quenching of the molten phase results in freezing a highly disordered glass structure during the ATEC. This effect is absent during the BTEC where ionization effects without any local melting dominate. Nonetheless, non-melting thermal spikes can be induced during the BTEC. It has been shown in our earlier work that He irradiation of the Au pre-damaged a-SiO₂ can lead to ionization of molecular oxygen (which itself was created during Au irradiation) and non-melting thermal spikes accompanying the He impact help induce diffusion of oxygen atoms which on recombination with the defects leads to partial defect healing.

Table-IV: Ion track thresholds of the BS3, ISG and SON68 glasses evaluated from swelling, microhardness and Raman spectroscopy.

Specimen	Ion track thresholds (keV.nm ⁻¹)		
	Swelling	Micro-hardness	Raman spectroscopy
BS3	3.5 ± 0.7	2.5 ± 0.5	2 ± 0.7
ISG	3.5 ± 0.7	3 ± 0.6	

4.2. Morphology of ion tracks

The stopping power curves in Fig. 4 (c) show that the electronic energy loss (or the total energy loss) decreases as a function of the specimen depth. As ion track cross-section depends on the magnitude of the electronic energy loss, it follows a similar trend as a function of the depth as shown in Fig. 4 (b). This suggests that the ion tracks in the studied energy range have a conical shape as a function of the energy loss until the energy loss falls below the ion track threshold. Due to a higher cross-section of these conical tracks near the surface, regions closer to the surface are damaged faster and reach the saturation state whereas the regions far from the surface require higher fluences to attain the damage saturation. This is reflected as a higher degree of increase in the R-band position at a given fluence near the surface. This is also the reason why swelling requires higher fluences to saturate because it is influenced by the entire ion path. When ion tracks are reasonably well separated from each other at low fluences, the depth dependence of the R-band position directly reflects the conical shape of the ion tracks (e.g. as seen in the blue curve in Fig. 4 (a)). Thus, it is possible to obtain a reasonable estimate of the ion track morphology directly from the low fluence data provided the track overlap is avoided. At higher fluences, the ion tracks start to overlap and this leads to a progressive consumption of the any left out pristine material. After this, the R-band position itself cannot directly reflect the conical shape of the ion tracks. Once the ion tracks start to overlap, the correct morphology can be obtained using the direct impact damage model if full damage saturation is achieved along the ion path. It is worth highlighting that the depth dependence of the ion track morphology derived from Raman spectroscopy could in principle be employed to correctly deconvoluting the depth-dependent ion track cross-sections obtained from SAXS by incorporating the degree of depth variation reflected in the cross-sections derived from the Raman spectroscopy.

4.3. The similarity between the ATEC and Nuclear collisions

During the ATEC, the energy is lost in the form of electronic excitation and ionization whereas energy is directly transferred to the target atoms during nuclear collisions. Direct energy transfer to target atoms displaces them from their equilibrium positions which after multiple collisions with other target atoms come to rest. The displacement and motion of the target atoms is akin to a thermal effect which leads to an increase in the frequency and magnitude of the atomic vibrations and eventually to melting if the material is heated to high enough temperature. The velocity or energy distribution of the target atoms during nuclear collisions can be alternatively presented as a temperature distribution as done during a normal thermal heating scenario. The two are related through Boltzmann's constant as given below:

$$E = (K_B \times T) \text{ or } T = 11628 \times E(\text{eV}) \quad (1)$$

Where $E(\text{eV})$ is the kinetic energy of the target atoms in eV, K_B is the Boltzmann's constant ($8.6 \times 10^{-5} \text{ eV.K}^{-1}$) and T is the temperature in Kelvin. As the energy is transferred to primary knock-on atoms, they rapidly lose it to the surrounding target atoms and slow down. For instance, a 100 keV ^{238}U recoil atom can transfer average energy of about 1.5 keV and 1.2 keV to Si and O target atoms respectively. The projected range (R) of the 100 keV ^{238}U is about 40 nm and that of the 1.5 keV Si atoms is about 3.7 nm (r). If one assumes that the Si recoils are ejected perpendicular to the ^{238}U trajectory (for the maximum range), then one can roughly assume a cylinder of height R and radius r (volume = $\pi r^2 R = 1700 \text{ nm}^3$) in which the energy of the ^{238}U recoil is deposited. Furthermore, SRIM calculations show that only about 60 % of the energy is lost in nuclear collisions. With a typical target atomic density of $7 \times 10^{22} \text{ atoms.cm}^{-3}$, the cylindrical volume will contain about 1.2×10^5 target atoms. Distributing the 60 keV energy evenly among these atoms leads to an average energy of about 0.5 eV per atom. From equation (1), it translates into a temperature spike of about 5800 K. Similar analysis for the O atoms shows a temperature spike of about 4500 K. Nonetheless, such temperature spikes are strong enough to cause a rapid thermal spike and local melting of the material (ballistic melting) [57]. Also, a 100 keV ^{240}U recoil will stop after about $t = \frac{d}{v} = \frac{R}{\sqrt{2.E/M}}$ seconds, where R is the distance travelled by the recoil nucleus (40 nm) and M is the mass of ^{238}U recoil. Assuming continuous slowdown, it gives a time period of about 4 ps. Therefore, the high-temperature spike along the projectile path is induced very rapidly and upon rapid thermal equilibration with the surrounding matrix, a defective state is frozen.

This is very similar to inelastic thermal spike modelling of electronic energy losses wherein the energy transferred to electrons through inelastic collisions is returned to lattice through the electron-phonon coupling. The strength of the electron-phonon coupling determines the amount of the energy transferred back to the lattice. In this case, the atoms receive the energy indirectly via phonons rather than directly through atomic collisions as in the case of the nuclear collisions. This energy transfer through phonons causes the lattice to heat and if sufficient energy is deposited through electronic collisions and returned to the lattice, local melting can take place. A detailed description of extending the thermal spike calculations to nuclear waste surrogate glasses is given elsewhere [44]. Therefore, even though nuclear collisions and ATEC are fundamentally different processes, both of them can lead to local melting. The similarity between nuclear collisions and ATEC is only from the perspective of thermal spikes. It is the cooling and relaxation history of the melt phase that defines the final damage state and the results so far indicate that the final state does not depend on how the melt phase was attained. Any history of how the melt phase was created is potentially lost in the final state and only the relaxation history controls the end result. Thus, it is not surprising why the ATEC and nuclear collisions lead to a similar result. The inability of the BTEC, on the other hand, to cause any local melting makes the damage state very different resembling more closely to pure electronic excitations as observed during electron irradiations. It is important to highlight that the electronic energy losses during BTEC are usually 3 to 4 orders of magnitude higher than the electronic energy losses by electrons but there is no strong evidence yet that the damage states during these two scenarios are significantly different from each other.

