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Institute of Chemical Physics of the Academy of Sciences of the USSR, Moscow

U. D. C. 546.284

QUARTZ CERAMICS

P. P. Budnikov and Yu. E. Pivinskii

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I. INTRODUCTION

Quartz ceramics are a recently developed class of materials offering a range of valuable properties of particular interest in a number of new technological areas.

Modern technology often requires materials combining high dimensional stability over a range of temperatures with good thermal stability and low thermal conductivity.

Fused quartz has a very low coefficient of thermal expansion: it is used as a standard for assessing the relative temperature stability of materials and has been successfully incorporated in equipment for use at high temperatures [1-9]. However, because of the very high viscosity of molten quartz glass (exceeding that of ordinary glass compositions [10] by more than a factor of 100 at 2000°), and of its appreciable volatility, the fabrication of articles of quartz glass presents serious difficulties.

Furthermore, only a very limited range of sizes and configurations can be obtained by applying conventional glass technology to the production of quartz glass articles. Hence, we must look for alternative routes to the production of articles made from fused quartz.

The limitations in shape and size are being overcome by the success achieved in recent years in applying ceramic technology to the problem.

It should be noted that an established terminology for ceramic materials based on amorphous or crystalline silica is still lacking, and some clarification is essential. In the American literature we find the term "slip cast fused silica", in the German Democratic Republic "Quarzglaskeramik" (quartz glass ceramic) and "schlickergegossenes Quarzgut" (translucent quartz glass made by slip-casting). In the USSR, the terms "kvartsevaya steklokeramika" [3] (quartz glass ceramic) and "kremnezemnaya steklokeramika" [11] (silica glass ceramic) have been proposed for materials based on quartz glass (fused quartz), and "kersil" for a ceramic based on synthetic amorphous silicon dioxide [12].

We consider the term "steklokeramika" (glass ceramic) an unfortunate choice, because it implies a crystallised glass of the "Pyroceram" type. Our suggested term "kvartsevaya keramika" [13] (quartz ceramic) can be applied to all ceramic materials prepared by ceramic techniques from one of the following: fused quartz, synthetic amorphous silica, or crystalline silica. It is important also to distinguish between the various forms of raw material used for the ceramic (crystalline silica, quartz glass, silicic acid gel), because the type of raw material plays an important role in the technology and in determining the properties of the product.

Several methods of preparation of quartz ceramics are known. The first, proposed by Skaupy and Weissenberg [14,15], consists in fusing (at 1650–1680°) cold-formed articles of quartz sand.

The second method, proposed by Solomin [11], consists in preparing articles of finely powdered quartz glass by the slip-casting method, with a subsequent heat treatment.

The difference between these methods lies in the choice of starting material. In the former, the starting material is quartz sand or rock crystal, which is converted to the desired state in the finished article. This requires a much higher temperature than is used in the second method. In the latter method the starting material is finely divided fused quartz. However, the basic technological operations needed to prepare the ceramic from fused quartz and from crystalline silica are identical. The fields of application of the second method and the quality of the articles made from fused quartz are such that this method is emphatically the better.

Botvinkin and Zaporozhskii [3] have described a method of preparation of quartz ceramics devised in an attempt to develop a material with a higher thermal stability than ordinary quartz glass. Aqueous silica gel was used as a binder for the fine grains of a thermally stable glassy composition, thus duplicating the natural conditions for the formation of cementoquartzites, whose thermal stability is equal to that of optical quartz glass.

It was shown [3] that the high thermal stability is due to the specific properties of the solid silica gel which binds the crystalline grains of natural quartz, itself of indifferent thermal stability. A series of materials with a binder of the silica gel type was synthesised, in which finely divided, transparent or translucent quartz glass was the filler.

Heany [16] suggested a method for preparing articles from finely disperse silica obtained by the decomposition of various silicone compounds. The castings were fired at 1200–1500° for various times.

The many papers published in the last few years [17-53] have considerably extended the scope and the applications of this new material, have suggested a number of valuable improvements in the technology of its production, and have discussed some of its properties.

II. MATERIAL PREPARATION

The starting material for the preparation of ceramics from quartz glass consists of waste, transparent or translucent, quartz glass [23,30], or fused quartz with SiO_2 content of the order of 99.5% (as reported by Schulle [23]). The quartz glass should be carefully melted and free from coarse heterogeneous inclusions such as graphite, slag, etc. In the preparation of the ceramic from silica, the starting material is pure silica sand or rock crystal. Schulle and Ulbricht [24] find that quartz sand with SiO_2 content of not less than 99.6% is essential for high-quality articles. By studying separate fractions they showed that the impurities in the sand are concentrated in the fractions of less than 0.1 mm and more than 0.3 mm grain size: the 0.1–0.3 mm fraction, which accounts for over 90% of the quartz sand, was therefore used for preparing articles.

In order to increase the SiO_2 content, the sand was treated with 12% hydrochloric acid in a ball mill for one hour. The chemical composition of the milled and washed quartz sand and glass, and the size distribution of quartz glass [23,24], are given in Table 1.

TABLE 1. Chemical composition of quartz sand and quartz glass, and granulometric composition of quartz glass.

	Quartz sand, wt. %	Quartz glass, wt. %	Size of fractions, μm	Fractions, %
SiO_2	99.83	99.51	40	0
Al_2O_3	0.07	0.31	22—40	15.1
Fe_2O_3	0.01	0.03	10—20	8.6
CaO	0.03	0.06	5—10	12.3
MgO	0.01	0.04	2—5	24.6
$K_2O + Na_2O$	0.01	0.05	2	39.4

Impurities of alkali metal oxides are the most detrimental, because they induce and catalyse the cristobalite transformation.

Amorphous synthetic silica also may be used as a raw material for the preparation of quartz ceramics. The first technological operation in this case is to bake the raw silica in order to drive off the large amounts of adsorbed water. It has been reported[3] that as much as 70–100 g of water per 1 kg of charge can be removed from synthetic silica in 24–72 h by baking at 1000–1200°.

Certain impurities are frequently added to the charge in order to improve sintering and inhibit crystallisation. In this case the SiO_2 content becomes correspondingly lower.

For example, Palatskii[51] mentions the addition of kaolin and low-melting glass frit, which lowers the sintering temperature to 1050–1100°. A slight lowering (by 20–30°) of the sintering temperature of a ceramic made from fused quartz can be achieved by adding synthetic SiO_2, whose sintering and crystallisation temperatures are both lower. Other workers[37] have added B_2O_3 to inhibit crystallisation.

Quartz ceramics based on quartz glass have undergone by far the most intensive development in recent years: all the results quoted in this review will therefore apply to this type of ceramic unless accompanied by a statement to the contrary.

Quartz glass is comminuted in a jawbreaker or other type of crusher; still finer particles are obtained in a ball mill. Size analysis of the fine powder is carried out in a centrifugal air separator[49].

Fine milling is done in ball mills with quartz liners and quartz balls; vibratory mills also can be used[35]. In cases of iron pick-up magnetic separation must be resorted to[49,50]. The fineness of the powder can be controlled on a PSKh-2 apparatus[35]: fine powders with a specific surface area as large as 8000–10 000 $cm^2 g^{-1}$ have been prepared both for semi-dry pressing and for slip casting[35].

III. FORMING

Quartz ceramics are manufactured in various forms: with medium porosity (up to 20–30%), high porosity (up to 80%), foamed quartz ceramic[34,39-42,44], and ceramic from cast[20,32] or granular material[35]. The following methods of forming quartz ceramic are known: wet slip casting, semi-dry pressing, hot pressing in graphite moulds, hot casting from wax, extrusion, etc.

The slip casting method is the most widely used, probably because of the requirement for hollow articles, which are most conveniently formed by this method.

The slip consists of a concentrated suspension of very fine particles of SiO_2 in a dispersion medium (water).

The particles must be fine enough to prevent fast settling under the influence of gravity during the time needed for the casting process. From the difference in density between the solid and the liquid phase and a number of other factors it can be calculated[54] that the particle size should be in the range 0–10 μm. The size of the bulk of the particles should be such that the interactions between particles are determined essentially by surface forces rather than by gravity.

The dispersity of the material is characterised by the particle size distribution, which is measured by sedimentation analysis, but as an overall characteristic of the dispersity we can use the computed mean surface diameter given by the formula

$$d_{mean} = \frac{100}{\sum \frac{a_i}{d_i}},$$

where a_i is the proportion of each fraction in % and d_i is the nominal mean diameter of the respective fraction in μm.

