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Amorphization of α -Quartz under Irradiation

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Abstract. — The course of radiation induced damage produced in α -quartz by neutrons, ions, electrons or photons — commonly known as metamictization — has been re-analyzed by careful comparison of available experimental data. Specific interest was devoted to confront experimental metamict state features with current structural models. It comes out that the metamict state of irradiated quartz should exhibit some structural characteristics of the modulated structure proposed for vitreous silica. The metamictization process is consistent with a structural relaxation process of a highly defective quartz matrix. According to this new point defect analysis, structural relaxation should be triggered by a critical concentration of oxygen vacancy point defects likely to significantly lower the connectivity of the SiO_2 network. Various experimental results are interpreted by incorporating the influence of the SiO_2 crystalline polymorph and the influence of the nature of the irradiating particle to the point defect model.

Résumé. — Nous avons étudié les modifications de propriétés et de structures de monocristaux de quartz α , consécutives à une irradiation sévère par des neutrons, des ions, des électrons ou des photons. Ce phénomène d'altération du quartz sous irradiation porte le nom de métamictisation. Notre travail exploite les recoupements de travaux antérieurs. Une attention particulière a été portée à la confrontation entre les données structurales expérimentales disponibles sur l'état métamictite du quartz et les modèles structuraux proposés. L'état métamictite du quartz présente ainsi les caractéristiques structurales du modèle de structure modulée, avancé pour décrire la structure de la silice thermique. Le mécanisme de métamictisation procéderait par relaxation de la matrice cristalline fortement endommagée. Ce phénomène de relaxation serait initié par l'apparition d'une concentration critique de défauts ponctuels de type lacunes d'oxygène responsables d'une forte augmentation des degrés de liberté des tétraèdres élémentaires SiO_4 au sein du cristal. Ce modèle de défaut ponctuel permet, par la prise en compte de la nature de la forme cristalline du dioxyde de silicium et la nature du projectile utilisé, de rendre compte de l'essentiel des données expérimentales.

Introduction

The effect of irradiation on silicon dioxide has been extensively studied both experimentally and theoretically. This interest reflects the technological importance played by SiO_2 material in modern applications. Indeed, silicon dioxide is today widely used for microelectronic and

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optoelectronic devices, *etc.* Previous studies [1-5], have shown that upon various particle irradiations α -quartz, as well as silica, evolves towards a single amorphous state somewhat different from an ordinary vitreous silica. This amorphous state, classified by geologists as metamict, keeps raising a lot of structural controversies.

In this paper, we investigate the damage produced in quartz by neutrons, ions, electrons or photons, with a specific interest to the structural modifications of the quartz matrix. Particular efforts were made to systematically re-analyze various experimental results with current model of the metamict state. It comes out that the metamict state corresponds to the single structural relaxation product of a highly defective SiO_2 matrix. The metamictization process is probably triggered by a critical concentration of oxygen vacancy like point defects. In addition, by taking into account the influence of the crystalline precursor as well as the nature of the irradiating particle, the point defect analysis is likely to account for a wide range of experimental results.

In part 1, we briefly review the macroscopic property modifications produced in α -quartz by neutron, ion, electron or photon irradiations. Part 2 summarizes the significant experimental results of structural studies carried on metamict quartz. Part 3 is devoted to the discussion of the structure of the metamict state as well as a possible single metamictization mechanism.

1. Particle Induced Amorphization of α -Quartz

When α -quartz is irradiated, it gradually becomes disordered into an amorphous form. An important point here is that, in respect to macroscopic properties such as density, refractive index, rotatory power..., this amorphous end product exhibits at least three distinctives features:

- 1a) the amorphization end product of quartz is almost irrespective of the irradiation process, *i.e.* whether neutrons, ions, electrons or photons are used for the irradiation,
- 1b) the amorphization end product of α -quartz is nearly indistinguishable from the end product of the irradiation of an ordinary vitreous silica,
- 1c) the amorphization end product of α -quartz is somewhat different from an ordinary vitreous silica in that its density appears slightly higher by 3% to 4%.

1a) Amorphization of quartz has been reported for various particle irradiations and wide ranges of irradiation parameters. Interestingly, direct and indirect density or refractive measurements carried out on the irradiation end product appear irrespective of the nature of the irradiating particle [1-3, 6]. However, physical property changes follow different ways.