4.4. Defect healing by BTEC (athermal defect annealing)

From multiple studies involving irradiation with two beams, it is now reasonably well understood that electronic energy losses in certain materials can lead to defect annealing referred to as “athermal annealing”. We have simulated and discussed this in detail for the case of the He irradiation of pre-damaged amorphous-SiO₂ in our previous work [45] and also published some results on athermal annealing in the BS3[6][7] and SON68 [7] glasses. At least from the sequential ion irradiation studies on a-SiO₂, it is understood that defect healing is a result of He induced ionization of molecular oxygen (already created due to heavy ion irradiation) into atomic oxygen and its subsequent diffusion — leading to a re-integration of oxygen atoms into the damaged network which causes partial defect healing. The diffusion itself is aided by non-melting thermal spikes accompanying the He impact. Subsequently, we undertook studies (and some are underway) to explore in more detail the effect of the magnitude of the electronic energy loss on the degree of healing. Unfortunately, such studies are still scarce and at least in its current state are not to our satisfaction. Nonetheless, we will discuss the results of three different sequential irradiation scenarios we have studied so far to express our current understanding of the role of the electronic energy loss value on the defect healing processes.

The specimens of the BS3 glass were first irradiated with heavy ions where either nuclear collisions (14 MeV Au) or ATEC (96.6 MeV Xe) dominated the energy loss mechanism. These pre-irradiated specimens were subsequently irradiated with light ions with different electronic energy losses. Figure 19 shows a contour map of the electronic energy loss (keV.nm⁻¹) as a function of the projectile energy and projectile atomic number. The horizontal dotted line indicates the ion track threshold on this map and the spots marked 1-3 indicate the three different ions used for the sequential ion irradiations. The studies were aimed at selecting the second ion type from both sides of the ion track threshold to understand what happens to athermal defect healing when the ion track threshold is surpassed. Labels 1-3 correspond to ⁵⁸Ni (17.4 MeV, S_e ~ 6 keV.nm⁻¹), ¹²C (12 MeV, S_e ~ 1.4 keV.nm⁻¹) and ⁴He (2 MeV, S_e ~ 0.3 keV.nm⁻¹) ions respectively. Note that the Ni ions undergo ATEC whereas the He and C ions undergo dominant BTEC.

Figure 19: Electronic energy loss contour map as a function of the projectile Z and projectile energy (MeV). The colour bar units are in keV.nm⁻¹. The horizontal dashed line indicates the ion track threshold which demarcates the ATEC and the BTEC. The numbers 1-3 indicate the energy and Z of the ions used for the sequential ion irradiations to study athermal defect healing.

In the case of the He sequential irradiation, the BS3 specimens were first irradiated with 14 MeV Au ions and some of the results from this study showing athermal defect annealing have been already published elsewhere [6][7][45]. In the case of the C sequential irradiation, the specimen was first irradiated with 96.6 MeV Xe ions up to 4×10^{13} ions.cm⁻² to induce a saturation damage state and then with 12 MeV ¹²C ions up to 8×10^{13} ions.cm⁻². Unlike the case of the He where fluences as high as 1×10^{17} ions.cm⁻² were used, only one fluence was studied in the case of the C irradiation. Raman spectroscopy and swelling measurements both indicated a defect healing taking place as shown in Fig. 20 (a, b). Figure 20 (a) shows a decrease in the step-height by about 12 % (~ 47 nm decrease) following the irradiation with C ions. The Raman spectra of the BS3 glass are shown in Fig. 20 (b). The region near 600 cm⁻¹ shows a decrease in the intensity tending towards a less damaged glass structure after C irradiation. For a comparison, the spectra of a 25 MeV Kr irradiated BS3 glass are shown in Fig. 20 (c) for various fluences. The intensity near 600 cm⁻¹ can be seen to progressively increase as a function of the fluence. In fact, the spectrum after irradiation with 7×10^{12} Kr.cm⁻² resembles very closely with the 4×10^{13} Xe + 8×10^{13} C spectrum shown in Fig. 20 (b) whereas for higher Kr fluences the specimen is fully damaged, resembling with 4×10^{13} Xe spectrum shown in Fig. 20 (b). To see a measurable change in the R-band position, a damage fraction change of about 15 to 20 % is usually needed (this is because the R-band shifts by about 12 cm⁻¹ and 15 to 20 % of this gives a measurable shift in the peak position). The degree of the recovery induced by the C ions is however just below this and it explains why changes in other Raman peaks are difficult to see.

Figure 20: Step-height measurements and Raman spectra of the BS3 glass. (a) Step-height measurements after irradiation with 96.6 MeV Xe ions up to 4×10^{13} Xe.cm⁻² and then with 12 MeV C ions up to 8×10^{13} C ions, (b) Raman spectra of the pristine, Xe, C and, Xe+C irradiated BS3 specimen. The inset highlights the region near 600 cm⁻¹, (c) Raman spectra highlighting the 600 cm⁻¹ region of the BS3 specimens irradiated with 25 MeV Kr ions to various fluences (see text for details).

For the case of the Ni irradiation (the case of ATEC), the specimen was first irradiated with 96.6 MeV Xe ions up to 4×10^{13} ions.cm⁻² (as in the case of the C) and then with 17.4 MeV Ni ions up to 3×10^{13} Ni.cm⁻² as per the methodology shown in Fig. 21 (a, b). The step-height measurements did not show any measurable changes between Xe and Xe + Ni irradiated regions whereas Ni irradiation of the pristine BS3 resulted in a step-height of 112 nm (~ 1.6 % swelling). A section of a 3D interferometry image is shown in Fig. 21 (c) showing the steps between different regions. Unlike He and C sequential irradiations, Ni irradiation had no impact on the Xe pre-irradiated region. These results show that ATEC (note that S_e for Ni ~ 6 keV.nm⁻¹) do not cause any damage healing unlike the BTEC.

Nonetheless, any systematic studies exploring in detail the recovery as a function of the fluence and electronic energy loss are still lacking. Such type of studies would be of interest in the future (irradiation with oxygen ions of 4 MeV are already planned at the moment). It would be interesting to explore if the degree of recovery depends on the magnitude of the electronic energy loss for BTEC. Such a hypothesis is plausible because if non-melting thermal spikes play a role in defect recovery, then their magnitude can be changed by increasing the electronic energy loss of the ions which may lead to faster defect diffusion and efficient defect annealing.