A very important process takes place during milling of quartz materials: formation of silica gel, as a result of which the non-plastic material acquires some measure of plasticity. Gel formation results from the disruption of the crystal lattice at the surface of the quartz particles during milling, accompanied by chemical reaction between water and the SiO_2.[55,56] When the grain size is less than 0.5 μm the disturbance of the crystal lattice can extend throughout the bulk of the particle, as shown by differential thermal analysis curves[24].

All types of silica (quartz, cristobalite, vitreous silica) can be considered as SiO_2 aggregates[57]. If the exact stoichiometry SiO_2 is retained, a truncated tetrahedron must be present at the point of contact of tangential surfaces. A surface of silicon atoms tends to complete its tetrahedral coordination: at a water interface the coordination can be completed by the formation of OH groups at the surface of SiO_2. Hydration of the silica proceeds at the surface and is limited by the size of the particle.

It is possible to obtain a silica slip (by wet milling) without any binder or plasticiser additives. The slip is prepared (by "wet" milling) in ball mills with silicon or quartz balls and a quartz liner. Rubber-lined mills with silica balls can also be used. The use of other types of mill is not recommended if pick-up of harmful impurities is to be avoided. The slip is made up of distilled water and quartz powder ground in the mill until the required consistency and the prescribed particle size distribution are obtained. The milling time can vary over wide limits (20–100 h), depending on the size distribution of the starting quartz, on the amount of water present, and on many other factors. Nishanova and coworkers[35] prepared a slip of satisfactory quality by milling for 30 h a powder of 10 000 $cm^2 g^{-1}$ specific surface area. The water content of the slip is between 25 and 30%: at higher moisture levels shrinkage increases and the quality of the castings deteriorates.

When the impurity content of the starting material increases, the minimum permissible water content rises to 33–35% or higher. Since a decrease in the water content of the slip can have an effect on the subsequent production stages, attempts have been made[35] to minimise the wetness of the slip by using vibration during casting (vibro-casting). The slip used in this work had a water content of 20%. The optimum time of vibration of the moulds (50 Hz frequency, 1 mm amplitude) was 3 min.

The degree of milling of the slip must be such that 40–50% of the solid particles have a diameter less than 5 μm. If the solid phase in the slip has a coarser size, fast settling results, giving poor casting properties and castings of low mechanical strength. The correct size distribution of particles is also essential. Preponderance of one fraction leads to increased shrinkage, lower strength, and lower density, which hampers the subsequent sintering.

The viscosity of the slip is very important in slip casting. The most satisfactory method of measuring viscosity under these conditions is to time the delivery of 100 cm^3 of the slip from a pipette (Engler's apparatus). It has been shown that the optimum pH value for a slip containing crystalline SiO_2 is 1; this value was obtained by adding hydrochloric acid, which does not introduce undesirable impurities into the slip[24].

The present writers have found[45] that the minimum viscosity of a slip based on fused quartz is reached at pH 3–3.5. Addition of hydrochloric acid lowers, however, the strength of the castings. For example, when the pH was lowered from 5.9 to 1.6 the strength of the castings under bending decreased from 4.0 to 1.4 kg cm^{-2}. This can obviously be ascribed to decomposition of the silica gel formed during the wet milling process, which acts as a binder in this case.

However, the pH changes continuously during wet milling due to the formation of silicic acid, reaching pH 3.5–5 at the completion of milling from an initial value of 7. Thus, the optimum pH value is obtained without adding acid.

The slip casting method is used for manufacturing hollow articles; the mould material is plaster of Paris, and the passive part of the mould is made of aluminium, plastics, etc. Ceramic or paper moulds can also be used[18,38].

The high thixotropy of SiO_2 slips is noteworthy. The limiting to apparent viscosity of thixotropy varies between 2 and 3, and increases steeply with particle size.

Using a thixotropic slip, articles cast in wooden moulds have shown adequate strength. The moulds were then dismantled and the articles dried[32].

The most important criterion of the quality of slip casting is the density of the casting obtained. This is because a high density is very beneficial to the relatively low mechanical strength of the dried castings, and it minimises shrinkage during drying and firing (particularly important in the manufacture of items of large dimensions and complex shape). Sintering also is easier and faster with high-density castings. The density depends on the particle size of the solid phase present in the slip, and on the size distribution over the various fractions, because separate loose aggregates of particles lower the density of the casting. Equally important is complete removal of air bubbles from the slip, which can be achieved by vacuum treatment. Under otherwise identical conditions, the density and the mechanical strength of the dried slip vary almost linearly with grain size (Fig. 1).

One of the features of ceramics manufactured from fused quartz is the possibility of obtaining castings of low porosity and high mechanical strength as compared with other types of ceramic.

The present writers have shown[45] that the casting properties of the slip are improved by lengthy storage after milling. Depending on the characteristics of the slip, the optimum properties were developed after 3–7 days: the

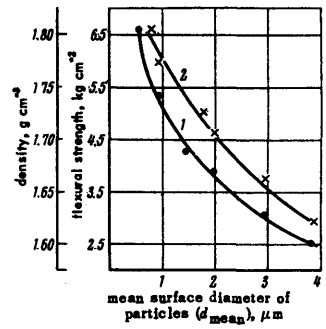


Fig. 1. Variation of density (1) and of flexural strength (2) of dry specimens with mean surface diameter of the particles (d_{mean}).

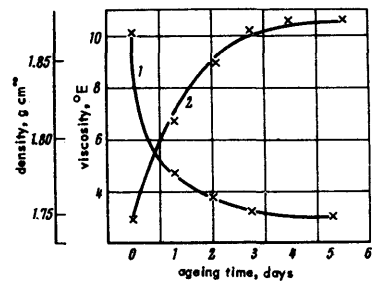


Fig. 2. Effect of ageing time on the properties of the slip and of the castings:
1) viscosity of the slip; 2) density of the castings.

viscosity decreased 2–8-fold, and the viscosity ratio changed from 2–3 to 1.2–1.3. Castings made from this slip can have a porosity of less than 12% and a strength of 25 kg cm^{-2} in transverse bending (Fig. 2).

We interpret the favourable effect of storage as follows. The silica gels formed during the wet milling process age with time; this is accompanied by evolution of the dispersion medium (water) from the diffusely bound to the free state, and therefore also by a decrease in viscosity. During the setting process closer packing can take place, because the diffusion layer around the particles is thinner.

Both the overflow and the pouring methods of casting can be used for the manufacture of quartz ceramics. Radome castings 750 mm in height and 450 mm in diameter have been made by the former method, which lends itself to the production of large articles without difficulty[18]. A radome 1220 mm in height also has been made by slip casting[36].

A mould release agent is used to prevent adhesion of the articles to the mould: for example, sodium alginate, which allows the passage of water[18]. However, the sodium alginate must be removed from the surface of the articles before baking, because it can cause undesirable crystallisation if it is allowed to penetrate into the material. In most cases, even a small shrinkage of the casting in the mould is sufficient to free the object without using release agents.

It is worth stressing that the shrinkage during drying is very small (0.1–0.5%, depending on the particle size and on the water content): hence, the size of articles which can be made by slip casting[18] can reach several metres, corresponding to a weight of 500 kg.

Quartz ceramics are also formed by using the slip casting method with 3–10% additions of a water-soluble gum. The article is dried, and the gum is hardened at 150–200°, which raises the strength of the unbaked articles in bending to 500 kg cm^{-2}. The gum burns off during sintering, but there is a loss of mechanical strength proportional to the amount of resin binder. Impregnation is used to achieve greater strength. The main advantage of this method of forming is that it allows the article to be machined on a lathe before baking. In this way one can make components with machine-cut screw-threads, electrical insulators of any shape, and nose cones for guided missiles[23].

A modification of slip casting is casting from compositions with a granular filler (casting compositions); another modification is casting from foaming slip. Casting from casting compositions consists essentially in adding to the normal slip a filler of granular fused quartz[31,35] of particle size between 0.25 and 1 mm.

To make larger castings, the maximum fraction size is increased. Under these conditions the ratio of slip to granular filler is of the order of 1 : 1. It is recommended that 100 parts by weight of the filler should be triturated with 2 parts by weight of water immediately before mixing with the slip. By using vibration during casting it is possible to lower the water content of the slip to 14.5–17.5%.[35]

Drying quartz ceramic presents no difficulty because the shrinkage is very small (less than 1%), and there are no distortion or crack formation problems. Both spontaneous drying at room temperature and forced drying in drying chambers can be used. A combination of the two methods is most common: 24 h at room temperature followed by treatment at 120° in a special drier[18]. The drying time is determined by the wall thickness of the article. For 10–15 mm wall thicknesses, drying is practically complete in 3–4 days at room temperature.

