PHYSICAL REVIEW VOLUME 133, NUMBER 2A 20 JANUARY 1964

# Ionization Expansion of Compacted Silica and the Theory of Radiation-Induced Dilatations in Vitreous Silica*

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(Received 22 July 1963)

Vitreous silica compacted by pressure at room temperature expands at a very rapid rate when irradiated with soft x rays or in a reactor, about in the ratio of the ionization doses received. A dose $\sim\frac{1}{2}\,10^{22}$ eV/cm$^3$ (i.e., $10^8$R) of absorbed ionization energy caused the "release" of about 1/3 of the compaction.

It is shown that the effect cannot be explained as a static electrostatic effect or a transient general thermal annealing effect (thermal spike). It must be a rapid transient effect associated with the local distortion or energy deposition of the ionization event. The efficiency of the process indicates that each ionization in moderately pressure-compacted silica (4–9%) must be effective or multiply-effective in "releasing" compaction. The relation of the compacted states of silica—pressure compacted, radiation compacted, shock wave compacted—is discussed.

## INTRODUCTION

WHEN vitreous silica is placed in a nuclear reactor, its density increases by some $2\frac{1}{2}$–3%.[1–4] Changes are also observed in x-ray diffraction patterns[5,6] and in infrared absorption spectra[2,6]; and it was pointed out by Simon[6] that these changes are the same as those found when silica is compacted by the application of high pressure.[7] It thus became of interest to (a) compare the compacted silica with radiation-damaged silica, and (b) to study the effect of radiation on the compacted silica.

Keiffer, Szymanski, and their students[8] studied the behavior of compacted silica when it was heated. They found that it behaved quite unlike silica irradiated in a nuclear reactor. Silica irradiated in a nuclear reactor begins to anneal between 300 and 400°C, and the annealing is not completed until the temperature is raised above 1000°C. Their compacted silica began to anneal not far above room temperature ($\sim$100°C) and the annealing was 3/4 completed by 650°C. The percent of compaction annealed plotted against temperature was nearly linear. A broad range of activation energies was indicated. Preliminary calculations of the frequency factor required to relate portions of the activation energy distribution calculated on the basis of the theory of large temperature range annealing for successive step annealings gave unexpectedly low values, $\ll 10^8$, and this should be reinvestigated.

The compacted silica used by Keiffer, Szymanski, and their students was from the same samples which are described here.

## EXPERIMENTAL

### Material

Four small cylinders were cut from each, Corning high-purity silica and Herasil (Heraeus Quarzschmelze, Hanau, Germany).[9] These were forwarded to R. H. Wentorf, Jr., at the General Electric Company Research Laboratory in Schenectady who subjected the cylinders (surrounded with pyrophyllite and hexagonal boron nitride) individually to high pressures. For most, pressures of 100 000 to 110 000 atm were reached in 2–4 min, held for 8 min, and then decreased to atmospheric in about 12 min. Two of the specimens blew out at 85 000 atm.[10] All of the specimens were fragmented. The experiments described here were performed with small individual grains of silica selected from these fragments. The density varied considerably from one grain to another, even from the same compression run. Some grains were found which possessed densities over 9% greater than ordinary vitreous silica, others as little as 3/4% greater than ordinary vitreous silica. It is probable that even within a single grain the density was not uniform and that the grains were badly strained.

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* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

† AEC Contract No. At 30-1-1810.

[1] W. Primak, L. H. Fuchs, and P. Day, Phys. Rev. **92**, 1064 (1953).

[2] W. Primak and L. H. Fuchs, J. Am. Ceram. Soc. **38**, No. 4, 135 (1955).

[3] W. Primak, Phys. Rev. **110**, 1240 (1958).

[4] W. Primak and E. Edwards, Phys. Rev. **128**, 2580 (1962).

[5] J. S. Lukesh, Phys. Rev. **97**, 345 (1955).

[6] I. Simon, Phys. Rev. **103**, 1587 (1956); J. Am. Ceram. Soc. **40**, 150 (1957).