Figure 21: Schematics of Xe and Ni irradiation of the BS3 glass and a 3D-interferometry image taken after the ion irradiations. **(a)** A part of the specimen was masked with Al foil before Xe irradiation; **(b)** the mask was then rotated by 90° and the specimen was irradiated with Ni ions, **(c)** a 3D interferometry image taken after Xe and Ni ion irradiations. The steps can be seen between; pristine and Ni irradiated regions, pristine and Xe irradiated regions, Ni and Xe+Ni irradiated regions. No measurable step was seen between Xe and Xe+Ni irradiated regions.

4.5. Thermal annealing of defects (step-height annealing)

Annealing experiments on the thermal recovery of irradiation-induced tracks in glasses [58] and experiments on the recovery of alpha tracks in polymer detectors [59] have shown that the thermal recovery processes in these materials can be described by simple exponential models. In line with these models, the data in Fig. 18 was fitted with an exponential equation of the form

$$\frac{H(t)}{H_0} = A + B \cdot \exp^{-\alpha(T) \cdot t} \quad (1)$$

Where H_0 and $H(t)$ represent the initial step-height and the step-height after annealing for time 't', $\alpha(T)$ is the annealing coefficient and A and B are constants. If it is assumed that the recovery is induced by a single diffusion process, then the annealing coefficient is given by

$$\alpha(T) = \alpha_0 \cdot \exp^{-E_a/k \cdot T} \quad (2)$$

Where, α_0 is the annealing constant, E_a is the activation energy, k is the Boltzmann's constant (8.6×10^{-5} eV.K⁻¹) and T is the annealing temperature in Kelvin. Using equation (2) in equation (1) and taking logarithmic on both sides, one can write

$$\ln\left(-\ln\left(\frac{H(t)}{H_0}\right)\right) = c - \frac{E_a}{k.T} ; \text{ Where, } c = \ln(\alpha_0) + \ln(t) + \ln A + \ln(B) \quad (3)$$

One can plot the left-hand side of equation (3) against $1/T$ with the slope of the line being equal to E_a/k . The graph for the data in Fig. 18 for specimen-2 is shown in Fig. 22 yielding activation energy of 0.47 eV for the recovery of swelling in the BS3 glass.

Figure 22: Data based on the annealing of step-height of the BS3 glass irradiated with 96.6 MeV Xe ions up to 10^{14} Xe.cm⁻². The y-axis shows the left-hand-side of equation-3. The activation energy (as given by the slope) is equal to 0.47 eV.

In addition to the approach taken above to evaluate the activation energy, one can combine the isothermal and isochronal data shown in Fig. 18 for specimen-2 to evaluate the activation energy using equation (4) [60]

$$\ln\left(\frac{\Delta t_{it}}{\Delta t_{ic}}\right) = \frac{E_a}{k} \cdot \left(\frac{1}{T_{it}} - \frac{1}{T_{ic}}\right) \quad (4)$$

Where Δt_{it} is the time interval during which in isothermal annealing performed at a temperature T_{it} the same amount of defect recovery is obtained as during isochronal annealing performed at a temperature T_{ic} for an isochronal time period of Δt_{ic} . Unfortunately, the data between 300 °C to 590 °C in Fig. 18 is not available and would have been excellent for this type of analysis. Most of the data available in the literature on defect annealing in a-SiO₂ show that the defect recovery as a function of the temperature follows an exponential form (Arrhenius equation) at high temperatures. This would be expected in our case for temperatures higher than 300 °C. Nonetheless, to get an upper estimation of the activation energy, we assume a linear equation between the data point at 300 °C and at 590 °C (which will lead to an underestimation of the rate of recovery) and for a 30 % recovery in the step-height (~100 nm decrease in the step-height; $\Delta t_{it} = 205$ minutes, $\Delta t_{ic} = 40$ minutes, $T_{it} = 300$ °C, $T_{ic} = 342$ °C), we obtained activation energy of 1 eV. This only represents an upper limit and indicates that the activation energy of 0.47 eV evaluated using equation (3) is very reliable. This is very close to the activation energy for self-diffusion of oxygen atoms in soda-lime silicate glasses (~0.4 eV) [61].

Some work on isochronal annealing of defects in gamma-irradiated borosilicate glasses has been presented by Griscom (using EPR) [40]. Although he has presented data on the annealing of boron oxygen hole centres (BOHC), non-bridging oxygen hole centres (NBOHC) and peroxy-radicals, no estimates of defect activation energy were presented in his work. Using the approach presented in equation (3), defect activation energies for BOHC and peroxy-radicals in Griscom's gamma-irradiated specimens were evaluated giving values of 0.27 and 0.42 eV for BOHC and peroxy radicals (this data is presented in Supplementary Fig. S4 in the SI). This again shows that borosilicate glasses have fairly low defect activation energies which are in good agreement with our values of heavy ion irradiated specimens. However, it is important to note that a broad spectrum of activation energies in the range of 0.2 to 0.5 should be expected depending on the defect type.

4.6. Energy deposition and damage saturation.

As mentioned earlier, ions undergoing ATEC created a higher degree of damage than the ions with BTEC. For instance, ATEC resulted in -3.3 %, -35 % and +12 cm⁻¹ change in the density, hardness and R-band position in the BS3 glass. On the other hand, the maximum property changes in the case of the BTEC were only 30 to 50 % of the changes seen during the ATEC. Figure 23 shows the saturation dose (electronic, nuclear, total and effective total) as a function of the specific energy of the ions (kinetic energy divided by the mass number) based on the results of the Raman spectroscopy for the ions with either dominant ATEC or dominant nuclear collisions. The saturation dose was calculated by multiplying the average energy loss in the first two micrometres of the specimen surface (~ Raman depth resolution) and the saturation fluence corresponding to 95 % change in the R-band position (from Fig. S2 in the SI). One can notice that for specific energies > 0.2 MeV/u (ATEC) the saturation dose remains fairly constant (linear fits to the data in this region are also shown in the figure). The nuclear dose (red circles) in this region is negligible (~2 % of the total dose) and the average value of the total saturation dose (blue up-triangles), contributed mainly by the ATEC, is about 4.7×10²⁰ keV.cm⁻³ (~ 30 MGy ~ 7 eV/atom) (± 4 % as the standard error of the mean). It highlights that once the ion track threshold is surpassed, the ion mass and/or energy do not play any role in controlling the magnitude of the maximum damage level and the saturation dose. For specific energies < 0.2 MeV/u a sharp rise in the saturation dose can be observed in Fig. 23. The electronic energy loss in this region is just near the ion track threshold or below. Because of the near or sub-threshold electronic energy loss the changes are actually induced by the nuclear collisions whereas the electronic energy loss has no to negligible effect because, as discussed earlier, the BTEC induce very small changes requiring significantly higher doses to induce those changes. Therefore, the total saturation dose appears high simply because the electronic dose adds up but actually does not contribute to the material changes, which are brought about almost entirely by the nuclear collisions.