We may expect, however, complications to arise in the drying process as a result of the strong tendency of the slip towards gel formation when the particle size is made very small or the milling time is increased. This is because silicic acid gel does not readily give up OH groups on drying. In this case the drying procedure must be milder, and must be chosen to suit the fineness of milling, the degree of gel formation, and the size of the casting.

Foamed quartz ceramics are becoming very common: they are produced by slip casting with a suitable foaming agent in the slip.

Budnikov and Duderov have developed a new method for preparing highly porous articles on the basis of fused quartz[34]. The fused quartz, finely divided to an average particle size of 1–3 μm, is mixed with acid aluminium phosphate and with glyceryl adipate, and the foaming agent "Product 102-T" (methylphenylene di-isocyanate) is added to the resulting suspension. The starting mass has the following composition (in wt.%):

fused quartz	45.0
ester	20.9
foaming agent	13.2
aluminium phosphate	20.9

A mass of the above composition is foamed in closed steel moulds, allowing accurate control over the profile of the article. Foaming occurs as a result of the evolution of carbon dioxide by the reaction

$$n\mathrm{O{=}C{=}NRN{=}CO} + n\mathrm{H\dot{O}\dot{O}CR'C\dot{O}\dot{O}H} \rightarrow n\mathrm{CO_2} + n\mathrm{O{=}C{=}NRNH{-}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}{-}R'{-}\underset{\underset{\mathrm{OH}}{|}}{\mathrm{C}}{=}O}.$$

di-isocyanate (foaming agent); ester

The volume expansion obtained is greater than a factor of 10. The polymerisation of the polyester, which occurs at the same time as the evolution of carbon dioxide, strengthens the porous structure and gives it increased rigidity. Firing temperature 950–1000°, density of the finished article 0.33–0.40 g cm^{-3}, proportion of open pores 80–88%.

According to Walton, aluminium phosphate (which was examined as a possible impregnating material) induced cristobalite transition of the siliceous masses[33]. However, X-ray diffraction analysis of the specimens fired at 1000° for 28 h, and also at 1100°, did not reveal a more intense peak than the one formed during normal heat treatment and ascribed to cristobalite (Fig. 3). Hence it was suggested that the observed peaks are associated not with cristobalite (as assumed by Walton) but with cristalorphite, the cristobalite form of $AlPO_4$. The absence of cristobalite was later confirmed by differential thermal analysis, petrographic analysis, and dilatometric analysis.

According to an American patent[45], insulators are made from silicic acid and glycerol (1–5%): after mixing, the mass is dried at 120–300°, ground to 100 μm particle size, and furnaced at 1260–1650°, when the silica expands forming hollow microspheres. The density of the final product is 0.7–1.2 g cm^{-3}.

Hot casting from wax can be used as a casting method. The density of the articles in this case is lower than when slip casting is used. Articles of simple shape can be made by semi-dry pressing, using a specific pressure of between 800 and 1200 kg cm^{-2}. The water content of the powder lies between 8 and 10%. The granular composition is approximately the same as in slip casting. According to Nishanova and coworkers[35] the specific gravity of the pressings and their apparent porosity vary with the pressure used as shown in Fig. 4. The relatively high porosity of the semifinished product is worth noting, as it causes difficulties in the subsequent sintering. Owing to the low mechanical strength, reaching 4–6 kg cm^{-2} in bending after forming and 2–3 kg cm^{-2} after drying[24], additives are commonly used.

Ethyl silicate-40, an ester of silicic acid, has been found[23,24] to be a very effective additive. Under the influence of water this compound hydrolyses to give SiO_2 gel, and binds the quartz particles together. The binding effect persists at elevated temperatures, which makes this binder superior to dextrin, starch, etc.

Ethyl silicate-40 decomposes to amorphous silica which is transformed to cristobalite only after prolonged heating at temperatures in excess of 1000°. Furthermore, ethyl silicate-40 does not increase the tendency to crystallisation of a quartz ceramic, and does not introduce contamination.

Alternatively, 0.2% additions of urea–formaldehyde resin have been used[35].

Vasilos and Wagner[27] have described a method of preparation of quartz ceramics from ground quartz glass by hot pressing in graphite moulds, which involves the simultaneous application of heat and pressure. Hot pressing

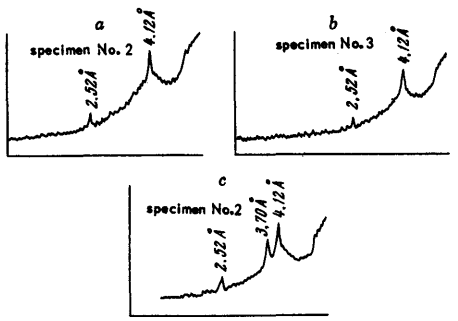


Fig. 3. X-Ray diffraction patterns of specimens: (*a*) fired at 1000°; (*b*) fired at 1100°; (*c*) fired at 1000° for 28h.

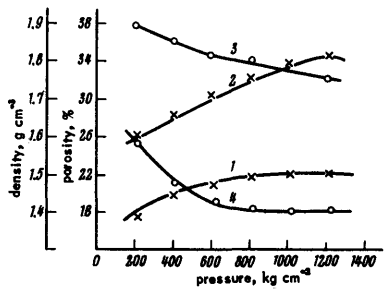


Fig. 4. Variation of the apparent porosity and of the density of a quartz ceramic with the porosity and the density of the raw material and with the applied pressure:
1) density before firing; 2) density after firing;
3) porosity before firing; 4) porosity after firing.

was achieved by applying pressure for 3 h at 1050–1450°. Graphite, which burns at ~800°, is added to the powdered quartz glass. Sintering under pressure results in relatively large shrinkage, which can amount to 5–15% or more according to the compressive strain. The porosity of the resulting material is less than 3%. If necessary, quartz glass articles with regions of different porosity can be manufactured by this method.

Vasilos[26] used three arbitrarily chosen fractions of fused quartz in the range 5–300 μm, prepared by grinding followed by acid leaching and separation on sieves.

Studies carried out on the hot pressing apparatus have shown that at 1100°, 1150°, and 1200°, and pressures in the range 70–170 kg cm^{-2}, for pressing times up to 90 min, the dispersity of the fused quartz has a negligible effect except for fractions up to 300 μm in size.

IV. THE ONE-COMPONENT SYSTEM AND ALLOTROPIC TRANSFORMATIONS OF SiO_2

The existence of the following modifications of silica is now recognised: quartz, tridymite, cristobalite, coesite, kitite, fibrous silica, stishovite, and quartz glass.

Fenner's well known phase diagram for SiO_2 clearly shows all the most important states of silicic acid (quartz, tridymite, cristobalite). It does not, of course, include all the recently discovered modifications listed above: for a detailed discussion of these allotropes and of contemporary ideas on silicon dioxide the reader is referred to the original papers[58–64].

Fenner's diagram shows the variation with temperature of the vapour pressure of the various modifications of SiO_2: polymorphic transformations are presented graphically.

Second-order transitions (within a given modification) are fast, but first-order transitions of the quartz–cristobalite type are slow. Hence, the temperature limits of stability of the individual modifications are meaningful only for prolonged heating in the presence of strong mineralisers. The smaller the difference in structure of the crystal lattices of two polymorphic forms of SiO_2, the faster is the transformation (under otherwise identical conditions).

In Fenner's diagram quartz is shown as thermodynamically stable from low temperatures up to 870°, tridymite from 870° to 1470°, and cristobalite from 1470° to the melting point.

The following problems are important in a study of the technology, structure, and properties of quartz ceramics: (1) the transformation of pure (upwards of 99% SiO_2) silica, quartz glass, and amorphous synthetic SiO_2 at the heat treatment temperatures into cristobalite, and the kinetics of this transformation; (2) the transition from high-temperature to low-temperature cristobalite; (3) the influence of impurities, of the gas medium, and of various other factors on these transformations.

Fenner's phase diagram for silica was not re-examined for many years. More recently it has been repeatedly pointed out that quartz is not converted into tridymite in the absence of mineralisers, and that Fenner obtained tridymite by using Na_2WO_4 as a mineraliser[65–69]: revision of the diagram therefore seemed desirable[70]. It was subsequently shown that pure silicon dioxide under atmospheric pressure can be converted into quartz or cristobalite by heating[71,72].

