

Amorphous Polymorphism: Norbert Kreidl's Hypothesis, Experimental Proof, New Theory

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1. Introduction. Polymorphism "glass-glass" – Kreidl's hypothesis

The study of radiation effects in crystalline silica and silica glass began fifty years ago, and the first researchers [1-3] interpreted the observed effects as "irradiation damage" to its structure. The interpretation seemed to be the only one possible since it was drawn from the analogy with amorphization, that is, disordering of irradiated silica crystals of quartz, cristobalite and tridymite (see the review by Lell, Kreidl and Hensler [4]). There are two fundamentally intriguing facts which have not been considered at a time and which could have undermined the concept of "irradiation damage". The first fact: the high-pressure silica polymorphs stishovite and coesite do not amorphize in a fast neutron fluence. High temperature and high pressure inside this fluence provide conditions for evaporation of silica however after its condensation crystallization readily recurs while no amorphous matter is formed. The second fact: amorphous structure that is obtained by fast neutron irradiation of quartz is identical not only to those of irradiated cristobalite and tridymite but also to that of irradiated silica glass (fused quartz). All properties stabilize with fluence reaching $2.2 \times 10^{20} \text{ n/cm}^2$, regardless of the original modification. Figure 1, replicated from [4], illustrates this fact using density as an example. It shows the density changes attendant upon neutron irradiation of quartz and silica glass. Similar dependencies can be plotted for other properties that are influenced by irradiation as described in [4]. In this work, Kreidl with co-authors not only reviewed and discussed almost 300 publications but also suggested a pioneer idea of the formation of amorphous polymorphs of a glass as an alternative to its irradiation damage.

The hypothesis of polymorphism "glass-glass" was formulated in [4] as follows: "The fact that all forms of silicon dioxide are transformed to optically isotropic glass-like

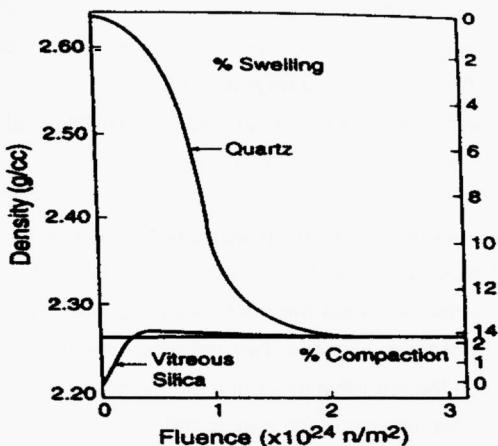


Figure 1. Density changes in neutron-irradiated quartz and silica glass [4].

material with virtually identical density, thermal expansion, elastic properties and absence of X-Ray pattern led to the conclusion that neutron irradiation produces a new phase of silicon dioxide which is independent of the original phase before irradiation.” The next sentence in [4]: “This new phase was named metamict phase, adapting the earlier designation for minerals disordered by radiation in the geological past” contains certain inaccuracy. The term “metamict” was indeed adapted from geology and this is well described in [5]. In the glass science literature, however, the words “metamict phase of silica” were applied solely as a descriptive term, in other words, the formation of metamict silica was never considered a phase transition.

2. Polymorphism “glass-glass” – Critical Experiments

Kreidl’s hypothesis required staging some critical experiments in order to prove the following positions.

1. Monotonous change in the properties of macro-samples that is experimentally observed in transformation “silica glass ↔ metamict silica” is a result of a change in concentration of each phase during discrete changes in the structure of micro-areas (the changes in the local structure).

2. There is latent heat of a transition “metamict silica ↔ silica glass” that occurs upon heat treatment of metamict silica.

3. Metamict silica being an independent phase of silica can be obtained not only radiolytically but by other methods and ways as well.

Such experiments were performed and proved the existence of polymorphism “glass-glass” that can be named “Kreidl’s polymorphism”.

2.1. Change in homogeneity of amorphous silica irradiated by fast neutrons

As a result of irradiation by fast neutrons, the density of silica glass changes from 2.20 g/cm³ to 2.26 g/cm³, while the refractive index changes from 1.458 to 1.468. Studying the kinetics of these changes does not allow determine whether it is the monotonous change in the refractive index of a mono-phase system or a change in the ratio between the two phases of the system “silica glass-metamict silica” that is responsible for the changes in physical properties.