[7] I. Simon and P. W. Bridgeman, J. Appl. Phys. **24**, 405 (1953).

[8] D. Keiffer (unpublished work); A. Roaldi and Szymanski (unpublished work); R. L. Kuczkowski, thesis, Canisius College, 1960 (unpublished).

[9] From the same stock described by W. Primak and D. Post, J. Appl. Phys. **30**, 779 (1959).

[10] R. H. Wentorf (private communication).

## Irradiations

Two kinds of irradiation are described in this paper: within fuel elements of the nuclear reactor CP 5, and by x rays from a Machlett beryllium window x-ray tube operated at 40–50 mA and 50 kV.

For the CP 5 irradiations the specimens were placed in pairs (consisting of two easily distinguishable ones) in silica thin-wall capillary tubes which were constricted at the ends to prevent loss of the specimens, but sufficiently open to permit them to be filled with liquid. The capillaries were placed in perforated aluminum cans and irradiated in process or loop water (temperature $<55°C$) near centerline of the reactor.

For the x-ray irradiations, specimens thinner than 0.024 cm, the logarithmic decrement (approximately) of the soft x-ray intensity in silica were chosen. They were placed on double-backing Scotch tape on a metal cylinder standing in an ice and water mixture held in a Thermos bottle. In addition to the conduction cooling thus provided, further cooling was obtained by directing an air jet between the specimens and the window of the x-ray tube.

A chemical determination of the x-ray intensity from the x-ray tube gave the result about $6\times10^{16}$ eV/cm$^2$ sec. This corresponds to a dosage about $1.5\times10^4$ R/sec in silica. From the logarithmic decrement the average x-ray wavelength is estimated as 1.4 Å, energy $0.9\times10^4$ eV.

## Measurements

The density was measured by techniques described in previous papers.[11] In the present experiments methylene bromide diluted with a mixture of equal parts of *n*-propyl alcohol and *i*-butyl alcohol was used as the flotation liquid. This mixture was much more stable than those used in the previous work. All determinations were made near or slightly above room temperature and desiccation of the liquid was not required. In the annealing work in which these techniques were described, it was possible to place the fragment in a capillary tube and perform all of the operations and measurements without removing the specimen from the tube. This was not possible in the present experiments and several specimens were lost in the course of the work.

## Results

Specimens of a wide range of densities, some above and some below the saturation value obtained on long pile irradiation, were chosen.

Results obtained on pile irradiation are shown in Fig. 1. Seven specimens of pressure-compacted silica and one specimen of ordinary vitreous silica were carried through 2 successive 10-MWh irradiations. Two specimens of the pressure-compacted silica, one of density above the pile irradiation saturation value and one below, and the ordinary vitreous silica were carried along for a third irradiation of 27 MWh. It is seen that the exposure produced only a very small increase in the density of ordinary vitreous silica. However, there was a very rapid and large decrease in the density of the pressure-compacted silica amounting to some 40% of the density increase produced by pressure.

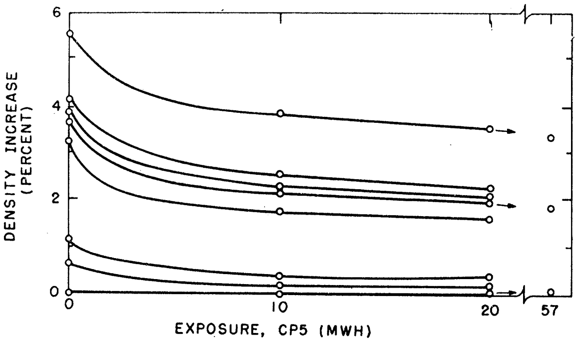

Fig. 1. Density change resulting from irradiation of several specimens of compacted vitreous silica in a fuel rod of nuclear reactor CP5. The ordinates are the percent greater density than ordinary vitreous silica.

The results obtained on x irradiation are shown in Fig. 2. The same general effect is seen on x irradiation as on pile irradiation, a rapid decrease in density. For comparison of the effect of x irradiation on ordinary vitreous silica see a previous paper[4]; an increase of density in the fractional hundredths percent range was found, too small to be detected by the methods used here.