Flörke electrolysed crystalline samples of tridymite[73] in the temperature range 870–1470°. Under these conditions, the tridymite in the anodic region was converted into cristobalite (for electrolysis temperatures above 1000°) or into quartz (at temperatures below 1000°), suggesting the breakdown of the tridymite structure by the removal of a stabiliser.

Thus, the stability of tridymite is due to impurity atoms of alkali metals introduced into the lattice during the synthesis of tridymite.

The structure of tridymite, like that of other modifications of silica, consists of a particular sequence of layers of SiO_4 tetrahedra. When free from defects, tridymite should have a twofold periodicity of layers of SiO_4 tetrahedra, i.e. an AB|AB|AB|AB structure.

Like cristobalite, real crystals of tridymite contain regions showing twofold periodicity and others showing threefold periodicity. However, in contrast to cristobalite which is made up mostly of three-layer regions, two-layer regions are predominant in tridymite.

According to Flörke, tridymite should be treated as a highly defective form of cristobalite, and should not appear in the phase diagram. Flörke's revised phase diagram, shown in Fig. 5, includes only quartz and cristobalite, with a transition temperature in the region of 1050°: pure cristobalite does not change into any other crystalline form[74,75].

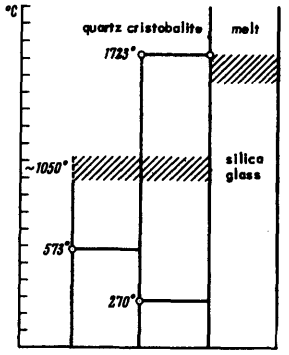


Fig. 5. Tentative revision of the phase diagram of pure SiO_2 (after Flörke).

Thus, whether we start from pure quartz, pure cristobalite, or from an amorphous form of silica (such as quartz glass or dehydrated silica gel), tridymite is not formed even after lengthy treatment in the temperature region 870–1470° (the stability region of tridymite according to Fenner). However, in the presence of small quantities of alkali metal oxides, tridymite forms quite readily in the stated temperature region. It follows that two phase diagrams for silica are needed, depending on the experimental conditions. When very pure silica is used (by far the commonest case in the preparation of quartz ceramics) the transformations are dictated by Flörke's diagram, but if the silica is in contact with other substances (in particular with alkali metal salts) Fenner's diagram should be used[58].

During the last few years many papers have been published on the allotropic transitions of SiO_2 and on the kinetics of crystallisation, and on the influence of various factors on these processes[82-110].

V. CONVERSION TO CRISTOBALITE AND ITS KINETICS

It has often been observed that the transformation of quartz to cristobalite, a solid-state reaction[95], begins at the free surfaces of grains, both internal and external. under the influence of high temperatures the cristobalite transformation of quartz spreads from these surfaces. The transformation of quartz follows this course because the free surface is the site of broken bonds between $[SiO_4]$ tetrahedra, which facilitate the rearrangement of the lattice through the enhanced mobility of the tetrahedra. The accurate and constant correlation between the crystallographic directions of quartz and of the resulting cristobalite is evidence that this transformation occurs in the solid phase.

By treating quartz glass as a non-stoichiometric material with a definite proportion of oxygen defects, Boganov and coworkers[104] explain the formation of a crystalline layer on the glass surface as follows.

When the surface of the glass is exposed, at high temperatures, to an oxygen-containing atmosphere, oxygen atoms penetrate the glass network by thermal diffusion. During some induction period, a fraction of the oxygen atoms dissolved in the boundary layer of glass fills, at random, vacant anion sites to an increasing depth below the original surface. However, formation of a local crystalline block in the region which has been made stoichiometric is possible only when this region reaches a definite critical size. This size is determined by the conditions of equilibrium between the deformation forces associated with the excess energy of a stoichiometric but disordered region and the bond-breaking forces at the surface of the resulting crystalline block. If the supply of the required amount of oxygen to the subsequently formed blocks is fast as compared to the characteristic formation time of the block the crystallisation process should proceed at a constant rate.

The temperature at which the cristobalite transition occurs during firing of a quartz ceramic is of the utmost importance, because the forms of quartz most resistant to the transformation (quartz glass) offer the best prospects of dense sintering and therefore also of improvements in a number of properties. The high-temperature α-cristobalite formed during heat treatment goes over to the low-temperature β-cristobalite during cooling: the attendant decrease in volume loosens the structure of the ceramic and degrades its thermal stability.

A more detailed study of the cristobalite transition temperature and of its dependence on a number of factors is therefore essential. The cristobalite transition temperature (1050°) given in Flörke's diagram is not associated with any particular heating time or with various other factors often found to be critical. According to Walton[31-33] and others, a fused quartz ceramic converts to cristobalite at temperatures above 1093° (2000°F). According to Schulle[23], conversion to cristobalite at 1100° occurs only after upwards of 20 h heating.

Verduch[82] studied the effect of time and temperature on the rate of formation of cristobalite, and showed that three stages are involved in cristobalite formation: the formation of crystal nuclei, fast crystallisation, and the subsequent (slow) crystallisation. The amorphous SiO_2 used for the investigation (silicic acid) began to crystallise at a temperature as low as 945° after 41 h, and at 985° crystallisation set in after 10 h.

The temperature variation of the nucleation process is described by the equation

$$\log t = \frac{22462}{T} - 13.32,$$

where t is the time needed for the formation of nuclei in seconds and T is the absolute temperature in degrees.

When the temperature is raised from 945° to 1085° the nucleation time decreases from 41 h to 0.5 h.

The next stage is the growth of a cristobalite structure. The amount of cristobalite formed is given by the equation

$$\log K = 5.98 - \frac{11122}{T},$$

where K is the amount of cristobalite formed per second (%), and T is the absolute temperature in degrees.

On raising the temperature from 945° to 1085° the quantity K increases from 7.87×10^{-4} to 7.00×10^{-3}.

The temperature at which cristobalite is crystallised from silicic acid determines the interplanar spacing of the cristobalite lattice, which decreases from 4.0825 Å to 4.062 Å when the temperature is raised from 1080° to 1425° (corresponding to a perfect cristobalite structure at 1425°).

The ordering of the structure proceeds from the centre of the crystal towards the periphery. The kinetics of the conversion of pure quartz into cristobalite depend on the

crystallite size. When the grains are small (~50 μm) the transformation in the temperature region 1270–1450° follows the equation

$$\log\alpha = -\frac{3ut}{r},$$

where u is a constant, t is the heating time, r is the initial radius of the quartz particle, and α is the fraction of quartz converted.

With coarser grains (~138 μm) the transformation proceeds in 2 stages: in the first stage cristobalite nuclei are formed on the surface of the grains and in the second stage cristobalite formation proceeds into the bulk of the grains. The rate of reaction for the first stage is lower than for the second, but the duration of the first stage decreases steeply on raising the temperature (from 1270° to 1450°). The rate constant for the first stage includes the surface factor $1/r^2$; the rate constant for the second stage includes the quantity $3u/r$, and is therefore proportional to $1/r$.

When the quartz particles are fine, the rate constants of the two processes are comparable, and the reaction proceeds, as it were, at a constant rate from beginning to end. The kinetics of the transformation of quartz are altered by the presence of a mineraliser (which can be either in the solid or in the liquid state at the transformation temperature).

If the mineraliser acts in the solid phase, the transformation of the quartz is fast only in the immediate vicinity of the grains of the mineraliser: hence, the mineralising activity is of short duration, and the remainder of the reaction proceeds slowly by the mechanism which operates in pure quartz. Increasing the amount of mineraliser increases the amount of quartz converted in the initial period, but the rate of reaction in the final period is significantly lower.

If the mineraliser forms a liquid phase at the conversion temperature its influence becomes much more marked, because the area of contact with the quartz grains is increased by capillary action[100].

It should be noted that there is a significant difference between the temperatures of fast cristobalite formation of amorphous and of crystalline SiO_2. Thus, whereas Brazilian quartz is converted into cristobalite at temperatures of the order of 1500°, quartz glass and silicic acid gel convert even at 1200° (after 4–5 h).

This disparity between the crystallisation temperatures of crystalline and amorphous SiO_2 arises because bonds have to be broken in crystalline SiO_2 before cristobalite formation can occur, and the process is therefore more hindered and slower than crystallisation from the gel[83].