The changes produced in quartz by fast neutron (n energy > 0.1 MeV) exposures in nuclear reactors have been early considered [1, 7]. Neutron irradiation damages are generally described according to a three fluence scheme. For low n fluences ($\phi_n \leq 1 \times 10^{18}$ n cm^{-2}), the effects of the irradiation is to induce point defect creation [8, 9], mainly E' centers and Oxygen Hole Centers (OHC). The point defect concentration increases as a power function of the fluence. For medium n fluences (1×10^{18} n $\text{cm}^{-2} \leq \phi_n \leq 1 \times 10^{20}$ n cm^{-2}) α -quartz undergoes an $\alpha \rightarrow \beta$ transition soon followed by a complete amorphization for n fluence greater than $\phi_n \geq 1 \times 10^{20}$ n cm^{-2} . Experiments [10-12] suggest that the amorphization proceeds from a progressive disordering of a highly defective β matrix.

The disordering of α -quartz by implantation of He^+ , B^+ and Ar^+ ions at room temperature has been investigated by Fischer *et al.* [13]. For this kind of ions, radiation damage is produced by nuclear processes only. The damage is dependent on the density of nuclear deposited energy. At low nuclear deposited energy, generation of point defects is predominant, then amorphized

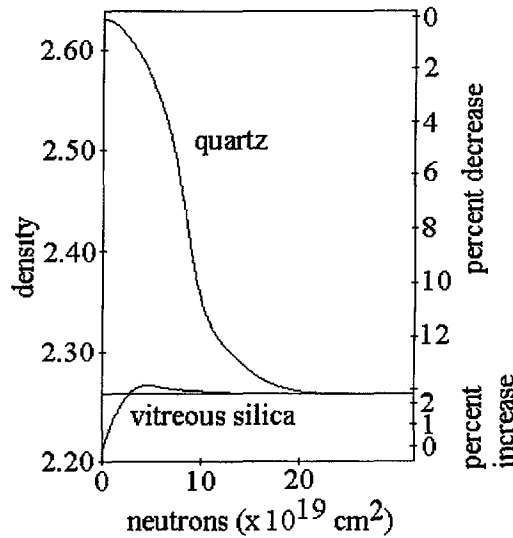


Fig. 1. — Change in density of α -quartz and vitreous silica upon irradiation by fast neutrons (after Lell [16]).

microregions are formed around each particle trajectory up to a complete transition of the damage material into an amorphous state at $2.5 \times 10^{23} \text{ eV cm}^{-3}$

Amorphization of quartz by ionization processes has also been reported. Douillard *et al.* [3] studied the modifications induced in α -quartz by an energetic ion bombardment, *i.e.* kinetic energies of several MeV/a.m.u. (electronic regime). Radiation damage is dependent on the electronic deposited energy and scales from point defect creation (E' centers, OHC . .) to latent track formation, *i.e.* formation of a continuous trail of an amorphous SiO_2 material.

Electron irradiation damages in quartz have been investigated *in situ* by Transmission Electron Microscopy (TEM) [4, 14]. Experiments suggest a progressive crystalline to amorphous transition of electron irradiated quartz. Amorphization is complete above $6 \times 10^{27} \text{ eV g}^{-1}$. Radiation damages scale with ionization cross-section, *i.e.* decrease with increasing electron energy and were therefore attributed to ionization mechanism.

Note that, from a close comparison of multiple irradiation experiments, it is now generally admitted that the amorphization of silica is complete for a deposited energy $\geq 3 \times 10^{23} \text{ eV cm}^{-3}$ into nuclear processes or $\geq 2 \times 10^{26} \text{ eV cm}^{-3}$ into ionization processes [15].

1b) Upon irradiation, α -quartz transforms into an amorphous state which is very similar to that resulting from the irradiation of silica. Direct density measurements [1, 16], as well as refractivity measurements [1] performed on neutron irradiated quartz and silica show no difference between both end products (see Fig. 1). Similarly, X-ray diffraction experiments carried on neutron irradiated quartz and silica exhibit identical scattering spectra within the experimental error [7]. In a study of ion implanted SiO_2 material, Katenkamp *et al.* [2] showed that in ion implanted quartz the refractive index approaches the value of implanted fused silica at high implantation dose.