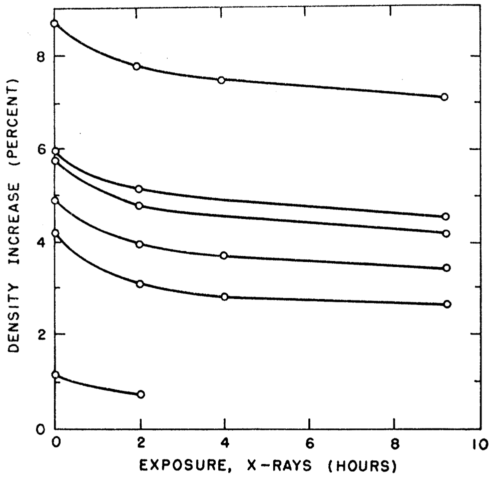

Fig. 2. Density change resulting from irradiating several specimens of compacted vitreous silica with soft x rays. The ordinates are the percent greater density than ordinary vitreous silica.

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[11] Cf. W. Primak and H. Szymanski, Phys. Rev. **101**, 1268 (1956).

## DISCUSSION

### Comparison of Dilatations

The comparison of dilatations of vitreous silica[4] found on irradiating in a nuclear reactor near fuel are made in Table I according to their magnitude and according to their period relative to the period for disordering quartz. Period is defined as the radiation dosage required to produce $(1-e^{-1})\sim 2/3$ of the maximum effect. The ionization expansion of compacted silica reported here is seen to be remarkable both for its rapidity and magnitude. This expansion occurred at rates about in the ratio of the ionization dosage both on soft x-ray irradiation and on pile irradiation and is therefore attributed to ionization.

### Static Effects of Ionization on Density

The static effects of ionization on density have been treated in the theory of ionic solutions. Two major effects, the monopolar (electrostriction) and the dipolar both lead to a contraction. The number of charge centers is important in this calculation but is unknown for irradiated silica. We reject a number like that obtained for the displacements in a calculation like Seitz's, $\sim 10^{21}$, on the basis of optical[12] and magnetic[13] work and assume the correct number is $\sim 3\times 10^{19}$ (i.e., $\sim 1.5\times 10^{19}$ dipoles). An elementary calculation of the electrostatic effects gives

$$\text{Monopolar}\qquad \frac{\Delta V}{V_0}=-\frac{2\pi}{B}\,\frac{k-1}{4\pi}\,\frac{2+k}{3}\,\frac{1}{k^2}\,\frac{e^2}{r_0}N,$$

$$\text{Dipolar}\qquad W=\frac{N\alpha e^2}{2kr}\,\frac{\Delta r}{r}=\frac{B}{2}V_0\left(\frac{\Delta V}{V_0}\right)^2$$

| Quantity | Definition | Magnitude |
|---|---|---|
| $B$ | bulk modulus | $0.38\times 10^{12}$ dyn/cm$^2$ |
| $k$ | dielectric constant | 3.8 |
| $e$ | electronic charge of center | $0.48\times 10^{-5}$ esu |
| $r_0$ | effective radius of center | $1.4\times 10^{-8}$ cm |
| $W$ | electrostatic work of dipole separation | |
| $N$ | number of monopoles or dipoles | (3 or 1.5) $\times 10^{19}$/cm$^3$ |
| $V_0$ | original volume | |
| $\Delta V$ | change in volume from that electrostatic effect | |
| $r$ | average charge separation | |
| $\Delta r/r$ | $(1/3)\Delta V/V_0$ | |
| $\alpha$ | Madelung constant | $\sim 1.7$ |

TABLE I. Comparison of dilatations of vitreous silica found in a nuclear reactor near fuel.

| Effect | Relative[a] exposure | Magnitude ($\Delta V/V_0$) |
|---|---|---|
| [Disordering of quartz] | [1] | [0.2] |
| Homogenization, stress relaxation | 1 | 0.0001 |
| Contraction | 1/7 | 0.03 |
| Initial rapid contraction | 1/140 | 0.002 |
| To change from ionization contraction to ionization expansion | 1/500 | 0.0001 |
| Ionization expansion of pressure-compacted silica | 1/1400 | 0.02 |

[a] Relative to the exposure period for disordering quartz.