The transformation of quartz, quartz glass, or silicic acid gel proceeds with formation of an intermediate phase called metacristobalite[106–109]. Metacristobalite is rapidly converted into the stable cristobalite, but in the presence of the required concentration of alkali metal cations it is converted into tridymite. The reaction scheme is the following:

crystalline silica, quartz glass, silicic acid gel
↓
metacristobalite
↓
cristobalite

The density of metacristobalite is close to that of cristobalite, 2.30 g cm^{-3}, and is therefore identical to the density of the disordered phase formed by bombarding quartz with neutrons[97].

Chaklader and Roberts[110] have put forward a hypothetical scheme for the conversion of quartz into cristobalite, which was subsequently developed by Chaklader[76].

The high-temperature α-form of cristobalite changes to the low-temperature β-form on cooling, with an appreciable volume change.

It has been shown that the temperature of the $\alpha \rightleftharpoons \beta$ cristobalite transformation is a function of the thermal history of the sample, and usually lies[85,89] in the range 200–280°.

Cristobalite formed at relatively high temperatures also shows a higher transition temperature to the β-form. According to Flörke[70], the ideal cristobalite structure shows a threefold periodicity of layers of SiO_4 tetrahedra, which can be expressed as a structure of the type ABC | ABC | ABC. Cristobalite is often obtained in a different structure, including regions of twofold periodicity. This type of cristobalite has a lower $\alpha \rightleftharpoons \beta$ transition temperature.

The transition temperature can also show hysteresis, the transition from the high-temperature to the low-temperature form occurring 35° lower than the transition in the opposite direction[83].

VI. EFFECT OF IMPURITIES ON CRYSTALLISATION

The cristobalite formation process can be accelerated by a wide variety of foreign ions. The specific effect of alkali cations does not depend on the formation of a liquid phase, nor does it depend on their concentration, although it is now well established that the presence of a liquid phase can greatly activate the cristobalite formation process[63,64].

The transformation of quartz to cristobalite is induced by introducing cations into the quartz crystal lattice because the lattice is thereby deformed and the activation energy of the transformation is accordingly lowered. The deforming effect of the added ion is expected to increase with the ionic radius of the cation within any one group of the Periodic Table. Thus, the efficiency of K^+ towards cristobalite formation should be greater than that of Na^+ and that of Ba^{2+} should be greater than that of Sr^{2+}, Ca^{2+}, and Mg^{2+}, as has been experimentally confirmed.

Impurity ions also show different catalytic effects towards cristobalite formation in quartz glass, as was established by the systematic researches of Kainarskii, Degtyareva, and others. Kind and Makhlina studied the influence of various additives on the crystallisability of translucent fused quartz[105]. The impurities investigated were mainly oxides present in the sand as natural impurities, as well as some other oxides (B_2O_3, ZrO_2, P_2O_5). In every case it was found that alkali and alkaline-earth oxides had a negative influence, increasing in the sequence $Na_2O \rightarrow K_2O \rightarrow$ $\rightarrow CaO \rightarrow MgO$, and aluminium oxide had a positive influence. The crystallisability of the quartz samples was measured in a high-temperature gradient furnace in the region 1420–800°, for 24 h.

These measurements showed that practically all oxides, and the alkalis and alkaline earths in particular, increases the crystallisability of translucent fused quartz. The crystallisation of samples containing added Al_2O_3 was

unique: an addition of 0.05% inhibits the crystallisation, the effect increasing with concentration. The negative influence of the basic oxides and the positive influence of Al_2O_3 on the properties of translucent quartz glass are explained as follows. The ions of alkaline and alkaline-earth oxides are not glass-formers: they fill the voids in the three--dimensional network, thus altering and loosening the structure of the quartz glass and breaking Si–O bonds. Since very many defect sites are present, the viscosity of the glass in the softening temperature region decreases, and other properties also are affected.

The aluminium ion (Al^{3+}), having sixfold coordination, can behave as a glass-former under the right conditions and be incorporated in the three-dimensional glass network at a tetravalent SiO_2 site.

In this case one positive charge is lacking in order to satisfy the valence requirements: this can be provided, for example, by an Na ion. As a result, the points of attack created by the presence of Na ions in the quartz glass are neutralised. The Na ion is fixed in the vicinity of the aluminium ion without giving rise to a point of attack. The glass structure is stabilised, and the crystallisability is lowered. Beyond the optimum concentration the Al ion apparently remains in the six-fold coordination but behaves as a glass modifier rather than as a glass former. When Al_2O_3 is added to translucent fused quartz the coordination of the Al ion can change under certain conditions: this leads to neutralisation of the negative influence of alkali oxides.

According to Kainarskii and Degtyareva, the crystallisation of quartz glass is inhibited by the presence of 1.5% by weight of Al_2O_3,[64] whereas small additions of Al_2O_3 enhance the crystallisation.

VII. EFFECT OF ATMOSPHERE ON CRYSTALLISATION

The atmosphere used for heat treatment also plays an important part in the crystallisation process. Lipinski and Schwiete demonstrated the effect of different gaseous atmospheres during firing on the formation of cristobalite. Specially pure synthetic amorphous silica, containing no more than $2-3 \times 10^{-3}$% Na_2O, was investigated. The extent of crystallisation was measured at temperatures of 1200°, 1300°, 1400° in the following ambients: vacuum, air, N_2, O_2, Ar, CO_2, CO. The crystallisation was shown to be significantly retarded in a medium of Ar, N_2, or CO_2. For example, at 1200° in air crystallisation began after 2.5 h, but in an atmosphere of CO_2 the time needed was 32 h. At the same temperature, crystallisation is extremely slow in CO, CO_2, and Ar during the first 20–25 h, whereas it reaches 80% after 8 h in air[101].

The crystallisation of industrial quartz glass produced in the Soviet Union has been investigated. The samples were prepared from transparent vitreous mouldings which contained a large number of fine tapered channels due to the particular production technique. Crystallisation was induced at 1300° in an air atmosphere over a period of 10–15 h. A crystalline layer several tenths of a millimeter thick was obtained, and crystallisation occurred on the inner surfaces of the open channels as well as on the external surface of the sample, but not on the surfaces of the closed channels[104].

This observation is a clear illustration of the undeniable influence of atmosphere on the crystallisation of the glass.

In a vacuum of the order of 1×10^{-5} mmHg, however, crystallisation was not merely delayed but completely absent after 30–50 h treatment at 1300°. These experiments also provided ample indirect evidence that silica undergoes intensive dissociation in the region of its melting point, giving off free oxygen, so that the melt becomes oxygen-deficient and is partly reduced.

It was also established that glasses prepared by melting in high vacuum under identical conditions behave quite differently when subsequently heated in oxygen, nitrogen, hydrogen, and air. The role of oxygen and water vapour as the main activators of the crystallisation process was also confirmed.

The increase in weight during crystallisation, which can amount to 0.1%, can be taken as proof that the crystallisation process is indeed closely associated with chemical oxidation of the glass during conversion to cristobalite.

As a result of their experimental work, the authors came to the following conclusions.

The crystallisation of quartz glass is primarily a chemical process rather than a thermodynamic relaxation process. Crystallisation occurs when the glass gains enough oxygen to form the stoichiometrically much more perfect cristobalite. No crystallisation takes place unless the stoichiometric formula SiO_2 can be achieved by some method or other.

Fused quartz is a chemical compound of formula SiO_{2-x}, showing no tendency to crystallise under conditions which allow the retention of this non-stoichiometric composition.

The discrepancy between Lipinski and Schwiete's results for vacuum heat treatment and those of Boganov and coworkers must be stressed.

Whereas Boganov et al.[104] reported that cristobalite formation was completely suppressed, the other investigators found that crystallisation in a vacuum was even more marked than in air, but the quality of their vacuum was not stated.

The crystallisation process is affected also by a number of technological factors. Botvinkin and Zaporozhskii have described an investigation of pure quartz glass (containing $1-2 \times 10^{-2}$% of impurities) prepared by different methods (high-frequency, vacuum compression, and oxy--hydrogen)[3].

The first crystals visible under the microscope appeared on the surface of the gas-melted glass after 72 h heating at 1350°, whereas with glass samples prepared in contact with graphite (high-frequency and vacuum compression method) crystals first appeared after 2–2.5 h at the same temperature. Thus, the rate of generation of crystallisation centres is approximately 30–35 times smaller for the electrically melted glass than for the gas-melted glass.

It should be noted that the crystallisation conditions of pure amorphous or crystalline SiO_2 cannot be the same as those of quartz ceramics, because crystallisation can be speeded up by the porosity and the high degree of dispersity of the starting materials.