Because the BTEC have a very little contribution, one could remedy this artefact in the total saturation dose at low values of the ion specific energies by simply subtracting the electronic dose in these subthreshold collisions. For this purpose, we define a new quantity called as “Effective total dose” obtained by subtracting the ion track threshold of 3 keV.nm⁻¹ from the total energy loss (called as “Effective energy loss” and given by the denominator in equation 5) and multiplying this effective energy loss by the saturation fluence. As it turns out, it gives a fairly straight line whatever the specific energy of the ions and is valid whether one is in the ATEC regime or dominant nuclear collisions regime. This data (pink squares) and its straight-line fit are shown in Fig. 23. Furthermore, it leads to an easy working formula that the researchers can use to calculate the saturation fluence whether the ion is undergoing dominant nuclear collisions or ATEC. This working formula is given in equation 5 and will be referred to as the Saturation Fluence equation (SF equation).

$$\text{Saturation fluence (ions.cm}^{-2}\text{)} = \frac{3 \times 10^{13}}{(S_t - S_{eth})} \quad (5)$$

Where S_t is the total energy loss at a given point and S_{eth} is the ion track threshold of the glass (both in keV.nm⁻¹). Note that the equation is valid as long as $S_t > S_{eth}$ and should be evaluated locally and not for the projected ion range. For instance, if a certain characterization tool probes a depth “x”, the saturation fluence for each point from the surface up to the depth “x” can be different depending on how the stopping power curve is changing within this depth. It is essentially the region with the lowest total energy loss that will dictate the saturation fluence and that is where the value of the S_t should be taken. For the cases where $S_t < S_{eth}$ and $S_n > S_e$, the limited data available so far indicates that the denominator in equation (5) can simply be replaced by S_t and the resulting saturation fluence would need to be multiplied by a factor of 10 at most to get the actual saturation fluence (this happens to be the case for 400 keV Kr irradiation).

The implication of introducing the “Effective total dose” or “Effective energy loss” is that a minimum energy deposition is needed during an electronic collision before the material can be driven to an irreversible high damage state. This minimum energy is used to create a threshold defect concentration or a sufficient enough temperature spike such that any additional amount of energy drives the system beyond full recovery; leaving it in a permanent high damage state. It is worth mentioning that molecular dynamics simulations of collision cascades in borosilicate glasses suggest that the modifications saturate after an energy deposition of

about 4 eV/atom ($\sim 2.8 \times 10^{20}$ keV.cm⁻³ ~ 18 MGy) [23] to 8 eV/atom (5.6×10^{20} keV.cm⁻³ ~ 36 MGy) [62]. These values are in reasonable agreement with the experimental data presented here.

At this point, it is worth highlighting the difference in the magnitude of the deposited energy and the actual stored energy. Differential scanning calorimetry studies of actinide doped specimens[13][63] have shown that the energy stored in waste glasses ranges from about 100 to 170 J/g (0.02 to 0.03 eV/atom). This is about two orders of magnitude smaller than the saturation deposited energy (~ 7 eV/atom) as shown above. One of the reasons for this is the fact that a major fraction of the deposited energy is lost in radiative and non-radiative transitions as the excited electrons return to their ground states. Furthermore, a fraction of the deposited energy is also lost by the atoms in thermal vibrations. Therefore, a direct comparison between the stored energy and deposited energy is not very meaningful unless various energy dissipation pathways are accounted for. Nonetheless, the results show that only a small fraction of the energy is actually permanently stored in the form of the defects. It is these defects that result in a higher enthalpy state of the radiation damaged glass.

Also, one of the things to point out here is some potential differences amongst the ions with BTEC. During 2 MeV He irradiation, first visible structural modifications were observed after about 6×10^{21} keV.cm⁻³ (2×10^{15} ions.cm⁻²) whereas it required only about 1×10^{21} keV.cm⁻³ (8×10^{13} ions.cm⁻²) during 12 MeV C irradiation for any visible structural modifications. This points to a potential dependence of the damage evolution on the electronic energy loss in the BTEC regime. Therefore, more research is needed in the BTEC region to understand whether the maximum damage state and its evolution has a dependence on the electronic energy loss of the ions.

In the case of the nuclear waste packages, the total damage results from a combination of the alpha particle and recoil nucleus damages. The accumulation of nuclear and electronic doses due to alpha decays in a typical nuclear waste glass is shown in Fig. 23 (b) (the data is linear on the Log-Log scale). Two important observations can be made viz. (i) The electronic dose is about 70 times higher than the nuclear dose at any point in time and, (ii) the saturation nuclear dose of about 2×10^{20} keV.cm⁻³ is reached after about 1×10^{18} alpha decays per gram. Given that the electronic collisions in nuclear waste packages are all BTEC and such collisions require about 100 times higher dose for the damage saturation, it is clear that the BTEC in waste packages can induce modifications in parallel to the modifications induced by the nuclear collisions if one were to assume that the damages due to these two processes were additive. However, even in this case, the changes due to electronic energy losses will be completely masked by the magnitude of the changes induced by the nuclear collisions because of the higher magnitude of the damage level associated with nuclear collisions. Therefore, the damage evolution would appear to be dictated by the nuclear dose rather than the electronic dose. For this reason, it is not surprising why the damage evolution in actinide doped glasses seems to show a good agreement with the nuclear dose deposition [14].

Nevertheless, alpha particles will induce an athermal defect recovery and the saturation damage will neither be dictated by alpha particles nor by the recoil nuclei alone. In the current study, SON68 glass was shown to swell by about 1.5 % from single beam ion irradiations whereas actinide doped SON68 is known to swell by about 0.5 % only [11]. These low swelling values of the SON68 glass have recently been observed by employing dual-beam ion irradiations where alpha-induced athermal defect recovery take places simultaneously with damage formation bringing down the swelling to less than 1 % [44]. Furthermore, NMR spectroscopy of the doped glass has also confirmed the presence of latent defect healing taking place in nuclear waste glasses [15]. This indicates that the changes in properties (structural and mechanical) due to alpha particles can compete with the changes induced by the nuclear energy loss and a probabilistic approach incorporating the alpha-induced defect recovery and damage formation to better predict the damage evolution in waste packages should be developed.

Figure 23: Doses during ion irradiation and self-irradiation **(a)** Saturation of the electronic, nuclear, total and effective total dose as a function of specific energy of the ions. The lines are linear fits to the data (see the text for more details) **(b)** Variation of the electronic (dashed-red) and nuclear (black) dose due to the accumulation of alpha decays in a typical nuclear waste glass. Note that the data is linear on a log-log scale.