[*Note added in proof:* The terms monopolar and dipolar are used in the sense of C. Zwikker, *Physical Properties of Solid Materials* (Pergamon Press, Inc., London, 1954). They may perhaps better be called ion-dipole or polarization and ion-ion interactions.] The monopolar effect is one or two orders of magnitude too small to account for the radiation compaction of vitreous silica, $\Delta V/V_0\sim 3\%$. The general dipole effect is four orders of magnitude too small. These electrostatic effects are of the order of magnitude of the ionization contraction of ordinary vitreous silica. They are of the wrong sign and far too small a magnitude to explain the large dilations observed in irradiation of silica.[14]

### Transient Effects of Corpuscular Irradiation

The stopping of Si and O atoms formed in the scattering of fast neutrons has been studied most. The energy of the atoms is largely dissipated in $\sim 10^{-15}$ sec, instantaneous for present considerations; and there is deposited $\sim$20 000 eV in the atomic system, the remainder being dissipated in the electron system, diffusing so rapidly it may be neglected. We consider that the region through which the 20 000 eV of energy is diffusing passes through a labile series of states until a volume equal to the total volume divided by the number of events which occur in the "period" of the effect is encompassed, and this state is "frozen in."[15] This state is described as approximately:

| | |
|---|---|
| Time from the scattering event | $\frac{1}{2}\times 10^{-11}$ sec |
| Temperature | 5000–10 000°C |
| Pressure | 3000–7000 atm |
| Volume | 10 000 atoms |
| Dimensions | 50–80 atomic diameters. |

The time, temperature, and dimensions follow when considering the flow of heat[16] in the above calculated volume and the total energy available; the pressure

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[12] Progress Reports of the Solid State Division, Oak Ridge National Laboratory Report No. ORNL 1959, 1962 (unpublished).

[13] Reported by J. H. Crawford, Jr., and M. C. Wittels, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955* (United Nations, New York, 1956), Vol. 7, p. 654.

[14] Note, however, local forces may be large. Average dimensions for the Si-O network (i.e., across the network from one strand of Si-O tetrahedra to another) are about 7 Å. A dipole separated by this distance in silica gives local forces about $\sim 10^4$ atm. This is pursued further below.

[15] Some thermal annealing may be superposed as a secondary effect.

[16] W. Primak, Phys. Rev. 98, 1854 (1955). The constants used here are more suited to what we suppose to be the state of the material.

from Gruneisens equation of state, $PV=\gamma E$ ($\gamma$ must be between 0.02 and 0.04).

We have applied this method to the data given by Hines and Arndt[17] for the stopping of energetic He and Ne in vitreous silica and obtain results consistent with the above. The approximate total energy deposition to the atomic system in the "period" for the effect is:

| | |
|---|---|
| Neutrons (i.e., O and Si) | 2.2 ($10^{11}$ ergs/cm$^3$) |
| He | 2.8 |
| Ne | 1.5. |

A smaller efficiency may be expected for He because the volume of the region affected is small, and probably somewhat elongated. However, the above data are not precise enough for such considerations. The similarity of the values is taken to confirm the similarity of the mechanism. Our conclusions differ from those of Hines and Arndt because they assumed the energy to be contained in a sphere of the diameter of the range; in fact, the state frozen in is one in which the energy has as yet encompassed only a much smaller volume.

We conclude that this radiation effect is in the nature of a phase change; the compaction achieved is that characteristic of the transient condition described above. The conditions are compared with other conditions in which compaction of silica has been reported.

