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Infra-red studies of vitreous silica at elevated temperatures

EDWARD GÖRLICH, KRYSTYNA BŁASZCZAK, GRAŻYNA SIEMINSKA
Laboratory of Silicate Chemistry, Institute of Materials Science, School of Mining and Metallurgy, Cracow, Poland

The purpose of this paper is to present a new approach to the problem of structure of the ordered regions in X-ray amorphous silica glass. The problem is open because of the differences in scientific opinion as to which polymorph of silica is the true crystalline model of vitreous silica.

Infra-red absorption spectra of cristobalite and silica glass taken at temperatures ranging from room temperature to 500° C were used to identify a characteristic low-high temperature polymorphic transition relaxed in X-ray amorphous silica after heating at 210° C for at least 10 h.

The infra-red spectrum of silica glass from various sources was identified as the spectrum of high-cristobalite, the spectrum after the polymorphic transition in silica glass is identical with that of low-cristobalite.

The results give a strong support to the high-cristobalite/cubic/model of normal silica glass, with ordered regions in metastable form at room temperature.

1. Introduction

These studies were inspired by the fact that there is no common agreement as to which polymorph of silica is to be regarded as a crystal model of amorphous silica. Nearly every possible form of crystalline silica was proposed by various authors as a probable model for silica glass structure on the grounds of X-ray or infra-red investigations.

What might be now considered as an experimentally established fact is that the extent of order in the X-ray amorphous silica must be much larger than accepted in the original network theory of Zachariasen and Warren. We refer here especially to the recent X-ray and neutron diffraction work done in the United States by Konnert and Karle [1, 2]. The significance of their work lies in the method of truncating applied to the radial distribution function and enhancing the precision of results obtained.

There are many earlier papers presenting studies which used the Debye equation to connect the broadening of the X-ray reflections with diminishing size of the crystals, as well as conclusions reached from the radial distribution functions of atoms or (better) electrons obtained from X-ray or (better) neutron diffraction [3-13]. All these and many other studies suggest that the size of the ordered regions in glass should be from 10 to 30 Å in comparison to the 7.6 Å suggested by Warren. Not only X-ray, neutron diffraction and infra-red studies but also the accumulative evidence of many types of investigations on glass and liquids done to this day point unmistakably to the failure of the random statistical theory of glasses and liquids.

Proceeding along these lines we studied first the progress of the polymorphic transition in crystalline cristobalite from low to high-temperature form with temperature. This process is a slow one and the intermediate stages of conversion, i.e. the growth of the domains of the high-temperature form in the hybrid crystals of the low-temperature form are easily observable, suggesting an equilibrium of the two forms at each temperature within the transition temperatures range. These observations were based on the gradual disappearance of the 620 cm^{-1} absorption band which is only characteristic for the tetragonal low-cristobalite.

The next step was to overcome the difficult nucleation, or rather initiation, of the polymorphic transition in silica glass due to the very small dimensions of crystalline regions. After a prolonged heating the polymorphic transition was achieved in silica glass at 210°C. The appearance of the 620 cm^{-1} absorption band can only be interpreted as a sign of transition from the metastable high-temperature cristobalite to the stable low-temperature form. This change is readily reversible within the range of temperature at which transition occurs.

In view of our experiments, it is evident that the silica glass in its normal form is to be considered as a very small-grained polycrystalline high-cristobalite aggregate, metastable at normal temperatures.

2. Review of the problem of proper crystalline model of silica glass

There is still a divergence of scientific opinion as to which polymorph of silica should be employed as a crystal (or lattice) model for vitreous silica. The absorption bands in the medium infra-red range suggest a resemblance between vitreous silica and low-temperature tridymite [14]. Gaskell [15-17] has obtained reflection spectra of high-temperature cristobalite at 300°C which also resemble those of vitreous silica. He has accepted (also in accordance with X-ray studies by various authors [4-18]) the cubic structure of high-temperature cristobalite (HTCr) as the "standard structure" for vitreous silica.