1c) Amorphized quartz evolves into an amorphous form somewhat different from ordinary relaxed silica in that it exhibits a constant compaction effect of 3% to 4%. This compaction effect has been ascertained by numerous studies dealing with various measuring techniques and various particle irradiations. Primak [1] performed direct density and linear expansion

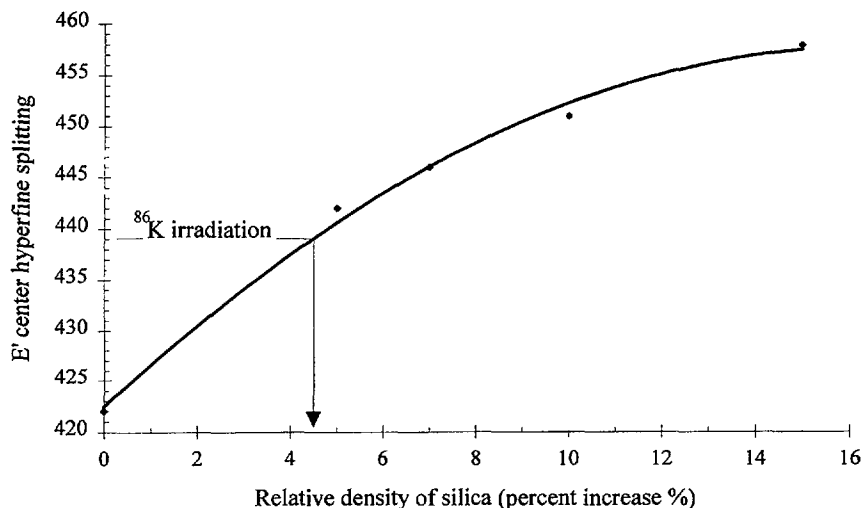


Fig. 2. — Variation of the E' ^{29}Si hyperfine splitting as a function of the relative density of silica (after Devine and Arndt [17]). ^{86}Kr (8.2 MeV/amu, 6×10^{12} ions cm^{-2}) irradiation of quartz induces a compaction effect of about 4% (Douillard *et al.* [3]).

measurements on neutron irradiated quartz. Experimental results show a decrease in the density of quartz by about 15% corresponding to a 3% compacted vitreous silica. Katenkamp *et al.* [2] studied the ion implantation damage by the refractive index technique. In ion implanted quartz the refractive index decreases slowly with the deposited nuclear energy and reaches a constant value at high dose ($> 4 \times 10^{24}$ eV cm^{-3}) similar to that measured for high dose implanted silica. This refractive index change corresponds to a decrease of the density of implanted quartz, whereas it indicates a compaction effect for fused silica. Douillard *et al.* [3] estimated the density of the material constituting the core latent tracks in swift ion irradiated quartz. By measure of the increase of the Electron Spin Resonance (ESR) E' center hyperfine splitting and comparison with experimental data collected on plastically densified silica [17], a mean compaction effect of about 4% was determined (see Fig. 2). Eernisse and Norris [6] used stress measurement to determine the specific volume change of ion and electron irradiated silica. Experimental results give a unique and constant compaction percentage of about 3.4% after either ion or electron bombardment. Compaction effect of SiO_2 material after photon irradiation has also been ascertained by ESR [5] (qualitative comparison of ESR E' center signatures) and birefringence experiments [18].

2. Structural Analysis of Particle Amorphized α -Quartz

The crystallographic structure of α -quartz, schematized in Figure 3, corresponds to an ordered lattice of corner-sharing SiO_4 tetrahedra. The hexagonal unit cell is defined by $a = 4.913$ Å and $c = 5.405$ Å [19]. The structural tetrahedral unit is nearly perfect. First Si-O interatomic distances are distributed in two close sets: 1.608 Å (2 bonds) and 1.611 Å (2 bonds); the intratetrahedral angle (O-Si-O) ranges from 108.74° to 110.54° and is therefore not significantly different from the value expected for a regular tetrahedron (109.34°). The corner-sharing tetrahedra form threefold spirals around the optical axis Z . This spatial arrangement determines an inter-tetrahedral (Si-O-Si) angle θ of 143.6° and a second interatomic distances Si-Si of 3.06 Å.