## Comparison of Compacted States

The static experiments of Roy and Cohen[18] show that at a given pressure, the compaction is greater at higher temperature. At 4000 atm a 3% compaction (about that attained in a neutron irradiation) would be obtained at 900°C. For his shock-wave experiments Wackerle[19] reported a very rapid, effectively instantaneous, irreversible compression. Since his experiment was of duration $\sim 10^{-6}$ sec, it may be concluded the changes are at least as fast as $\sim 10^{-8}$ sec. Even in his lowest pressure experiments, the pressures were much greater than computed above for the corpuscular irradiation case. It is not proper to proceed from the static experiments and the shock experiments to the radiation experiments and conclude the compaction occurs in times $\sim 10^{-11}$ sec. The processes are quite different. In the radiation case there is no compression of the material (indeed, an expansion surely occurs) whereas in the shock experiment the compression attained exceeds the compaction of the recovered material. In the shock experiment for compression above some value Wackerle recovered uncompacted material, evidently because temperatures were reached which persisted long enough to anneal the compaction. In the radiation case the much higher temperatures, because they are present in smaller volumes, do not persist long enough to permit complete annealing.

In accordance with the suggestions of Simon and Bridgeman,[7] we assume the compacted state to result from an infolding of the Si-O network. In the compressed material the infolding occurs at normal temperatures when the volume is decreased. In the radiation case it is arrived at to accommodate the increased thermal motion, and possibly also to balance electrostatic repulsion from ionization in the region. These compacted states are thus different phases in the thermodynamic sense.

## Thermal Effect of the Photoelectric Process

A thermal effect of the photoelectric process by which the x rays are absorbed by the compacted silica arises largely from the released electrons, $\sim 10^4$ eV energy. Their cross sections for ionization are $\sim 10^{-18}-10^{-17}$ cm$^2$, hence the energy is dissipated in $\sim 10^3$ atomic spacings. In the disordered insulator much of this energy is stored temporarily in excited and ionized states and appears eventually as local vibrational energy: i.e., thermal energy. It is shown below that the number of photoelectric events in the "period" of the effect is $\sim 10^{18}$. Following the procedure used above for corpuscular radiation, if the ionization expansion is to be accounted for by the thermal effect, each event must affect a volume containing $5\times 10^4$ atoms, a volume encompassed by the thermal wave in $10^{-11}$ sec.

Consider now the maximum possible annealing which can result from such a process. The ionization and excitation energy must be largely degraded to thermal energy in $\ll 10^{-11}$ sec and the temperature rise is $\sim \frac{1}{2}\times 10^3$°C. According to the method of Primak and Szymanski, annealing would proceed to activation energies, $\epsilon=\tau \ln At$, where $\tau$ is the average thermal energy (eV/atom), corresponding to $\sim 800$°K in the present case, $A$ is a frequency factor, $10^{14}$ sec$^{-1}$ maximum, and according to preliminary calculations by Keiffer, much smaller in the present case, and $t$ is $10^{-11}$ sec. Annealing would proceed then to activations energies $\sim 0.4$-eV maximum, far too small to affect the material since room-temperature storage permits annealing to proceed to $\sim 1$ eV. It would require times $>10^{-5}$ sec to produce any significant annealing at temperatures of 800°K.

It is obvious that a generalized thermal annealing will not account for the ionization expansion of compacted silica by x rays. A local effect (i.e., one in the immediate neighborhood of a small group of atoms strained in the compaction process) must be involved.

## Efficiency of the Ionization Expansion of Compacted Silica

A structural formalism is required for this estimate. On the average, the three-dimensional network of ordinary vitreous silica is composed of "nets" of 6 Si-O tetrahedra. The volume of Si ions is negligible, less than

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[17] R. L. Hines and R. Arndt, Phys. Rev. **119**, 623 (1960).

[18] R. Roy and H. M. Cohen, Nature **190**, 798 (1961); H. M. Cohen and R. Roy, J. Am. Ceram. Soc. **44**, 523 (1961).

[19] J. Wackerle, J. Appl. Phys. **33**, 922 (1962).