Recent work by Bock and Su [19], however, rejects the cristobalite model of Gaskell, as well as the random net-work approach of Bell and Dean [20] and takes the low-temperature quartz structure as the crystal model for vibrational analysis of vitreous silica.

A high-temperature quartz model is accepted by Bates [21] on the grounds of Narten's work [22]. Narten states that the X-ray diffraction pattern of vitreous silica could be interpreted by assuming a high-temperature quartz lattice structure containing about 12% vacancies. According to Bates, the infra-red and Raman spectra of vitreous silica are consistent with lattice dynamics calculations of the optical modes of high-temperature quartz. Further, Bates positively excludes high-temperature cristobalite as a possible lattice model for vitreous silica on the evidence of Raman spectra of vitreous silica obtained by Hass [23] and those of high-cristobalite obtained by himself. The 420 cm^{-1} band is absent in high-cristobalite but is very strong in vitreous silica.

Inferring from radial distribution functions obtained from X-ray and neutron diffraction data, Konnert and Karle [1, 2] reached a conclusion that these data are consistent with the assumption that the structure of vitreous silica is composed "nearly entirely" of ordered crystalline regions with dimensions of at least 20 Å. They suggest that these regions possess a tridymite-like structure. It is a similar conclusion to that reached by Hanna [14] from infra-red studies, but neither Konnert and Karle nor Hanna made any attempt to obtain data on high-temperature polymorphs of silica in order to compare them with the vitreous silica.

3. Infra-red investigations of polymorphic transitions in cristobalite and tridymite

By using a specially constructed heating stage for powdered samples in KBr pellets, attached to a Zeiss UR-10 model infrared spectrometer, we were able to follow changes in the transmission infra-red spectrum of tridymite and cristobalite in the temperature range from room temperature up to 500°C. Cristobalite and tridymite crystals were powdered to 900 mesh and a pellet with KBr (ca. 2 mg sample in 800 mg KBr) was made.

The KBr disc was inserted in a heating stage which was then placed in the Zeiss UR-10 spectrophotometer. The sample was heated from room temperature to the required temperature and then kept at this temperature for 30 min and the absorption spectrum recorded at that temperature. Then the temperature was raised to a higher value and the same pellet was heated further, the absorption curve registered and so on.

Changes in the spectrum of tridymite with temperature (Fig. 1) are much less spectacular than those found in cristobalite (Fig. 2). Above 270°C the 620 cm^{-1} band which is characteristic of low-temperature cristobalite (LTCr) disappears completely – the three other bands remaining practically unchanged (Table I).

By completing the cycle through obtaining an absorption spectrum at room temperature of a sample of cristobalite previously heated at 500°C, (Fig. 2), we have established a correspondence between the polymorphic changes LTCr $\rightleftharpoons$ HTCr and appearance and disappearance of the 620 cm^{-1} absorption band (Fig. 3: DTA curves for the same samples).

DTA curves show the thermal effects of the polymorphic transitions in crystalline tridymite and cristobalite. The peaks indicate the transition

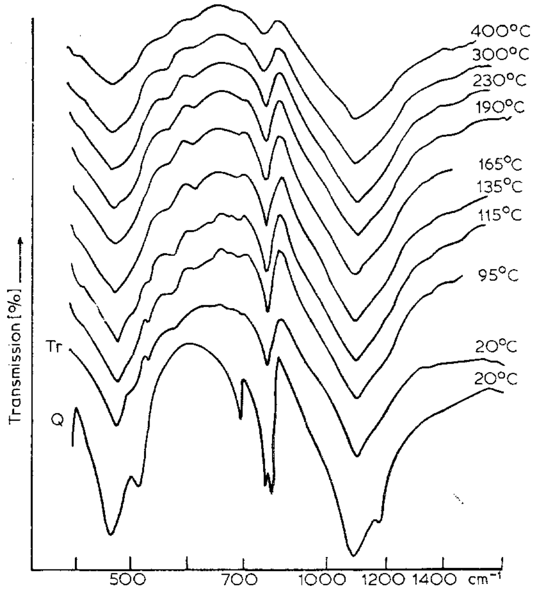

Figure 1 Transmission infra-red spectra of quartz (Q) at 20°C and of tridymite (Tr) at 20, 95, 115, 135, 165, 190, 230, 300 and 400°C.