4.7. Global contribution of fission fragment damage.

In addition to the alpha decays, spontaneous fissions will also take place in the waste packages. In the preceding discussion, the contribution of the spontaneous fissions to the overall damage formation was ignored. Fission fragments have typical energy and mass of about 100 MeV and 120 amu each (the two fragments, in reality, have unequal masses and energy leading to two distinct humps in the fission fragment mass spectrum. A common example is fission fragments Xe and Kr). It is worth mentioning that the fission fragments for most of their path will undergo ATEC and induce ion tracks in the waste matrices. The fission fragments will travel a distance of about 12 μm each, which is about 400 times the distance travelled by alpha recoil nuclei. The average damage cross-section of the ions of this mass and energy is about $4 \times 10^{-13} \text{ cm}^2$ (Fig. 4) which is roughly 5 times the damage cross-section of a typical recoil nucleus. A single spontaneous fission event would create a damage zone equivalent to about 4000 alpha recoil nuclei damage zones ($\sim 2 \times 400 \times 5$). A homogeneously distributed spontaneous fission element concentration giving rise to 2.5×10^{-4} decay events is thus equivalent to one recoil nucleus damage event. Taking into account the activities of different minor actinides present in the nuclear waste glass and a total minor actinide oxide content of 1.2 weight percent (typical of waste after 33 GWd/ton burnup and 16 wt. % oxide loading), the damage contribution of fissions fragments relative to the recoil nuclei damage is shown in Fig. 24. The overall contribution of the fission fragment damage is three orders of magnitude less than the alpha recoil damage. This shows that the damage from spontaneous fissions can be ignored in comparison to the damage due to recoil nuclei.

Figure 24: Damage contribution of fission fragments resulting from spontaneous fissions. The calculation takes into account the following parameters: Energy of fission fragments = 100 MeV, the mass of fission fragments = 120 amu, number of fission fragments per decay = 2, the average range of fission fragments = 12 μm , total path length travelled by the fission fragments = 24 μm (12×2), the ratio of the fission fragment path to recoil nucleus path = 800, the ratio of the average fission fragment to recoil nucleus damage cross-section = 5 and, damage zone of fission fragments relative to the recoil nuclei damage zone = 4000 (800×5).

4.8. Modifications in the glass structure and properties.

Structural modifications: Raman spectra of the heavy-ion irradiated (ATEC) glasses, both BS3 and ISG, qualitatively suggested an increase in the concentration of the BO_3 units and a decrease in the concentration of the BO_4 units. Similar changes but to a lesser degree were observed due to the BTEC. This is consistent with the already published results on NMR studies of the heavy-ion irradiated glasses (ATEC) [64] showing a decrease by about 23 % and 33 % in the BO_4 content in the BS3 and ISG glasses respectively. The Raman spectra of the ion irradiated glasses indicated network depolymerization, an increase in the concentration of the Q^3 species and, a decrease in the concentration of the Q^4 species. This is again in line with the previously published NMR results [64][38] on the subject. The modifications in the low-frequency side of the Raman spectra showed an increase in the frequency of the R-band suggesting a decrease in the mean Si-O-Si bond angle and modifications in the ring statistics.

Similar conclusions have been drawn from MD simulations of collisions cascades showing that BO_4 content decreases by about 14 to 30 % and 12 to 22 % in the alumino-borosilicate and borosilicate glasses respectively after ballistic collisions [23]. The transformation of BO_4 to BO_3 is not unusual as it is well known that BO_4 is unstable at high temperatures [65] and transforms to BO_3 . Such a transformation would be expected to take place in the high-temperature thermal spikes induced by the ATEC and fast quenching of the molten material would facilitate freezing a depolymerized structure enriched in the BO_3 content.

In comparison, electron irradiations of the BS3 glass irradiated up to 4.5 GGy [4] have shown a decrease of 6 % only in the BO_4 content and an increase in the Q^3 species by about 14 %. Because the changes due to BTEC and electron irradiations are very similar (based on the Raman spectra) we expect a similar change in the BO_3 and BO_4 contents in the glasses damaged by the BTEC. For studies in the near future, NMR studies of the glasses damaged by BTEC could be interesting and would allow a more quantitative comparison with electron irradiation effects with regards to the structural modifications. Furthermore, NMR studies of glasses irradiated with dual ion beams should be undertaken to quantify the effect of athermal defect healing on the BO_3 and BO_4 contents.

Microhardness: The indentation results showed that the hardness of the irradiated glasses decreased after irradiation with either ions or electrons. This is expected because both the electrons and the ions caused network depolymerization and therefore reduced the number of the bonds that the indenter encounters. ATEC induced a maximum hardness decrease of about 35 ± 1 % irrespective of the glass composition. BTEC, on the other hand, decreased the hardness by 18 ± 1 % (for BS3) and 14 ± 1 % (for SON68) — suggesting that the glass

composition plays a role during BTEC. Also, it has been shown in our previous studies that the hardness of the BS3 and SON68 glasses decreased by about $20 \pm 3\%$ and $10 \pm 3\%$ respectively after electron irradiation. This is in reasonable agreement with the results of the BTEC which showed a similar trend for these glasses — highlighting a similarity between the electron irradiation and BTEC. It has been demonstrated from electron irradiations of various multi-component alumino-silicate glasses that the addition of transition elements such as Fe and, mixed alkali effect, can reduce the sensitivity towards ionization effects leading to relatively radiation-resistant glasses [66][67]. In light of these studies, it is plausible to propose that the irradiation response during BTEC is affected by the glass composition because pure ionization effects are dominant during the BTEC. Nevertheless, these results are consistent with the structural modifications observed using Raman and NMR spectroscopies which showed that the ATEC induced the maximum structural modifications.

Similar results have been reported in other studies [38] after He and Au irradiation of the ISG and SON68 glasses (lesser change due to He irradiation). The authors of this study also reported a decrease in the reduced Young's modulus by about 8 % and 2% after Au and He irradiation of the SON68 glass respectively. Ion and electron irradiation studies of borosilicate glasses close in composition to the BS3 glass by Chinese researchers have also indicated the dominance of ion irradiation effects over electron irradiation effects [29].