VIII. SINTERING AND ANNEALING

Sintering of quartz ceramics prepared from pure silica materials proceeds without the appearance of a liquid phase. In the presence of impurities, however, whether deliber-

ately added or already present in the material, a liquid phase can be formed. The sintering mechanism of quartz ceramics can be visualised as viscous flow and volume diffusion.

According to Frenkel'[111], solid-phase sintering occurs by "viscous flow", and can be resolved in time into two phases: (1) the coalescence of particles, leading to the disappearance of open pores (cavities) and to the formation of disconnected closed pores of various shapes (spherical in the simplest model); (2) the shrinkage of closed pores under the influence of surface tension forces.

The first stage of the process proceeds at a constant rate, depending only on the surface tension and on the viscosity of the medium surrounding the pore:

$$\frac{da}{d\tau} = \frac{3}{4} \times \frac{\sigma}{\mu},$$

where a is the radius of the pore, σ is the surface tension, τ is time, and μ is the viscosity coefficient at the given temperature.

During the second stage the rate of the process decreases continuously because of the retarding effect of the gas trapped in the pores. The theory of Frenkel' does not take account, however, of a number of special features of the sintering process in real powdery bodies, such as the wide variety of particle size, the presence of pores of different sizes, etc.

Pines has shown[112,113] that these factors are of major importance in the sintering process. In particular, powdery bodies of different particle size sinter in different ways.

Following Pines and other workers we may assume that the sintering of a real powdery body results primarily from bulk diffusion, but also partly from surface diffusion. The mechanism of sintering in the absence of a liquid phase thus amounts to redistribution of the material in the body by directed self-diffusion. Interesting discussions of the sintering process can be found also in the papers by Kuczyński, Kingery, Coble, and Johnson and Cutler[114-117].

When considering the sintering of amorphous or crystalline SiO_2 one should first of all take into account the allotropic transformations of the compound, which are ignored by all the existing theories of sintering. Data showing the appreciable effect of these factors are available.

Nishanova and coworkers[35] have studied the sintering of a quartz glass ceramic containing a fairly high concentration of impurities (99.44% SiO_2). Their samples were prepared by pressing at 800 kg cm^{-2} powder from a vibro-mill having a specific surface area of 3100–9800 cm^2 g^{-1}. The bulk density of the samples before firing was 1.41–1.44 g cm^{-3}, their porosity was 34.5–36%. Annealing was carried out in a Silit furnace and in a gas-fired furnace. The results are summarised in Table 2.

The samples annealed in the gas-fired furnace gave somewhat different results, which confirms the influence of the gaseous medium.

Thus, the maximum strength was observed at 1250°, and further increase led to crystallisation. Somewhat greater densities and linear shrinkage factors were obtained in the gas-fired furnace.

The same workers also heat treated samples prepared by slip casting from a mass containing a granular filler. The filler, of fused quartz, included 0.25–0.5 and 0.5–1 mm fractions, and accounted for 30–50% of the total. Under these conditions the strength under compression reached 460 kg cm^{-2}. Summarising the findings of this paper, we note the rather low mechanical strength both under bending (up to 270 kg cm^{-2}) and under compression (up to 1490 kg cm^{-2}), due no doubt to low initial density and to the rather coarse size distribution.

TABLE 2. Influence of degree of comminution of the powder and of firing temperature in a Silit furnace on the sintering and crystallisation of specimens.

Specific surface area, cm^2 g^{-1}	Firing temperature, °C	Linear shrinkage, %	Density, g cm^{-3}	Apparent porosity, %	Strength under compression, kg cm^{-2}	Flexural strength, kg cm^{-2}	Cristobalite content, %
3100	1150	0.2	1.45	34.1	31	17	0
	1200	0.2	1.45	34.2	100	48	0
	1270	2.2	1.53	30.8	359	94	<1
	1300	3.1	1.55	30.0	—	74	3
	1350	3.9	1.58	30.5	—	56	51
9800	1150	0.5	1.47	33.2	104	45	0
	1200	3.7	1.58	28.5	326	94	0
	1270	5.8	1.73	21.8	673	187	<1
	1300	9.0	1.86	16.9	—	179	5
	1350	9.2	1.88	16.8	—	117	63

Popil'skii and Nishanova[42] also investigated the sintering of pressed specimens (5 × 5 × 50 mm) under a specific pressure of 800 kg cm^{-2}. The starting material was translucent quartz glass (99.9% SiO_2). Grinding was done in a vibro-mill (dry method) or in ball mill (wet method) to a specific surface area of 10 000 cm^2 g^{-1}.

Sintering was continued for 2 h at temperatures of 1100°, 1150°, 1200°, 1250°, and 1300°. All the fired specimens showed high porosity, relatively low strength, and in most cases a linear thermal expansion coefficient higher than that of silica glass.

The authors concluded that samples prepared from wet-milled quartz glass (whether transparent or translucent) exhibit slow sintering and crystallisation, but they were unable to explain this effect. They also reported that 0.15% iron contamination has no particular influence on sintering and crystallisation.

From the results set out in Table 3, summarising the measurements of sintering, crystallisation, and strength on specimens made from all the starting material examined, we may conclude as follows.

TABLE 3.

Paste No.	Treatment of starting material	Porosity, % at cristobalite temperatures, °C					Coefficient of thermal expansion 10^{-6} α_{mean} in the range 20–400 (% in brackets) at cristobalite temperatures, °C					Flexural strength, kg cm^{-2} at cristobalite temperatures, °C				
		1100	1150	1200	1150	1300	1100	1150	1200	1250	1300	1000	1150	1200	1250	1300
	Transparent quartz glass															
1	Vibro-mill 180 min	31.5	16.3	13.8	11.9	9.1	0.54	1.42	4.04	33.54 (78)	37.54 (82)	65	310	210	195	105
2	Vibro-mill 180 min, washed	31.2	17.0	16.1	13.8	10.0	0.54	1.01	23.84	37.54 (83)	38.54 (85)	165	355	150	130	160
3	Wet mill, washed	45.9	36.1	33.5	15.6	10.2	0.54	0.65	1.39	20.94 (44)	37.94 (86)	30	170	305	145	170
	Translucent quartz glass															
4	Vibro-mill 180 min	37.5	34.5	32.4	22.0	19.8	0.54	0.54	0.54	0.72	8.94	—	55	65	330	130
5	Vibro-mill 180 min, washed	34.0	32.0	27.1	17.8	11.8	0.54	0.54	0.54	1.44	21.84	40	105	180	340	175
6	Wet mill, washed	35.8	35.8	34.2	29.5	16.0	0.54	0.54	0.54	0.54	6.29	—	—	30	140	260

If we scrutinise the results from the standpoint of a minimum coefficient of thermal expansion, we note that specimens with a low expansion coefficient (0.54×10^{-6}) show a porosity of 31.5–45.9% (for transparent quartz glass as the starting material) or 32.4–34.2% (for translucent quartz glass); the strength under bending varies from 30 to 165 kg cm^{-2} and from 30 to 180 kg cm^{-2} for the two cases respectively.

If maximum mechanical strength is the criterion, specimens made from sintered transparent quartz glass and having a strength of 305–310 kg cm^{-2} exhibit a thermal expansion coefficient between 1.01×10^{-6} and 1.42×10^{-6}, i.e. higher than the expansion of fused quartz glass by a factor of 2–3; the porosity under these conditions is 16–33%. The corresponding values for specimens from translucent quartz glass of strength 260–340 kg cm^{-2} are $6.29 \times \times 10^{-6}$–$0.72 \times 10^{-6}$; the porosity is 16–22%.

Therefore, the results are unsatisfactory as regards optimising this set of properties in specimens made by any particular regime. Thus, the thermal stability (an essential property of this material) falls off as the thermal expansion increases. However, the low mechanical strength and the high porosity of samples having a low thermal expansion can impair the thermal stability and also various other properties.

Walton showed that the mechanical strength of quartz ceramics is raised by a small amount of cristobalite formed during firing (Fig. 6). He suggests that very small particles begin to crystallise during firing, and are converted into cristobalite. Since these fine particles are distributed throughout the bulk, a very intimate binder of cristobalite is formed and causes incipient sintering during the firing operation: in other words, cristobalite appears between the coarser grains of the remaining fused quartz and acts as a binder for these grains.

However, in view of the higher sintering temperature of cristobalite, the suggestion that sintering of this material can occur at 1250° is unconvincing.

It may be thought that a small amount of cristobalite surrounded by a mass of amorphous quartz will not raise the thermal expansion coefficient to the value calculated by assuming additive behaviour, because the expansion of the microscopic cristobalite centres can be checked by the substrate.