temperatures. These temperatures agree closely with the effects (disappearance of absorption bands) shown by the infra-red spectra (Fig. 2). The inflection point on Fig. 4 for LTCr $\rightleftharpoons$ HTCr transition in cristobalite, established from the gradual disappearance of the 620 cm^{-1} band, is at 259°C, the corresponding thermal effect (DTA) lies at 260°C.

At this rate (and therefore time) of heating, no thermal effect appears in the case of silica glass. Much more heating time is needed to relax the polymorphic transition in glass.

The degree of conversion of the LTCr phase into HTCr phase of cristobalite (representing the growth of the HTCr domains in hybridic monocrystals of LTCr) with temperature, is shown in Fig. 4. It is evident that a sort of equilibrium establishes itself between both phases at each temperature (samples were heated for $\frac{1}{2}$ h to reach the temperature required and then kept at that temperature for another $\frac{1}{2}$ h).

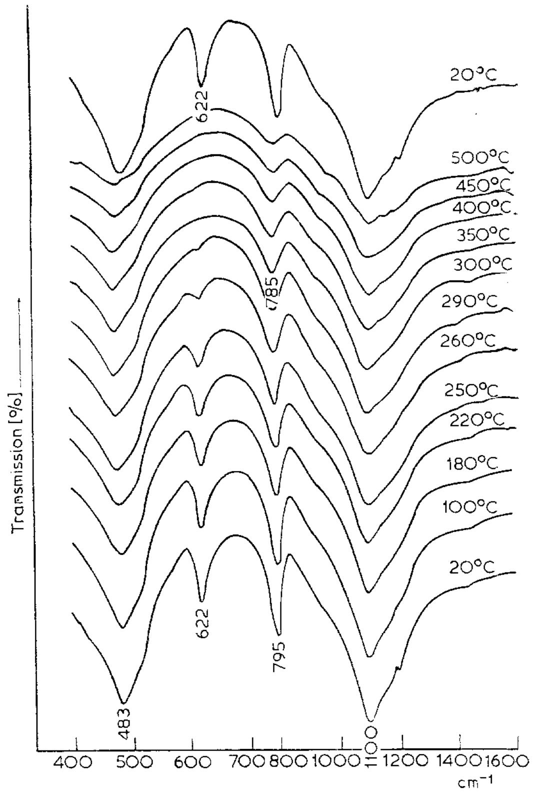

Figure 2 Transmission infra-red spectra of the same sample of cristobalite at 20, 100, 180, 220, 250, 290, 300, 350, 400, 450, 500°C and after cooling from 500 to 20°C.

4. Infra-red investigations of polymorphic transition in X-ray amorphous silica glass

The specimens of silica glass were tested by X-ray diffraction for any small amounts of crystalline phase and were found to be completely X-ray amorphous (Fig. 5). Each specimen was powdered to pass through a 900 mesh sieve. A sample of about 100 mg was taken and heated to 210°C in a silica glass container and kept at that temperature for up to 100 h in all but with intermittent cooling to as low as room temperature. Every hour or two about 2 mg of this

TABLE I Comparison of absorption bands (cm^{-1}) in different substances

Band	LTCr	HTCr (> 300°C)	Opal	Quartz glass	Quartz glass, high purity
I	484	478	476	467	473
II	622	—	—	—	—
III	795	785	790	800	800
IV	1105	1100	1102	1105	1107