In order to address this issue, in our study of irradiated silica [6] we used Shelyubskii’s method for determining homogeneity of glass [7]. The method allows measure heterogeneity index, σ^2 , of a bi-phase system that is given by

$$\sigma^2 \equiv (n_1 - n_2)^2 q_1 q_2 \quad (1)$$

where n_1 and n_2 are refractive indices, q_1 and q_2 – concentrations of the phases 1 and 2, correspondingly. In the experiment, σ^2 is determined from the intensity of scattered light therefore the values in the right part of Equation 1 are not considered in the calculations of heterogeneity index. Figure 2 shows the dependency of σ^2 on the fast neutron fluence in the progress from silica glass (phase 1) to metamict silica (phase 2). The existence of a maximum on curve 1 and its position agrees with the concept of glass-to-glass phase transition: n_1 and n_2 are constant, $(n_1 - n_2)^2 \equiv 10^{-4}$, $q_1 \equiv q_2 \equiv 0.5$, hence $\sigma^2 \equiv 22.5 \times 10^{-6}$ while the fast neutron fluence is 5×10^{-19} n/cm². With this fluence, the density of silica is 2.23 g/cm³ that being also the mean density for silica glass and metamict silica.

Metamict silica is a more homogeneous phase than silica glass and this is not a result of “dissolution” of heterogeneous inclusions that are normally present in silica glass, as it was suggested by Porai-Koshitz in [8], but rather a result of a phase transition during which concentration of phase 2 increases thus causing, at first, an increase in heterogeneity index of the bi-phase system as a whole. The process

suggested in [8] is based on the random network model of glass structure and it would have been described by a hypothetical curve 2 on Figure 2. Experimental data (curve 1) support the hypothesis of amorphous polymorphism and prompt to revert to the model of crystal similarity of the local structure in amorphous silica.

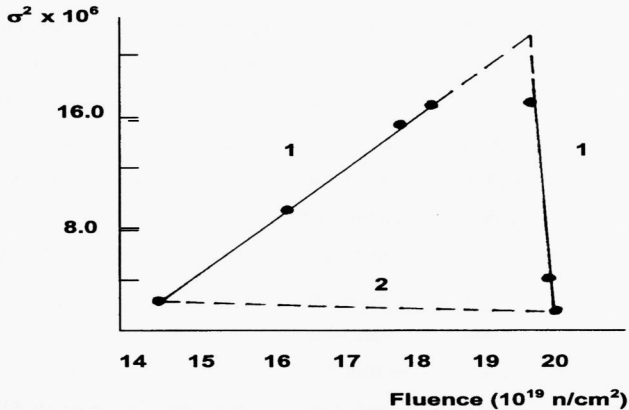


Figure 2. Changes in heterogeneity index in neutron irradiated silica glass transforming to metamict silica [6]. 1- experimental data indicating phase transition; 2 – hypothetical monotonous transformation.

2.2. Structural Model and Thermodynamics of Amorphous Polymorphism

The classical crystallite hypothesis of glass structure reached an impasse in consequence of the fact that it did not give (and could not give) a definition of a crystallite. This difficulty becomes critical in consideration of a long-range order, that is, of an elementary cell for which translation is its basic property. Diffraction methods have shown [9] that this very property is not realized in glass: the size of areas having local order does not exceed 7-8 Å thus corresponding to the size of one elementary cell in cristobalite. It is possible, however, to identify a crystal within one or two coordination spheres without a reference to the translation symmetry of a Bravais cell. For silica, this can be done in the following way [10].

K-structures (low-pressure) are defined by the cycles of 12 and 14 tetrahedra (2 primitive rings of 6 and 8 tetrahedra with common oxygen for quartz; 2 rings of 6 tetrahedra each for cristobalite).

Q-structures (high-pressure) are defined by the cycles of 8 tetrahedra (2 silicon-, or tetrahedron-sharing rings of 5 or 4 tetrahedra for keatite; 2 rings of 4 tetrahedra each for coesite).

S-structures (more dense high-pressure) are unique among silicas because of their six-fold coordination of silica to oxygen (stishovite).

Since the suggested classification does not comprise long-range order parameters, it can be related to the description of amorphous matters such as glasses and melts. Using this approach, Landa [11] proposed a crystalloid concept of the glass structure. In this model crystalloid is a genetic structural unit which is the same for a melt, crystal and glass of a given composition. The crystalloid concept differs from the crystallite model by lacking translation symmetry and from the random network model by extending beyond the first two coordination spheres. The size of a crystalloid in quartz and cristobalite is, correspondingly, about 635 \AA^3 and 545 \AA^3 .

Since according to Warren [9], the size of a short-range order domain in silica glass is about $2000\text{-}2500 \text{ \AA}^3$, it is plausible that it can comprise four crystalloids.