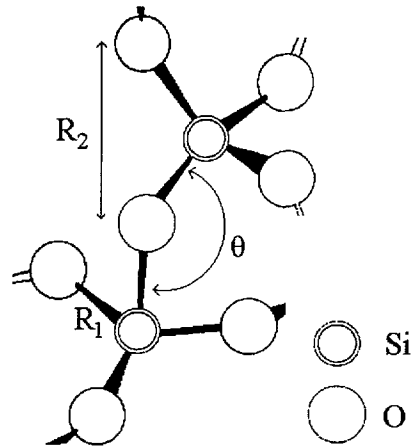


Fig. 3. — The relative orientation of two corner sharing tetrahedra $\text{Si}(\text{O}_{1/2})_4$ in α -quartz. $R_1 = 1.61 \text{ \AA}$ is the first interatomic distance Si-O, $R_2 = 2.60 \text{ \AA}$ the tetrahedral O-O edge and θ (Si-O-Si) the intertetrahedral angle between two adjacent tetrahedra.

The short-range order of the irradiation end product of α -quartz has been extensively investigated. X-ray [7], neutron [20] and electron [21] diffraction experiments indicate that the tetrahedral structural unit SiO_4 is very robust, *i.e.* is preserved intact upon irradiation. The first interatomic distance Si-O keeps a constant mean value of 1.61 \AA corresponding to the common first bonding interatomic distance encountered in many SiO_2 forms [19]: silica, quartz, cristobalite, tridymite... Only one study [3], based on an EXAFS structural analysis, suggests a slight increase by $0.02 \text{ \AA} \pm 0.01 \text{ \AA}$ of the first interatomic distance Si-O after irradiation by swift heavy ions. The oxygen coordination number is found to remain essentially unchanged or decreases slightly upon irradiation.

Most structural modifications concern the second interatomic distances. The distance from a silicon atom to the next nearest silicon atom (Si-Si) is smaller by about 0.05 \AA (3.01 \AA instead of 3.06 \AA) in irradiated quartz. This feature has been widely interpreted as a consequence of the decrease in the averaged inter-tetrahedral angle θ (Si-O-Si). According to the previously mentioned diffraction and EXAFS experiments, as well as Nuclear Magnetic Resonance experiments [9], the reduction of the inter-tetrahedral angle (Si-O-Si) is estimated to range from 7.5° to 12° . Similarly to the Si-Si distance, the second O-O interatomic distance initially 2.6 \AA in α -quartz and common silica is found to decrease slightly (-0.05 \AA) upon irradiation.

In addition, the end metamict state contains an important residual point defect concentration. Various ESR studies estimate the residual E' point defect concentration to be about $1 \times 10^{18} E'/g$.

Note that the structures of the amorphous end products are not rigorously equivalent. As shown recently by Hobbs [21], slight but significant structural differences exist between electron and neutron irradiated quartz.

Due to the amorphous nature of the irradiated material, very few is known about the intermediate range order of the irradiation end product. Comparison of diffraction profiles shows that the structure of the correlation function for irradiated quartz exhibits a strong amplitude reduction when compared to common vitreous silica, *i.e.* the more distant neighbor atom distributions are wider in disordered quartz than in vitreous silica [7,20]. This accounts for a

Table I. — *Local clusters, full ring descriptions and primitive ring densities of several common silica polymorphs (local clusters and full ring descriptions after Hobbs [21]).*

Silica polymorph	Number of primitive rings	Local cluster size (tetrahedra)	Density	Primitive rings / Å ³
Quartz	6 × 6-rings and 40 × 8-rings	63	2.65	1.22
Cristobalite	12 × 6-rings	29	2.32	0.26
Tridymite	12 × 6-rings	27	2.26	0.27
Metamict SiO ₂	~ 6-rings		2.26	
silica	< 6-rings		2.21	

lower degree of intermediate range order, probably corresponding to an increase in the inter-tetrahedral rotational disorder. More recently, Devine and Marchand [22] have given evidences for structural similarities between Chemical Vapor Deposited (CVD) and n irradiated SiO₂. According to the authors, the three membered ring density is significantly enhanced in both CVD and n irradiated silica with respect to bulk and relaxed silica and a considerably larger fraction of free volume is expected.