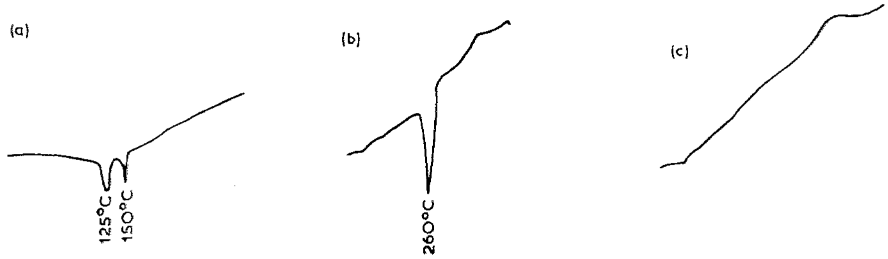

Figure 3 Differential thermal analysis of: (a) tridymite, (b) cristobalite and (c) vitreous silica (silica glass) between 20 and 400°C.

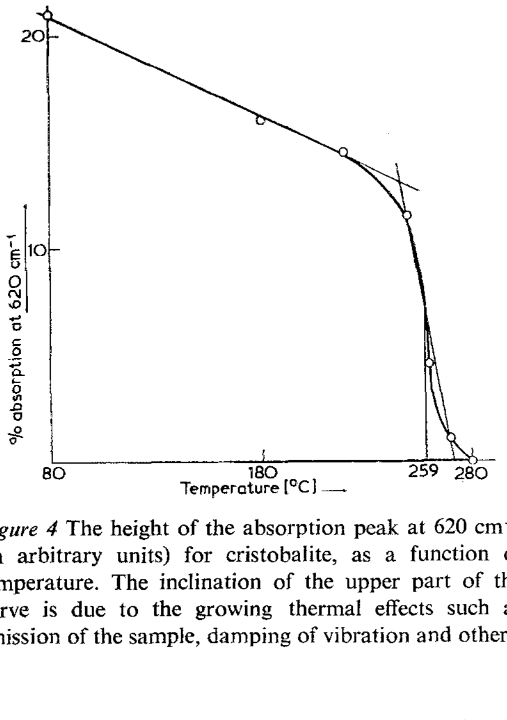

Figure 4 The height of the absorption peak at 620 cm^{-1} (in arbitrary units) for cristobalite, as a function of temperature. The inclination of the upper part of the curve is due to the growing thermal effects such as emission of the sample, damping of vibration and others.

sample was taken to prepare a KBr pellet in order to record an infra-red spectrum at room temperature. The experiment was repeated many times on samples from two different sources. The final intensity of the 620 cm^{-1} band was about the same as in the case of similar amounts of cristobalite crystals in the LTCr form.

Samples heated directly in KBr pellets do not show any trace of transition even after 180 h of heating. It is not possible at the present time to decide whether this is due to the presence of large amounts of K$^+$ cations or to the separation of grains of silica glass.

We obtained the absorption (Fig. 6) and reflection (Fig. 7) infra-red spectra of silica glass (high purity glass produced commercially from quartz, two kinds). The transmission spectra of vitreous silica are very nearly identical with the spectra of crystalline HTCr, as well as with a spectrum of opal, as given by Moenke [24] (Fig. 8). The glassy silica thus resembles the high-temperature cristobalite and none of the low-temperature polymorphs of silica.

The 620 cm^{-1} absorption band which is absent in HTCr, reflects the structural differences between cubic HTCr (O_h^7 or Fd3m space group) and the tetragonal LTCr ($P_{4_1 2_1 2_1}$ space group) and also the optical differences between isotropic and uniaxial crystals of cristobalite.

It is a well established fact that the polymorphic transitions are hampered if the grain size in polycrystalline material is very small, as the probability of nucleation is diminished. However, the driving force, i.e. the tendency to

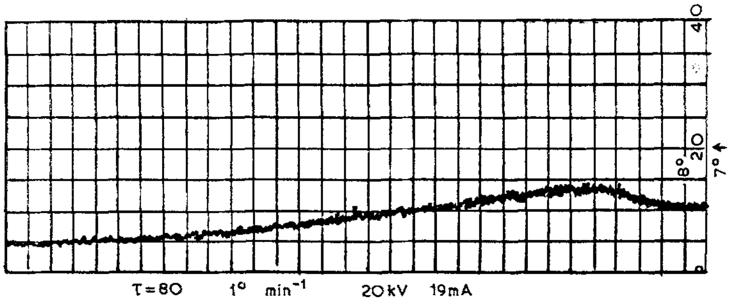

Figure 5 X-ray diffraction of the silica glass used in the experiments.