The hardness of a material essentially measures its resistance to permanent deformation. This depends on the strength of the bonds (spring constant), the density of the bonds (bonds per unit volume) and, on the resistance offered by various structural units to deformation (which may depend on the bond angle distribution and network connectivity). It is well known that amorphous-SiO₂ undergoes densification under ion irradiation unlike the borosilicate glasses studied here. But, irrespective of the density change, irradiation leads to a decrease in the hardness. In the case of the amorphous-SiO₂, the irradiation-induced densification (~3 % in amorphous silica) will lead to an increase in the bond density whereas irradiation of the borosilicate glasses (BS3, ISG, SON68) will lead to a decrease in the bond density. This indicates that a change in the material density (or bond density) by a few percent does not have a significant effect on the hardness. However, in addition to the modification in the density, irradiation also leads to the formation of punctual defects and network depolymerization introducing discontinuities in the network and, leading to a decrease in the density of the bonds. The irradiation-induced discontinuities reduce the number of constraints on the atoms which allows them to reconfigure relatively easily under any external stresses favouring viscous flow of the glass. It is essentially these additional broken bonds and network discontinuities introduced by the irradiation damage that result in a decrease of the bond strength and bond density that the indenter encounters. This is manifested as a decrease in the hardness of the irradiated glasses. The other effect of this is an increase in fracture toughness of the irradiated glasses. This is because a decrease in the constraints allows better network reorganization upon external stresses which helps to decrease the local stress concentration. This, in turn, leads to an increase in the fracture toughness of the irradiated glasses. These are also essentially the conclusions one can draw from MD simulations of nanoindentation of the pristine and irradiated glasses [62][68].

Both, a decrease in the hardness and an increase in the fracture toughness imply a better impact resistance of the irradiated glasses under geological disposal conditions. These two factors together may have positive effects with regards to leaching. The enhanced resistance to cracking may help reduce the fracture of large waste packages into smaller pieces and thereby help decrease the surface area exposed to water and leaching. Nonetheless, to the best of our knowledge, there are currently no mechanistic models incorporating the effects of radiation damage on the hardness and fracture toughness to estimate its impact on the long-term fracture of waste packages. That being said, any such positive aspects may be within the error margins of the cracking considered for the initial waste package.

Density change: The BS3, ISG and SON68 glasses showed ATEC and nuclear collisions caused swelling of $2.8 \pm 0.08\%$, $1.3 \pm 0.05\%$ and $1.5 \pm 0.06\%$ respectively. The swelling results of BTEC are detailed as part of the multi-particle ion irradiation studies elsewhere [44]; where it was shown that the BTEC resulted in a swelling of 0.8 % in the BS3 glass (observed after irradiation with 2 MeV He ions up to 1×10^{17} ions.cm⁻²). Electron irradiation of the BS3 glass also caused swelling of 0.8 % only as reported in our previous work [43]. This again shows that the electron irradiation and the BTEC behave similarly and that the ATEC cause the maximum swelling.

The density changes perhaps have their origin in the modifications in the ring statistics and the transformation of BO_4 to BO_3 . It is known that BO_3 units occupy a larger volume in comparison to the BO_4 units. Irradiation induced transformation of BO_4 to BO_3 can thus be expected to contribute to the glass swelling. It is however not clear as to what the individual contributions of the structural transformation and the changes in the ring distribution towards the global swelling are. MD simulations of sodium borosilicate glasses with $R = 1$ and K ranging from about 1.3 to 4.7 indicate that 5 to 7-member rings are the most probable in the pristine and radiation-damaged borosilicate glasses and that the ballistic damage leads to a broadening of the ring distribution with an increase in the large and small rings at the expense of the intermediate size rings [23] (the ratio of the rings before and after the radiation damage is shown in Fig. S5 in the SI). These simulations show that the irradiation-induced swelling ranges from about 4 % to 5.2 %. For the case of the BS3, the simulations indicate a maximum swelling of about 4.4 % which is about 58 % higher than what was observed experimentally during single beam ion irradiations in our study. An additional correction factor can be applied to the experimental data by also considering the small step-height created along the specimen edges in addition to the major step-height as measured on the irradiated surface after the ion irradiation. Optical micrographs and SEM images of a BS3 specimen taken along the irradiated cross-section indicated that a small step was formed after the ion irradiation. Unlike the sharp step created on the partially masked specimen surface, the lateral step along the irradiated cross-section seemed to follow a complicated topography. Starting from the end of the ion path, the step height slowly increased and attained the maximum height on approaching towards the surface. This led to complications in correctly evaluating the step height using either AFM, interferometry or mechanical profiler due to errors in correctly establishing the background. Nonetheless, by measuring the z-movement of the stage during confocal Raman spectroscopy to get the best laser focus, a rough estimate of the step height was obtained. By taking this into account, the revised BS3 swelling is about 3.3 % which is only 18 % higher than what we have reported so far (2.8 %). Even with this revised estimate, the simulations still predict a swelling which is about 33 % higher than the experimentally measured values. Despite the differences between the experiments and simulations, the general trends are correctly captured in the simulations. It is important to highlight at this point that MD simulations fail to deal with the formation of molecular oxygen as observed experimentally. The molecular oxygen is formed as a result of the recombination of non-bridging oxygen atoms (NBO) (e.g. $[\text{Si-NBO} + \text{Si-NBO}]_2 = 2[\text{Si-O-Si}] + \text{O}_2$) and such reactions have the potential of decreasing the concentration of the NBO atoms and cause a certain degree of re-polymerization. This can, in turn, change the ring statistics and potentially affect the swelling as well. Until issues like this are properly handled in MD simulations, one should not expect any better agreements between the simulations and the experiments.

4.9. Recommended ion types and ion energies

Based on the results so far, we aim to provide contour maps showing the projectile energy, projectile Z and, the energy loss to facilitate choosing the ions for ion irradiation studies to simulate the effects of ATEC, BTEC and athermal defect healing. Figure 25 (a-c) shows the electronic (S_e), nuclear (S_n) and the ratio of electronic to nuclear energy losses (S_e/S_n) respectively for elements from $Z=1$ to $Z=92$ (the energy losses are in keV.nm^{-1}) up to 30 MeV (maps up to 110 MeV are shown in Fig. S6 in the SI). These maps give a broad overview of the typical range of the electronic and nuclear energy losses covered by various ion irradiation studies of nuclear waste glasses available in the literature. For comparison, the typical values (average) of S_e and S_n are 0.2 and 2×10^{-4} keV.nm^{-1} for alpha particle, and 0.3 and 2.2 keV.nm^{-1} for the recoil nucleus respectively (indicated by the circles on the figures). The S_e/S_n ratios are between 1000 to 1400 for alpha particle and close to 0.1 for the recoil nucleus for the most of their path.

Figure 25: Contour maps of electronic energy loss (S_e), nuclear energy loss (S_n) and their ratio as a function of the projectile Z and projectile energy (MeV). The red circles indicate the typical values for alpha particle and recoil nucleus in nuclear waste glasses. The vertical dashed line in (a) indicates a 5 MeV energy limit discussed later on. The energy losses are in keV.nm^{-1} (data from SRIM 2008 for an ISG type glass with a density of 2.5 g.cm^{-3}).

Now we bear in mind the following points to make some recommendations on selecting the ion types and ion energies for simulating the alpha and recoil nucleus damage in nuclear waste glasses.