1% of the volume of the solid, and may thus be neglected. There are 12 O ions per "net," each of which is shared with a neighboring "net" in the network. Hence, for these statistical considerations we may assign 6 O ions per "net," and there is also free volume equivalent to 4 additional O ions. It is reasonable to ascribe to the infolding of a Si-O tetrahedron a volume of the magnitude of an O ion, and we name this a "kink." Thus, a 20% compaction (greater compactions have been attained with pressure) corresponds to 2 "kinks" per "net." A typical example of the ionization expansion may be described in this formalism as follows:

| | |
|---|---|
| *Silica data* | |
| $4.4\times10^{22}$ O ions/cm$^3$ | or $7\times10^{22}$ O volumes/cm$^3$ |
| 6% compacted silica | 1"kink" every other "net" |
| 1% volume expansion | $7\times10^{20}$ "kinks"/cm$^3$ removed |
| *Irradiation data* | |
| 2 h x rays $1.5\times10^4$ R/sec | or $28\times10^{20}$ eV/cm$^3$ h absorbed |
| $\sim$30 eV/transient ionization | $2\times10^{20}$ ions/cm$^3$ in 2 h. |

The efficiency of the process is thus of the order of magnitude of 1 or several events per ionization.

From its high efficiency it may be expected that the process is an individual one rather than a 2-ion interaction. The latter would increase with the square of the dose rate. The dose rate in the reactor experiment was estimated roughly as fivefold that of the x-ray irradiation. The volume change experienced in 2 h beneath the x-ray tube required about 15 min in the reactor, thus linear within knowledge of the relative dose rates.

## Transient Ionization Annealing

In the photoelectric process only a small fraction of the energy is transferred to the atomic system, $\sim$1/3 eV. The photoelectron dissipates its energy widely, mainly to the electronic system. Thus at no point is the energy of the photoelectric process localized enough to activate ($\sim$1 eV required) the process releasing a "kink." Two kinds of transient processes occur subsequently. First are the local interactions associated with the ionization: (a) alteration of the bonding in the Si-O tetrahedron and in the "net,"[20] and (b) distortion of the "net" by electrostatic forces across it as described above. These could serve to reduce the activation energy for annealing a "kink." A lifetime of $10^{-9}-10^{-11}$ sec for an ionized species in silica is not unreasonable and would be sufficient to permit the process to occur with high probability by thermal activation. The second is a radiative transition of ionized or excited atoms. Since several electron volts are involved, this process could activate the annealing of a "kink" in its vicinity. The probability of this process is unknown. If Keiffer's preliminary calculations of the thermal annealing data are correct and apply to this process, the probability may be quite low, $10^{-5}$.

In the Simon-Bridgeman[7] picture the infolding can be "keyed in," an additional explanation of the high efficiency of the process.

## Behavior of Other Compacted Silicas

It was shown by Primak and Edwards[4] that when neutron irradiated silica is irradiated in a nuclear reactor beyond a certain point (Table I) ionizing radiation causes an expansion. However, the effect was much less efficient than the one described here for pressure compacted silica. On the hypothesis developed here, this is accounted for as follows:

(1) silica irradiated in a nuclear reactor has already been subjected to intense ionization and further ionization causes a small effect; (2) annealing of the neutron irradiated silica requires a greater activation energy; (3) the "kinks" are present in lower concentration; (4) the "kinks" may be stabilized by the electrostatic effects of the ionized species.

It would now be interesting to compare the ionization expansions for pressure-compacted irradiated silica, partially thermally annealed pressure-compacted silica, and pressure-compacted silica prepared at various temperatures. It is hoped to do this.

## ACKNOWLEDGMENTS

We wish to express our appreciation to R. H. Wentorf for pressure-compacting silica specimens and to S. Gordon and J. Thomas for the chemical determination of the x-ray dose rate.

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[20] Such processes are considered by J. Durup and R. L. Platzman, Discussions Faraday Soc. **31**, 156 (1961) as arising out of the multiple ionization resulting from the Auger cascades. We find it necessary in the present case to consider such effects associated with every ionization.