The crystalloid concept predicts and explains the phenomenon of amorphous polymorphism. In the structural model suggested in [10] it is assumed that if melting of a crystal occurs under pressure of its stability and the melt is then quenched under the same pressure, it transforms into a glass with the same local structure as that of the original crystal and the intermediate melt. According to this model, metamict is considered a glass having local structure of a high-pressure silica phase, coesite, that is, a Q-structure while silica glass is considered a K-structure. Therefore, a structure similar to metamict silica can be formed under high pressure. Besides, at normal pressure, this amorphous structure may be thermodynamically more stable than the K-structures of the silica family, including crystalline.

Figure 3 replicated from the review [11] shows experimental data published by Landa et al. in 1984-1986. These are the results of calorimetric study of the transitions of amorphous Q-structures obtained by different methods into silica glass. Q-glass to K-glass transition occurs in a temperature range 900-1200 K and is accompanied by heat absorption, with endothermic effect of 15.2 kJ/mol for ultra-dispersed powder and 16.5 kJ/mol for monolithic glass. This is 1.5 times larger than latent heat of melting cristobalite. As it was suggested earlier [6, 10], various high-pressure phases of amorphous silica can be considered Q-glasses with local structure of keatite or coesite, for example, ultra-dispersed powders having specific

surface of about 300-380 m²/g, vapour-deposited silica films, monolithic samples of either metamict silica or silica glass heat treated under high pressure.

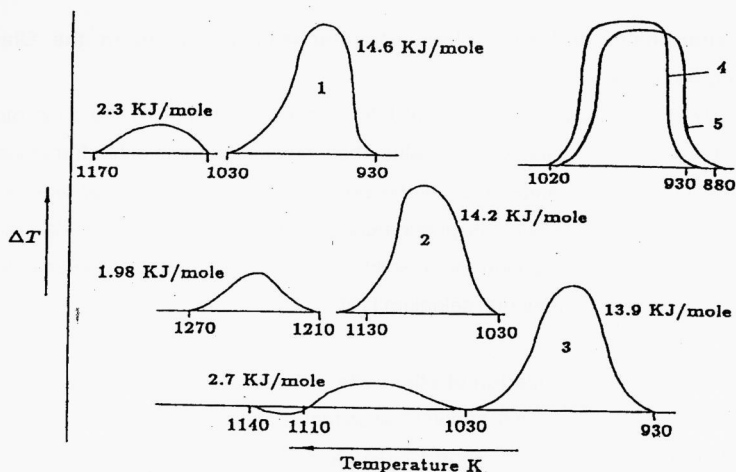


Figure 3. DSC data on enthalpic transition of Q-glass to K-glass [11].

Methods of obtaining Q-glass from silica glass:

1,2 – high pressure, high temperature treatment for 2 hours; 1 – T=920 K, P=0.2 GPa; 2 – T=1010 K, P=0.22 GPa;

3 – fast neutron irradiation (fluence 2.2×10^{20} n/cm²);

4,5 – ultra-dispersed silica with specific surface 300 m²/g (4) and 380 m²/g (5).

Standard Gibbs energy, G, of metamict silica is lower than that of silica glass by 16 kJ/mol and lower than that of crystalline quartz by at least 8 kJ/mol. Anomalous correlations between thermodynamic functions of a crystal and a glass do not contradict the principles of classic thermodynamics. Since $(\partial G/\partial T)_T = V$ and $(\partial G/\partial T)_P = -S$, a decrease in temperature results in stabilization of the phase with the lower entropy (crystal), while a decrease in pressure results in stabilization of the phase with the greater volume (glass or liquid). The latter is the case of Q-glass that is quenched from the high pressure of its formation [11]. One of the first works dedicated to high-pressure amorphous polymorphism of silica [12] reported the formation of a glassy phase that was, evidently, an S-glass with the local structure of stishovite. Thus independent experiments and structural models support Kreidl's

hypothesis of amorphous polymorphism "glass-glass" and bring it to the level of a theory.

3. Polymorphism and Anomalous Thermochemical Effects in the Glass-Forming Systems

Previously [11] we have observed that latent heat of a change in the short-range order can be greater, by its absolute value, than the latent heat of either formation or destruction of the long-range order. If the signs of the above referenced latent heat values are opposite, anomalous phenomena, such as endothermic crystallization and exothermal amorphization of a solid may occur. Those phenomena were observed in silica and elemental selenium [13].