- a. The ions should not induce any ion tracks due to their electronic energy loss (BTEC only). This limits the ion energies and ion types to the cases where the electronic energy loss is no more than 3 keV.nm^{-1} (the upper limit of ion track threshold). From Fig. 25 (a), this is true for all the ions from $Z=1$ to $Z=92$ if their energy is roughly about 5 MeV and less (indicated by the vertical dashed line). Note that the upper limit of the ion energy in principle depends on Z and it can be up to 10 MeV for ions with Z ranging from about 50 to 70. For the sake of simplicity, we recommend the energy limit as 5 MeV and no limit on the Z to avoid the formation of any ion tracks. Also, cross-sectional Raman spectroscopy of the specimen irradiated with Xe ions allowed studying the effect of S_e/S_n ratio from 1 to 136 and no relative changes were observed as a function of the S_e/S_n ratio.
- b. The changes due to BTEC are only about 30 to 50 % of the changes due to ATEC/NC, and it takes about 100 times higher dose level to attain the saturation damage state due to BTEC. Therefore, only ions with S_e/S_n ratio at least > 100 and $S_e <$ ion track threshold should be used to approximate the He ion simulation. Figure 25 (c), shows that for $Z < 10$, $S_e/S_n > 260$ for energies $> 1 \text{ MeV}$. This is more clearly visible in Fig. 26 where the contour maps for Z from 1-20 and 15 to 92 are shown in rows 1 and 2 respectively (up to 5 MeV). The region below the horizontal dashed line in Fig. 26 (c) indicates the region of interest for alpha particle simulation. Therefore, ions with $Z < 10$ and Energy $> 1 \text{ MeV}$ would be recommended for alpha particle simulation.
Currently, there is no evidence that higher S_e/S_n ratio is better and while it is trivial to propose that one should only use He ions for simulating alpha particle, there is no evidence that other lighter ions (like $Z < 10$) are not as good in terms of the nature of the final damage state. It is worth mentioning that cross-sectional Raman spectroscopy was performed on a BS3 specimen irradiated with 2 MeV He ions and no differences were observed in the Raman spectra along the cross-section. This allowed examining S_e/S_n ratios from 100 to 1000; indicating that S_e/S_n ratio in this range does not have any measurable effect on the final damage level.
- c. For the recoil nucleus simulation, Fig. 26 (f) shows that for most of the ions with $Z > 20$, S_e/S_n ratio is < 30 and $S_e <$ ion track threshold. Given that the changes due to BTEC are only about 30 to 50 % of the changes due to ATEC and nuclear collisions, ballistic damage will dominate in this region. The bottom right corner in Fig. 26 (d) ($Z = 15$ to 20 , $E > 4 \text{ MeV}$) has the highest S_e/S_n ratio of about 90. The recommended ions for recoil nucleus simulation would be $Z \geq 20$ and $E \leq 5 \text{ MeV}$ to maintain the S_e below the ion track threshold and the dominance of nuclear collisions. This is indicated by the region above the dashed line in Fig. 26 (f). Like the case of He, cross-sectional Raman spectroscopy was also performed on a 14 MeV Au ion irradiated BS3 specimen allowing to explore S_e/S_n ratios in the range of 0.8 to 2.4. No differences in the damage level were observed in this case as well.
- d. For recoil nucleus simulation using the ATEC, ions with $Z > 15$ and $E > (5 \text{ to } 10 \text{ MeV})$ would be required as indicated by the rectangular region of interest in Fig. 26 (g) ($E > 10 \text{ MeV}$ for some ions, especially for Z between 50 and 70 as seen in the contour maps shown in Fig. 26 (g) or Fig. 25 (a)). It is important to point out that while such ions would lead to the same damage state as nuclear collisions, they may potentially bias the leaching due to ion track formation. Studies in that direction could be interesting in the near future. These ions offer a particular advantage of increased ion range and thereby allowing to damage relatively larger quantities of material that can be characterized using various spectroscopic techniques such as NMR, EPR etc.

Figure 26: Contour maps of electronic energy loss (S_e), nuclear energy loss (S_n) and their ratio as a function of the projectile Z and projectile energy (MeV). Row-1 shows the data up to $Z = 20$. Ions with $Z < 10$ and $E > 1$ MeV (as indicated by the rectangle in (c)) can be used for alpha particle simulation. Row-2 shows the data from $Z > 15$. Atoms with $Z > 20$ and $E \leq 5$ MeV (as indicated by the rectangle in (f)) can be used for recoil nucleus simulation. For certain heavy ions, the upper limit can be up to 10 MeV. See the text for more details. Row-3 shows the electronic energy loss map up to 30 MeV energy. The rectangle shows the region of interest for simulating recoil nucleus damage using the ATEC (see the text for more details and other important conditions to consider).

4.10. Prospects and further scientific problems to address

Athermal defect healing: While we have shown so far that the BTEC can lead to athermal defect recovery, there are currently no studies addressing whether the degree of recovery depends on the electronic energy loss of the ions in the BTEC regime. It is, therefore, worth exploring in detail the contour map for the BTEC region shown in Fig. 19 to address this point. A typical study could involve irradiating the pre-damaged specimens (pre-damaged with an ion with ATEC/NC) using ions with S_e in the range of 1 to 3 keV.nm⁻¹ to various fluences and study the recovery as a function of the fluence until saturation in the recovery is obtained. We have discussed in our earlier study that the athermal defect recovery was a combined result of non-melting thermal spikes induced by the BTEC and ionization of the pre-existing molecular oxygen leading to a diffusion of oxygen atoms and their re-integration into the network. Since the temperature of the non-melting thermal spikes depends on the value of the S_e , it is, therefore, plausible to propose that the rate and perhaps the level of the recovery may increase with an increase in the S_e value in the BTEC region. Another interesting study would be to post irradiate the pre-damaged specimens with electrons/gamma-rays and study whether pure ionization effects due to the electrons/gamma-rays can induce the defect recovery. This would be a good way to differentiate the individual contribution of the ionization and non-melting thermal spikes to defect recovery. It offers a potential way of unambiguously exploring the role of the thermal spikes in athermal defect recovery.

The difference in the defects due to ATEC and nuclear collisions: So far, we have ascertained that the ATEC and the nuclear collisions induced the same damage state. This assertion was primarily based on the changes observed in the mechanical properties and to some extent on the results of the Raman spectroscopy. One of the difficulties in going into more detail into the defect formation under nuclear collisions lies in the fact that only a small specimen depth is damaged by heavy ions of few hundred keV energy and there are only a limited number of characterizations that can be reliably applied for such studies. It is therefore important that techniques such as XANES, EXAFS, XPS (with depth profiling) and IR/ATR should be explored and used more routinely. These characterizations can allow to better compare the changes due to ATEC and nuclear collisions and would be helpful in unambiguously establishing the compatibility (or incompatibility) between these two damage mechanisms.