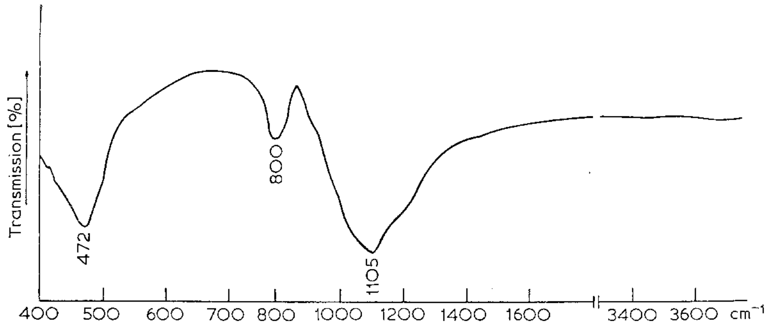

Figure 6 Transmission infra-red spectrum of vitreous silica (quartz glass) at 20°C.

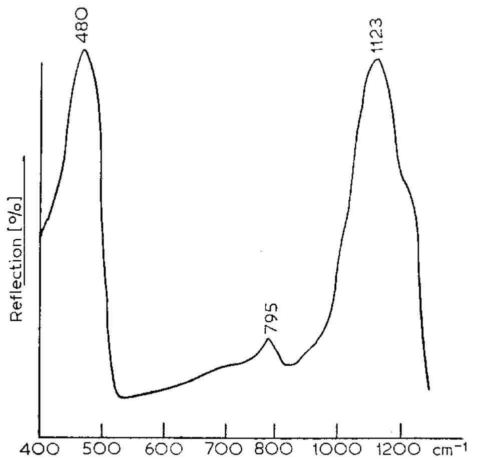

Figure 7 Reflection infra-red spectrum of vitreous silica (quartz glass) at 20°C.

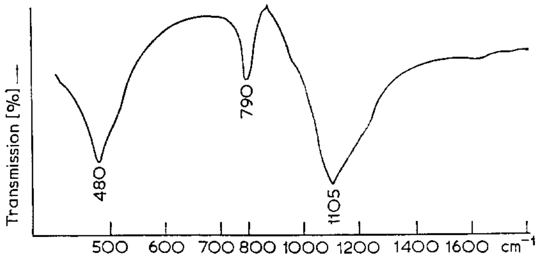

Figure 8 Transmission infra-red spectrum of opal (amorphous silica) at 20°C (after Moenke [24]).

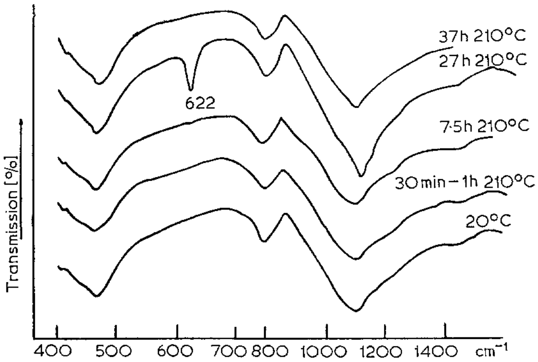

Figure 9 Transmission infra-red spectra of vitreous silica (quartz glass) at 20°C and when heated for 30 min, 7.5, 27 and 37 h at 210°C.