3.1. Exothermal amorphization of stishovite into silica glass

Stishovite is a rutile-like modification of silica that is stable at pressures higher than 10 GPa in a temperature range 1300-1900 K. At 1070 K, stishovite transforms into a glassy state during one hour [14]. According to Hess's law, the enthalpy change in this process can be given by either of the following expressions:

$$H^{\text{st}}(298) + \int_{298}^{1072} C_p^{\text{st}}(T) dT + \Delta H^{\text{am}}(1072) = H^{\text{gl}}(1072) \quad (2)$$

$$\Delta H^{\text{am}}(1072) = H^{\text{gl}}(1072) - H^{\text{st}}(298) - \int_{298}^{1072} C_p^{\text{st}}(T) dT \quad (2a)$$

where $H^{\text{st}}(298)$ and $H^{\text{gl}}(1072)$ are the enthalpies of stishovite at 298 K and of glass at 1072 K, correspondingly, $\Delta H^{\text{am}}(1072)$ is the latent heat of amorphization of stishovite, $C_p^{\text{st}}(T)$ is specific heat for stishovite, and the integral represents the enthalpy change of stishovite during its heating from 298 K to 1072 K.

According to [14], $H^{\text{gl}}(1072) - H^{\text{st}}(298) = 8.4$ kJ/mol. Since specific heat of stishovite at high temperatures is unknown one can use the value of specific heat of stishovite at 298 K instead. $C_p^{\text{st}}(298) = 42.9$ kJ/mol, hence Equation 2 can be re-written as follows

$$\Delta H^{\text{am}}(1072) < H^{\text{gl}}(1072) - H^{\text{st}}(298) - C_p^{\text{st}}(298) \Delta T \quad (3)$$

Specific heat of stishovite increases with an increase in temperature, therefore the integral $\int_{298}^{1072} C_p^{\text{st}}(T) dT$ in Equation 2a is larger than the component $C_p^{\text{st}}(298) \Delta T$ in Equation 3, and the equality (2) transforms into inequality (3).

Latent heat of the amorphization of stishovite can be estimated based on the experimental data available [11, 14]: $\Delta H^{\text{am}}(1072) < -24.8$ kJ/mol, and though the exact value is uncertain, the exothermic nature of the process itself is quite certain.

3.2. Endothermic Crystallization of Red Selenium into Monoclinic Metastable Phase

In [13], red amorphous selenium was obtained from its black glassy modification in two steps. At first, black selenium was dissolved in sulfuric acid (density 1.84 g/cm³) and green solution of SeSO₃ was obtained. This solution was cooled down and diluted with water. Residue of red selenium was thus formed. It was washed in deionized water and ethanol and dried in a dessicator. Crystallization was conducted in a Calve calorimeter at 312 K over 42 minutes. Figure 4 shows the experimental data. Crystallization of about 30% of selenium was accompanied by absorption of 0.35 kJ/mol therefore it is reasonable to assume that completion of the process would require heat absorption of about 1 kJ/mol. Considering that endothermic effect of crystallization was recorded in a direct experiment, no thermochemical calculation was necessary.

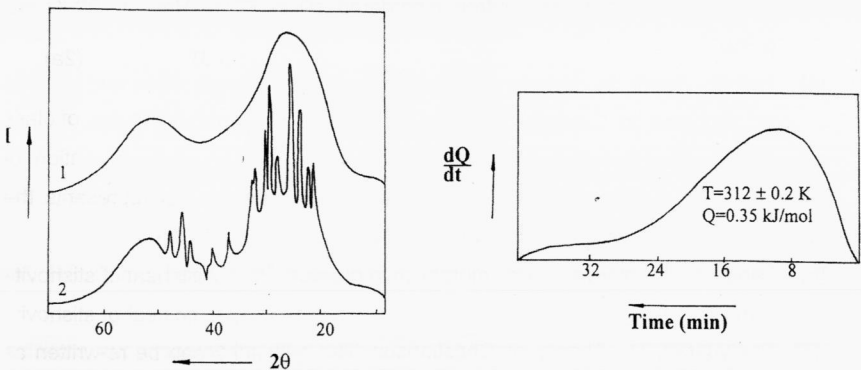


Figure 4. Crystallization of amorphous selenium [13].

- 1 – X-Ray diffraction pattern of the original amorphous selenium;
- 2 – X-Ray diffraction pattern of selenium after heat treatment at 312 K for 42 min;
- 3 – Endothermic peak of crystallization of amorphous selenium, calorimetric data.

4. Conclusion

The concept of amorphous polymorphism was proposed by Norbert Kreidl and co-authors back in 1966. In the following years, several researchers have contributed to the understanding of the phenomenon and proof of concept. The development of the concept continues at present (see, for example, 15-17). Further development planned by the authors will consider the systems glass-liquid based on the Landau's theory of the second order phase transitions. The authors had an honour and a pleasure of discussing the phenomenon of amorphous polymorphism and their experimental results and ideas with Norbert Kreidl at several international conferences. His vision and kind support was invaluable. This paper is an attempt to remind and remember Norbert Kreidl's contribution to the glass science and his impact on the lives of the glass scientists.

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