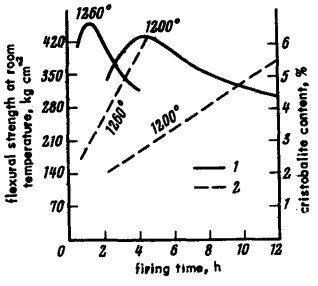


Fig. 6. Variation of the strength of a quartz ceramic with firing time and with cristobalite content:
1) limiting flexural strength; 2) cristobalite content.

A method of producing quartz ceramics from fused quartz has been patented[37], which prevents the formation of cristobalite by the addition of finely divided B_2O_3 to the starting composition, in conjunction with a protective gas atmosphere during sintering.

The amount of B_2O_3 added as a fine powder (up to 2–4 μm particle size) should be at least 1.2% of the weight of SiO_2; the mass to be formed is then prepared by a standard method. Firing must be done in a tightly sealed capsule or in a medium of quartz sand to prevent direct access of furnace gases. The firing temperature can be higher than the normal firing temperatures for quartz ceramics (up to 1350°). The firing time is 30 min. Sintering in a hydrogen atmosphere or in an atmosphere containing vapours of boron compounds produces good results.

Water vapour has been shown[47] to have a distinctly beneficial effect on the sintering of quartz ceramics. However, since water vapour also catalyses the crystallisation of amorphous SiO_2, the onset of cristobalite formation is lowered to 865° by water vapour[101].

The sintering of quartz ceramics to high relative densities without degrading the properties of the articles obtained is complicated by the devitrification phenomena leading to cristobalite formation discussed above. This accounts for the rather high porosity of quartz ceramics, which has an unfavourable effect on the properties. According to published data, the porosity of quartz ceramics varies between 10 and 30%.

To achieve high levels of sintering it is essential to take account of factors such as the density and particle size distribution of the preparation. Under otherwise similar conditions, a denser raw material and a finer granular composition lead to faster sintering at a given temperature. The variation of porosity and density after firing with the density and the porosity of the raw material is illustrated in Fig. 4.

The present writers[45] have demonstrated the profound effect of the state of comminution of the starting material on the sintering of fused-quartz ceramics. Fig. 7 shows the variation of the apparent porosity of specimens made by slip casting at firing temperatures of 1200° and 1250° with firing time, for different mean surface diameters d_{mean} of the particles (calculated by the formula given in Section III of this paper).

We have also shown[45] that a quartz-glass ceramic with zero apparent porosity can, in principle, be prepared, and that the strength and thermal expansion coefficient of this

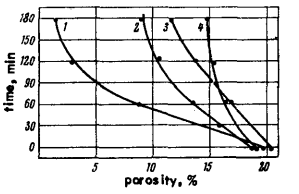


Fig. 7. Variation of apparent porosity with firing temperature and time and mean particle size:
1) firing temperature 1250°, d_{mean} 1 μm;
2) firing temperature 1250°, d_{mean} 2.5 μm;
3) firing temperature 1200°, d_{mean} 1 μm;
4) firing temperature 1200°, d_{mean} 2.5 μm.

material are close to those of quartz glass. The necessary conditions are: small particle size (60–70% of the particles below 5 μm), a very dense starting material (12–15% porosity), and firing at 1300–1450° for times varying from 1.5–2 h to 10–15 min according to the temperature.

The sintering of crystalline silica also is of interest. Dietz and Schulle[17] have investigated the sintering of quartz and cristobalite powders as a function of purity, particle size, temperature, and time. Pure cristobalite was obtained by firing powdered rock crystal at 1530° for 5 h. Specimens of the moistened powders were pressed at 1300 kg cm^{-2}. Quartz began to sinter at 1250°, as shown by an increase in strength and density.

Above 1450° a loss of strength was observed, and this was ascribed to the conversion of quartz into cristobalite. Cristobalite begins to sinter at temperatures beyond 1450°, but the effect of sintering on cristobalite is less marked than on quartz.

The sintering of siliceous materials proceeds in the solid phase, and the formation of a liquid phase as a result of the presence of impurities is of secondary importance. Dietz and Schulle[17] explain the densification and the increase in strength of the quartz by invoking an intermediate amorphous phase, formed during the transition of quartz to cristobalite induced by the mineralising effect of impurities. But this cannot account for the sintering of cristobalite, because no intermediate phase is formed in this modification of silica. The possibility of diffusion processes influencing the sintering of quartz and cristobalite is not excluded.

According to other workers[118], the decrease in porosity and the binding of quartz particles begins at 1580°, and sintering begins at 1605°. At 1620–1660° sintering is fast, and the pores between particles disappear. At 1660° the quartz crystals are converted into optically active cristobalite.

Chaklader and Roberts[110] examined specimens of pure (99.96% SiO_2) quartz, and observed intensive sintering during the first few hours' heating at 1500–1570°, followed by a loosening of the structure. Fig. 8 shows the strength under compression as a function of the time of heat treatment at 1570°. The loss of strength is due to the cristobalite transition undergone by the specimens. The authors suggest the following sintering mechanisms: surface or bulk diffusion, plastic flow, evaporation, or condensation. Sintering apparently occurs through a disordered surface layer on grains formed at high temperatures. Appreciable sintering is observed as soon as the transition phase is formed.

The sharp decrease in strength of the sintered specimens is explained by the formation of significant amounts of cristobalite, which does not sinter at these temperatures. The sintering process is explained by a mechanism involving the transformation of quartz into cristobalite. The expansion observed in the early stages of firing is the result of the conversion of quartz (density 2.65 g cm^{-3}) into a transition phase (2.30 g cm^{-3}) which is amorphous and has vitreous properties.

As soon as a thin layer of the transition phase is formed on the surface of the quartz particles, these particles tend to coalesce, and the strength accordingly increases. The shrinkage is due to the transfer of material to the pore volume. Necks are formed at the points of contact between particles under the influence of capillarity forces.

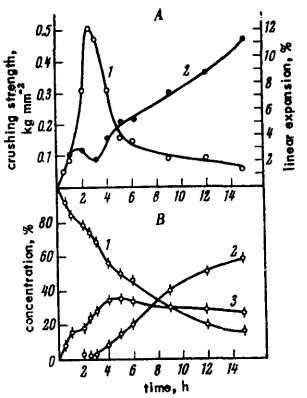


Fig. 8. Variation of crushing strength and relative amounts of quartz, intermediate phase, and cristobalite as a function of firing time of quartz specimens at 1570°.
A: 1) linear expansion in %; 2) crushing strength in kg mm^{-2}.
B: 1) quartz; 2) cristobalite; 3) intermediate phase.

A critical survey of available data on the sintering of crystalline silica, fused quartz, and amorphous synthetic silica leads to the following general propositions.

The occurrence of sintering and the sintering temperature are invariably associated with incipient crystallisation. The lower the temperature at which crystallisation of any particular form of silica begins, the lower will be the temperature of incipient sintering. There is also evidence that intense sintering occurs during the period immediately prior to crystallisation, i.e. during the stage of formation of metacristobalite. We have shown[45] that the specific gravity of a densely sintered ceramic made from fused quartz is often slightly higher than that of fused quartz (2.21 g cm^{-3}), suggesting partial conversion into metacristobalite not involving appreciable degradation of the properties. The method of formation and the pretreatment of the material also have an undeniable effect on the onset and on the kinetics of the sintering process.

In order to achieve higher densities in a ceramic based on fused quartz without at the same time causing the formation of cristobalite it is desirable to use finely milled powders. In this way the rate of sintering is increased more than the rate of onset of crystallisation. Conversely, coarser granular compositions retard the onset of crystallisation, but since sintering is very slow and much longer firing times are needed the amount of crystallisation is relatively large.

The initial density of the raw material plays an important part in quartz ceramics, high initial densities allowing extremely dense materials to be produced.

When specifying the firing schedule of an article it is important first of all to consider the possibility of cristobalite formation. The initial particle size distribution and the presence of impurities are also extremely important.

Fig. 9 summarises our results[45] on the effect of time and temperature on the onset of cristobalite formation for specimens prepared by slip casting from fused quartz containing 99.9% of SiO_2.

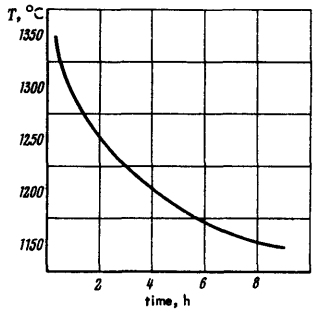


Fig. 9. Variation of the onset of crystallisation with temperature and time.