reach a lower value of free enthalpy G, remains and by heating vitreous silica for prolonged periods we hoped to induce a polymorphic transition in pure silica glass. An experiment confirmed our expectations and the 620 cm^{-1} band appeared in the spectrum of vitreous silica after 27 h heating at 210° C, i.e. in the stability range of both phases (280 to 180° C is the accepted range of the temperatures of transition for LTCr and HTCr, depending upon previous thermal history of the sample). The first barely distinguishable traces of the 620 cm^{-1} absorption peak appeared already after 8 h of heating at 210° C. After a further 10 h heating at the same temperature (210° C) the sample quite unexpectedly reconverted to HTCr and the 620 cm^{-1} band disappeared completely (Fig. 9). These experiments were repeated on the other kind of silica glass and the reverse transition to the HTCr form of glass (the disappearance of the 620 cm^{-1} band) sometimes occurred again. Evidently the thermal history, however slightly different, may cause unusual effects in the transition range. The time required for transition to occur can be as long as 72 or even 120 h, or as short as 10 h, depending on various factors.

Transition between HTCr and LTCr is a displacive one, with only a slight distortion of the original cubic symmetry, thus it does not require a large amount of activation energy to proceed. The nucleation of the LTCr form is one of the shear type, and no interphases between both forms exist. The domains of the new phase interlace with the old one forming a hybridic crystal. On the other hand, the volume change resulting from the transition is of the order of 1 cm^3 mol^{-1} in case of vitreous silica heated for 70 h at 1500°C [25]. The resulting internal strains lead to tensile stresses. This deformation energy is largely dependent upon thermal history of the sample and thus its share in the free energy function is not strictly defined. Therefore, the free energy curves of HTCr and LTCr do not intersect at one definite point, but cover a common region of temperatures and free energy values. In this region one or other form can be stable at the same temperature, depending upon previous thermal history which is not easily reproducible exactly. The transition between HTCr and LTCr can occur anywhere between 180 and 280°C, depending also on the purity of the sample and the kind and the distribution of impurities in the sample.

A crystallization of the vitreous silica when heated at 210°C for 27 h or less is out of the question, even if transition has shown itself less easily reversible*.

According to Nordwall and Stavely [26, 27] the spontaneous crystallization of glasses (devitrification) occurs during heating up from room temperature at a characteristic temperature, T_D. This temperature for silica glass is much above 1000°C. For different glasses it varies in a wide range from $T_D/T_F = 0.36$ to 0.70, where T_F is the equilibrium fusion temperature of respective crystals. According to the recent work by Florinskaya [13] the first vestiges of crystallization of silica glass appear after heating for 12 h at 1180°C.

Polymorphic transition LTCr $\rightleftharpoons$ HTCr needs only a comparatively small activation energy. On the contrary the crystal growth (crystallization-devitrification) needs a much higher activation energy, and the rate of this diffusion controlled process is insignificant.

5. Conclusions

In view of these experiments it is evident that the polymorphic changes in "amorphous", i.e. "short range" ordered, silica glass do occur exactly in the same manner as in the "long range" ordered crystals of cristobalite.

The discovery of appearance of the polymorphic transition LTCr $\rightleftharpoons$ HTCr in vitreous silica provides the most convincing evidence in support of HTCr as the proper lattice model for silica glass.

The occurrence of polymorphic transitions characteristic to the crystalline forms of silica in glasses containing, apart from silica, some amounts of sodium oxide (4%) and large amounts of boron oxide (26%) were known from the times of Lebedeev (1921). This was confirmed by the electrical conductance measurements done by Garman and Krasilnikova [28] through determining the Poole's coefficient and also by DTA methods. The effect was, however, observed only in glass samples which were first annealed for 150 h at 700°C. Such effects have not to our knowledge been studied so far in pure, unannealed silica glass using infra-red or other methods.

The X-ray amorphous silica is thus to be considered as a polycrystalline material with small grain sizes. Probably the best model of "vitreous silica" would be a "sintered powder model" with very small grained crystals of high (or low, after transition) cristobalite connected by "necks" containing a varying number of oxygen bridges. Thus a "sintered powder model" of glass presents a kind of much loosened network with micropores (see also Narten [22]) between crystal grains. The varying number of oxygen bonds in "necks" should be responsible for the lack of a constant temperature of fusion.

The size and size distribution of the grains remains to be established unequivocally.

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*At this temperature the viscosity is very high and diffusion is negligible.

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