The activation energy for defect annealing: There are only a very limited number of studies exploring the effect of time and temperature on the defect recovery in glasses of nuclear waste interest. Studies aimed at deducing the defect activation energies and long-term defect recovery that would occur under geological disposal conditions should be undertaken. Raman spectroscopy could prove to be an important tool for this purpose as hot stages can be readily set up allowing to precisely monitor the defect recovery as a function of time and temperature. Moreover, it requires only very small specimens and therefore a single pre-damaged specimen of about 1cm×1cm could be split into many pieces allowing to carry out both isochronal and isothermal studies on a single pre-damaged specimen. Similarly, annealing of step-height could be monitored by employing AFM at high temperatures ($T < T_g$; which is usually $< 600\text{ }^{\circ}\text{C}$ for nuclear waste glasses) for such purposes.

Ion tracks and leaching: While the ATEC create the same damage state as nuclear collisions and therefore offer a way of studying the effects of nuclear collisions, it would be pre-mature to ignore the effects the ion tracks may have on the radioisotope leaching. Ion tracks are highly directional which may act as fast diffusion channels for water, thereby, increasing the rate of radioisotope leaching. While studies on the rate of water and radioisotope diffusion through ion tracks are lacking, it would be wise to limit the leaching studies to specimens not irradiated with ions with ATEC.

5. A summary of the points to remember

- Ion track threshold of simple and complex nuclear waste forms are in the range of 2 to 3 keV.nm⁻¹. We recommend an upper limit of 3 keV.nm⁻¹ as a reference value for all the nuclear waste forms.
- The modifications induced by the ions with electronic energy loss above the ion track threshold (ATEC) are different from the modifications induced by the ions with electronic energy loss below the ion track threshold (BTEC).
- Nuclear collisions (NC) and ATEC induce similar modifications requiring about 3×10^{20} to 5×10^{20} keV.cm⁻³ (~ 19 to 34 MGy ~ 4 to 7 eV/atom) of energy deposition for damage saturation.
- The similarity between the NC and the ATEC arises due to the formation of thermal spikes and a melt phase which upon fast quenching freezes a defective state which has no memory of how the melt phase was created.
- In the bulk of the glass, BTEC and electron irradiations induce similar modifications; requiring at least about 3.5 GGy of energy deposition for the damage saturation.
- The modifications due to BTEC and electrons are only about 30 to 50 % of the modifications due to the NC and ATEC.
- BTEC collisions can induce athermal defect healing in the pre-damaged glasses.
- The electronic energy loss of the alpha particles, recoil nuclei and any other knock-ons in the waste forms is in the BTEC regime. This will potentially lead to a partial defect healing in the long-term.
- ATEC, BTEC and electron irradiations, all lead to changes in the ring statistics, network depolymerization, transformation of BO₄ to BO₃ and a decrease in the density and hardness (for the studied borosilicate glasses).
- The activation energy for defect healing in the simple sodium borosilicate glass BS3 is about 0.5 eV.
- Preferably use ions with $Z < 10$ and Energy > 1 MeV for alpha particle simulation (BTEC) and ions with $Z > 20$ and Energy ≤ 5 MeV for recoil nucleus simulation (NC).

- Preferably use ions with $Z > 15$ and Energy > 10 MeV for ion track formation (ATEC).
- Either when the total energy loss of the ions is greater than the ion track threshold or when nuclear collisions dominate, the saturation fluence can be given by the Saturation Fluence equation (SF equation) given below (equation 5 in the text. Where S_t and S_{eth} are the total stopping power and the ion track threshold respectively in keV.nm^{-1})

$$\text{Saturation fluence (ions.cm}^{-2}\text{)} = \frac{3 \times 10^{13}}{(S_t - S_{eth})}$$

Conclusion

Borosilicate glasses of nuclear waste interest were irradiated with various ions and characterized for modifications in the glassy structure and mechanical properties. The studies were aimed at understanding the role played by the ion mass and energy on the damage state to establish some standard ion irradiation conditions for correctly simulating the damage accumulation due to alpha decays. Many aspects of this mass-energy landscape were discussed and several other important scientific issues that remain unanswered were highlighted (section 4.10). Based on the results so far, recommendations were made on selecting the ion mass and energy for better simulating the effects of alpha decays (section 4.9). Also, a working formula, referred to as SF-equation, to calculate the saturation fluence was proposed based on the available experimental data which can allow to better plan the future irradiation experiments.

The results showed that borosilicate glasses have ion track threshold in the range of 2 to 3 keV.nm^{-1} — which is higher than the electronic energy loss of alpha decay products. The response of the glasses strongly changes around the ion track threshold. Above threshold electronic collisions (ATEC) induce larger modifications as compared to the below threshold electronic collisions (BTEC). Furthermore, ions with BTEC are capable of inducing partial defect healing in the pre-damaged glasses (pre-damaged by ATEC or nuclear collisions) and their effects in pristine glasses are very similar to the effects of high energy electron irradiation. The effects of the ATEC and nuclear collisions seem to be the same although further studies are needed in the future to support this point.

Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations. However, it can be made available upon request.

Declaration of Competing Interests

The authors declare no competing interest.

CRedit Author Contribution Statement

A H Mir: Conceptualization; Formal analysis; Investigation; Methodology; Visualization; Data curation; Validation; Writing – original draft writing.

S Peugeot: Conceptualization; Data curation; Funding acquisition; Project administration; Resources; Supervision; Validation; Writing – review & editing.

Acknowledgements

This work was funded by the CEA in the framework of the VESTALE project. A H Mir is also thankful to EPSRC U.K for funding under grants EP/ T012811/1 and EP/E017266/1 for continued research. The authors also acknowledge the support from the IAEA through their INWARD coordinated research project (Ion Beam Irradiation for High Level Nuclear Waste Form Development, F11022, 2018 to 2022) which is an ongoing project bringing together scientists from across the world for collaborative research on the subject. The experimental work was carried out by A H Mir from 2012 to 2019 with support from Sylvain Peugeot, Marcel Toulemonde and Serge Bouffard. The ion irradiations were performed at the GANIL and JANNUS facility and the authors are grateful to Isabelle Monnet and Clara Grygiel from GANIL and Sandrine Miro and Yves Serruys from JANNUS for

1504 supporting the ion irradiation experiments. The surface profilometry experiments were supported by Laurence
1505 Mechin from GREYC research group at the University of Caen and we are grateful to her for giving us
1506 unrestricted access to her lab. We also highly appreciate the MD data from Amreen Jan presented in the SI. And
1507 at last we would like to thank Christophe Jegou for very fruitful discussions over the years.

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