3. Discussion

3.1. RING DESCRIPTION OF SILICA POLYMORPHS. — During metamictization, quartz undergoes a crystalline to amorphous transition. Thus, classical crystalline models are no more relevant, and one needs a unified description of both periodic and aperiodic solids to further investigate such amorphization process. In the case of fully-connected silica networks, structures (whether periodic or aperiodic) can be uniquely described by a characteristic *local cluster based on a ring description* of the intermediate range order [23,24]. Indeed, the network of a silica polymorph can be viewed as to be composed of rings of corner sharing tetrahedra. The structurally significant rings, *i.e. primitive rings*, are those passing through the same single tetrahedron which cannot be decomposed into smaller rings. The medium range order of a specific silica polymorph is fully and uniquely defined by the set of all primitive rings. This set of primitive rings is called the *local cluster*. Table I reports the local clusters and full ring descriptions of several common silica polymorphs. For instance, the local cluster of cristobalite consists of 12 × 6-primitive rings comprising a total of 29 tetrahedra. Note that density scales with the ring size, *i.e.* larger rings mean higher density.

3.2. INTERMEDIATE RANGE ORDER. EXPERIMENTAL RESULTS. — The most striking features of the structural analysis carried on metamict quartz are: 1) the keeping of a *regular tetrahedron as a structural unit*, 2) the important *decrease of the mean inter-tetrahedral angle* θ (Si-O-Si). The latter change is accompanied by a broadening of the second Si-Si distance distribution which reflects the progressive loss of crystallinity. This broadening is probably responsible for the apparent decrease in the second O-O interatomic distance, *i.e.* the interatomic distance corresponding to the tetrahedral edge, see Figure 3. The slight increase of the first interatomic R_1 (Si-O) distance does correlate with the closure of the mean inter-tetrahedral angle θ (Si-O-Si). Indeed, according to Hill [25], these latter two structural parameters (R, θ) are related by the relation $\log(2R(\text{Si}-\text{O})) = 0.504 - 0.212 \cdot \log(\sin(\theta/2))$. Use of this relation

correlates a first interatomic $R_1(\text{Si} - \text{O})$ distance reduction of $\Delta R_1 = +0.02 \text{ \AA} \pm 0.01 \text{ \AA}$ with a closure of the mean inter-tetrahedral angle $\theta(\text{Si} - \text{O} - \text{Si})$ of $\Delta\theta = -17.5^\circ \pm 9^\circ$.

Thus, experimental results give a coherent view of the modification of the intermediate range order in quartz during the metamictization process. They suggest a decrease of the mean size of the primitive rings of the metamictized network with respect to quartz. As suggested by Hobbs [24], this reduction will be accompanied by the appearance of fractions of both smaller and bigger rings indispensable to accommodate the main shift in the ring distribution.

3.3. POINT DEFECT MODEL FOR THE METAMICTIZATION OF QUARTZ. — The fact that irradiation of quartz by ions, neutrons, electrons or photons gives nearly equivalent end products suggests that metamictization of quartz (as well as silica) may proceed through the same specific mechanism. To date previous works dealing with particle induced quartz amorphization refer to particle dependent mechanisms. As mentioned in Part 1, nuclear processes, *i.e.* atomic displacement cascades, have been used to interpret neutron and low energy ion irradiation damages, while ionizing processes are invoked to take into account irradiation damages by electrons and swift heavy ions. One common point to these irradiation mechanisms is the trend toward *stable point defect formation*. Thus, we suggest that the stable point defect may be the key idea to a unique description of particle induced quartz amorphization. Generalizing earlier conclusions by Hobbs and Pascucci [4], Douillard and Duraud [26] have proposed to identify this specific mechanism with *a structural relaxation process of a highly defective SiO₂ matrix triggered by a critical point defect concentration*. In a first step, the induced point defects progressively lower the network connectivity. This ends when the solid can no longer accommodate supplementary point defects and rearrangement of the damaged network takes place. This loss of crystallinity through multiple reorientation and rebounding of the corner sharing SiO₄ tetrahedra will pursue till complete loss of topological order, *i.e.* complete metamictization of the solid [24]. Careful comparison of significant particle irradiation experiments has allowed the authors [26] to estimate the lower value of the paramagnetic part of the involved critical point defect concentration to be of the order of $1 \times 10^{18} E'/\text{irradiated } g$. This two step point defect mechanism gives a qualitative interpretation of the unicity of the particle amorphization end products of quartz, and makes understandable the observed structural differences between particle and plastically compacted silica [26]. It explains as well the difference of three orders of magnitude observed between the nuclear and ionizing doses necessary to complete the silica metamictization. As a matter of fact, this ratio appears close to that found when comparing oxygen vacancy creation efficiencies by the two different irradiation processes [27] and so further suggest the important role played by point defect (like oxygen vacancies) in the damaging process of SiO₂ polymorphs.

It is worth noting that the present analysis by using the stable point defect as the basic idea for the interpretation of particle induced quartz amorphization shares common points with previously published models. For instance, in the case of a swift ion irradiation the Self-Trapped Exciton (STE) model [28], dealing with enhancement of transient point defect generation by excitation interaction, reduces to the present point defect analysis after the introduction of a transient-to-stable point defect conversion factor.

In our previous study [26], we focused on the most significant experimental facts. Following is a more complete description of the point defect mechanism taking into account: a) the influence of the crystalline precursor, b) the influence of the nature of the irradiating particles.

a) *Influence of the crystalline precursor.* — The resistance to the metamictization of a particular silica polymorph is a function of the relative importance of the topological redundancy of its intermediate range order, *i.e.* its local cluster. As a matter of fact, the *local cluster*

constitutes the *topological unit* of the network. Thus the minimum disorder necessary to initiate the metamictization process should correspond to the disordering of a local cluster size fraction of the irradiated solid. The critical concentration necessary to initiate the metamictization should thus correspond to the minimal point defect concentration providing the requisite freedom for the rearrangement of such a local cluster volume. In this view, the shape of the local cluster determines the resistance to the amorphization. Larger primitive rings can more easily convolute and double back on themselves leading important structural redundancy and allowing significant denser packings. As seen in Table I, the local cluster of both cristobalite and tridymite consist of 12×6 -primitive rings comprising 29 and 27 tetrahedra, respectively. In the case of quartz, the local cluster is dominated by larger 8-primitive rings. It contains exactly 40×8 -rings and 6×6 -rings encompassing a total of 63 tetrahedra. If one considers the fraction of primitive ring per unit volume as a measure of the structural redundancy of a local cluster, then cristobalite came first with $0.26 \text{ primitive ring} \cdot \text{\AA}^{-3}$, then tridymite $0.27 \text{ primitive ring} \cdot \text{\AA}^{-3}$ and finally quartz $1.22 \text{ primitive ring} \cdot \text{\AA}^{-3}$. Experimentally, complete electron metamictization takes place according to the above order, *i.e.* cristobalite first, then tridymite and quartz being the slowest [21]. Thus, the point defect mechanism is likely to take into account the influence of the crystalline SiO_2 precursors in the analysis of the particle induced quartz amorphization.

b) *Influence of the nature of the irradiating particles.* — The way the critical point defect concentration is created is particle dependent. Two main regimes should be distinguished: 1) during irradiation by particles such as electrons or photons, point defects are created randomly through the whole irradiated fraction of the quartz sample. The point defect concentration is spatially uniform and increases monotonically, exhibiting generally a power law dependence with particle fluence. This *accumulating point defect concentration* keeps increasing till the requisite critical concentration is reached, 2) in marked contrast with this accumulating process, irradiation by fast neutron, respectively by swift heavy ions, produces locally (\sim local cluster size) and instantaneously an important point defect concentration likely to exceed the critical one. So, the metamictization should be rapidly initiated giving way to progressive amorphization, respectively latent track formation.

The study by Douillard *et al.* [3] of the irradiation damage produces in quartz by respectively swift high Z (atomic number) ions and low Z ions gives an illuminating example of the balance between *accumulating and no accumulating damaging processes*. For swift heavy ions, *i.e.* high electronic stopping powers, the number of point defects created by ionizing process along the ion path is very important and could largely exceed the critical point defect concentration. Further local metamictization should rapidly take place, materializing irradiation damage as latent tracks. For light ions, *i.e.* small electronic stopping powers, the induced point defect concentration is too low to trigger local metamictization and no latent tracks are observed. From a solid state point of view, low Z ion irradiation of quartz appears to be equivalent to photon or electron irradiation (point defect creation).

According to this model, the latent track radius does correspond to the spatial extension of the small metamictized volume centered on the ion path. Since metamictization takes place in the region where the initial point defect concentration exceeds the critical one, the knowledge of 1) the radial energy loss distribution curve for a particular ion, and 2) the average point defect creation efficiency should, permit to correlate latent track radius with ion stopping power. To date, several alternative models have been successfully used to predict the radii of latent tracks

induced in quartz by swift heavy ions: 1) a STE model [28], 2) a thermal spike model [29] and 3) a critical energy model [30]. Due to close physical relationship with the STE model, the proposed point defect model will predict similar latent track dimensions for quartz. Further precise quantitative estimates will be necessary to validate or invalidate the proposed point defect mechanism.

3.4. STRUCTURAL MODEL OF METAMICT PHASE. — As pointed out by Hobbs [24], the metamict quartz should largely share the structural characteristics of the *modulated structure* proposed by Mariani and Burdett [23] for vitreous silica. The modulated network model consists of domains of ordered regions linked by interfacial less ordered regions. The ordered regions, while not fully crystalline, exhibit cristobalite-like or tridymite-like structure, *i.e.* 6-ring local clusters. The interfacial regions should contain rings of other sizes larger as well as smaller in the case of metamict phase. Depending on the relative fraction of ordered *versus* non ordered regions, a large variety of metamict structures can be considered. We suggest that the slight but significant structural differences reported between *n*-amorphized quartz and e^- -amorphized quartz, as well as between e^- -amorphized quartz and e^- -amorphized cristobalite or tridymite [24], correspond to different modulated structures. In other words, different metamict stages could be achieved depending on crystalline precursors, irradiating particles and absorbed doses yielding to different medium range orders of the damaged SiO_2 polymorph.

Experimental support for such a *metamictization scale* can be found in the annealing behavior of *n*-amorphized quartz. As a matter of fact, all annealing experiments can be interpreted by considering that with increasing the *n*-absorbed dose, the irradiated quartz contains smaller and smaller fraction of ordered regions likely to provide recrystallization nuclei until, eventually, no recrystallization can occur by annealing [1]. Interestingly, two *n*-irradiated quartz samples (quartz A at a dose of $1 \times 10^{20} \text{ n cm}^{-2}$ and quartz B at a dose of $2 \times 10^{20} \text{ n cm}^{-2}$), while both exhibiting the density of metamict SiO_2 material, present quite different annealing behaviors. On annealing quartz B becomes indistinguishable from ordinary vitreous silica, while quartz A although essentially amorphous exhibits a slightly greater medium range order than silica. This experimental fact shows that different metamict phases can possess similar macroscopic properties. It shows also that annealing experiments can be used to distinguish between different metamict states.

With increasing absorbed dose, SiO_2 polymorphs should evolve to the same ultimate metamict state, but due to the lack of correlated diffraction and annealing experiments, no definitive evidence can be given concerning the existence of such a single ultimate metamict phase.

4. Conclusion

Upon particle irradiations, α -quartz transforms progressively into a single particular amorphous state, known geologically as *metamict*. This metamict state is somewhat different from an ordinary vitreous silica in that its density is slightly higher by 3% to 4%. Extending previous conclusions obtained for electron irradiated quartz [24], we suggest that the structure of the metamict quartz corresponds to a *modulated SiO_2 network structure*, where ordered regions are linked by interfacial less ordered regions. We propose to identify the metamictization process to a *structural relaxation process* of a highly defective SiO_2 matrix. This *point defect model* should be triggered by a *critical oxygen vacancy like point defect concentration* providing structural freedom through the decrease of the SiO_2 network connectivity. Taking into account the influence of the *crystalline SiO_2 precursor*, as well as the *nature of the irradiating particle*, the point defect mechanism may explain the slight structural differences between metamict

states reported in the literature [21, 24]. Crystalline SiO₂ precursors determine the resistance to the metamictization of a particular SiO₂ polymorph with respect to the same irradiating particle. The nature of the irradiating particle determines the way the requisite critical point defect concentration is created in a particular SiO₂ polymorph and two regimes should be distinguished: an *accumulating process* (electrons, photons, light ions) and a *no accumulating process* (neutrons, heavy ions). An accumulating process gives a rather uniform metamictization, while a no accumulating process gives way to non isotropic metamictization observed as *latent tracks*. Depending on the crystalline precursor, the nature of the irradiating particle, as well as the absorbed dose, different metamict stages could be achieved, *i.e.* different intermediate range orders.

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