The maximum firing temperature is 1650–1680° for articles made from quartz sand, and 1250–1300° for articles made from fused quartz, The time of treatment at the maximum temperature is usually 1 h, but equally good results can be obtained for shorter times at higher temperatures.

Schulle and Ulbricht[24] have described the following firing schedule for articles made by slip casting from quartz sand. The specimens were heated at 1000° for 3 h in a Silit furnace before being subjected to the required firing temperature (1680°). After the prescribed firing time the specimens were removed from the furnace and placed in a cooling oven set at 900°, in which they were allowed to cool to room temperature.

Fleming[20] considers that 4 h at 1200° is sufficient for relatively small articles made of fused quartz, whereas larger articles need 1 h at 1260°.

The shrinkage during firing depends on the porosity of the starting preparation and on the maximum temperature and time of heat treatment, and is usually in the range 0.5–5%. With large articles there is a possibility of distortion of the lower parts.

IX. SURFACE IMPREGNATION AND SEALING

Quartz ceramics offer good electrical properties, similar to those of quartz glass. However, the unavoidable porosity associated with the conventional ceramic production techniques has an appreciable effect on the electrical properties. Furthermore, quartz ceramics have inadequate moisture resistance. In a number of applications both high density (absence of porosity) and moisture resistance are essential. However, the achievement of adequate density by sintering is made difficult by the cristobalite transformation discussed above.

In this connection, the following methods for achieving the required properties have been proposed: impregnation, glazing, surface melting, and hydrophobic coatings[31-33]. Impregnation consists, essentially, of soaking the fired porous article in a solution which can fill the pore volume and subsequent deposition of a solid phase from the solution. The rate, uniformity, and completeness of the soaking treatment depend on a number of factors: the magnitude of the surface tension at the interface between the impregnating solution and the body, the size and shape of the pores in the sintered article, and the viscosity of the penetrating solution.

The impregnation method has already been used in practice for powder-metallurgy articles. For example, porous sintered iron or steel is usually impregnated with various metals and alloys, mostly based on copper. In this application the sintered articles must be impregnated with much more fusible metals.

In the preparation of ceramic materials impregnation problems have attracted little attention so far, and the work discussed below is based exclusively on laboratory data[24,31-33].

The theoretical foundations of impregnation have been developed by Deryagin[119]. The basic postulates of his theory are essentially the following.

Let an element of the impregnation front move to a new position in a given time, filling a pore volume ΔV with a wall surface of ΔS:

$$p\,\Delta V = A\,\Delta S,$$

where p is the pressure drop across the layer l of impregnated volume due to the internal friction of the liquid and A is the specific work of wetting. Then,

$$l = k\frac{\Sigma}{\delta^2}\sigma\cos\theta,$$

where l is the thickness of the impregnated layer, k is the filtration coefficient, δ is the fractional pore volume, Σ is the specific surface area of the impregnated body, σ is the surface tension of the liquid, θ is the limiting contact angle.

Impregnation is carried out after a preliminary heat treatment, and is followed by drying and firing. The best results are obtained in practice by impregnating with true solutions of inorganic materials. Colloidally disperse silica does not give good results because of the very small pore diameter of quartz ceramics, which acts as a filter and removes the most finely dispersed colloids after a thin layer has been impregnated. Impregnation is achieved by using hydrolysed ethyl silicate: the concentration is adjusted so that the silica is held in solution low enough to ensure complete impregnation of the ceramic, whereupon the ethyl silicate forms a gel which deposits SiO_2 in the pores.

However, since these gels are aqueous, some residual porosity is unavoidable to allow the passage of the dehydration products during firing, and the method allows the porosity to be decreased but not completely eliminated.

When the porosity of the original ceramic is high, impregnation affords a significant improvement in strength and decrease in porosity[24].

As the porosity of the ceramic decreases, impregnation becomes slower. An aqueous solution of aluminium chloride has been examined as a possible impregnating agent[33]. Aluminium hydroxide was precipitated in the pores of the quartz ceramic by altering the pH. This material reacts with silica during sintering, forming mullite. However, since mullite is formed at temperatures above the crystallisation temperature of quartz ceramics, we are faced with the problem of avoiding the conversion of fused quartz into cristobalite and yet producing mullite, which can be sintered sufficiently to eliminate the porosity.

Glazing of quartz ceramics is difficult because of the very low thermal expansion coefficient of the material, which necessitates a glaze having either zero or a small negative thermal expansion coefficient.

Glazes of materials such as spodumene and petalite, which satisfy these requirements, have a flow temperature higher than the crystallisation temperature of quartz ceramics, and cannot be applied by ordinary methods. However, the glazes can be deposited by flame-spraying whilst retaining their low or negative thermal expansion coefficient. Surface sealing can be achieved also by fusing the surface layer of the glass ceramic with a plasma torch.

Both glazing and surface melting must be carried out whilst heating the ceramic to 1000–1100° to avoid large thermal stresses, and the article must then be annealed.

Hydrophobic coatings which are fired in flight by the temperature rise can be used for sealing antenna fairings [31].

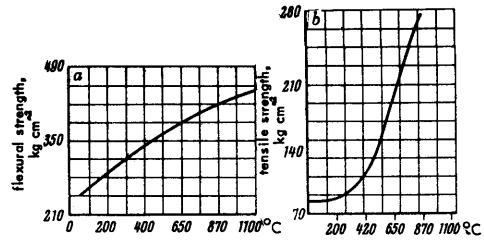


Fig. 11. Effect of temperature on the mechanical strength of quartz ceramics:
(*a*) flexural strength; (*b*) tensile strength.

X. PROPERTIES AND APPLICATIONS OF QUARTZ CERAMICS

Quartz ceramics made from fused quartz possess many of the valuable properties of the starting material: a low coefficient of thermal expansion, good high-temperature stability, good electrical parameters, high chemical stability. However, quartz ceramics also exhibit some properties which are not present in fused quartz (quartz glass). Unlike quartz glass, whose thermal conductivity rises quite significantly with temperature, quartz ceramics and quartz ceramic foams have a constant and fairly low thermal conductivity over the temperature range up to 1100°. As Fig. 10 shows, the thermal conductivity of quartz glass at 500° is approximately 5 times higher than that of quartz ceramics and 20 times higher than that of quartz foam.

A steep rise in the thermal conductivity of quartz ceramics is observed in the temperature region above 1100°, due to the formation of cristobalite. Furthermore, devitrified quartz glass breaks down on cooling, whereas the ceramic can retain its shape. A special feature of quartz ceramics in comparison with other types of ceramic is the increase of tensile and flexural strength with temperature, evidently associated with an increased plasticity and a lower brittleness [18,52]. The increase in strength is quite significant: as Fig. 11 shows, the strength under bending is much higher at 1100°. [18]

Another distinguishing feature of quartz ceramics as compared with other ceramic materials is their much smaller shrinkage both on drying (0.1–0.5%) and on firing.

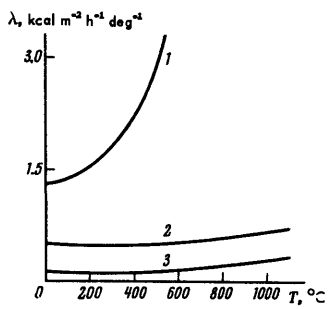


Fig. 10. Temperature dependence of thermal conductivity:
(1) transparent quartz glass, (2) quartz ceramic, and (3) quartz foam.

The main structural difference between quartz ceramics and quartz glass lies in their porosity, from which stem all the other differences in mechanical as well as electrical properties.

The influence of porosity on the mechanical, thermal, and dielectric properties of quartz ceramics has been investigated [46]. Specimens prepared by slip casting, hot pressing, and spray coating were divided into four groups: low (25–40%), intermediate (30–70%), high (85–90%), and very high (90–100%) density as compared with the theoretical density. It was shown that the properties of the ceramic depend on the type of raw material and on the method of preparation as well as on the pore volume, with the exception of the dielectric properties, which are determined exclusively by the porosity. The strength is as much a function of the method of forming as of the porosity.

The porosity of quartz ceramics is responsible for the low thermal conductivity of these materials, for their low mechanical strength (relative to that of quartz glass), and for the slight difference in electrical resistance. The ceramic, unlike quartz glass, is not transparent (having a white colour), and has a lower specific gravity. However, when the porosity is minimised (to the 1–2% level) the basic properties of the ceramic become almost identical to those of the glass.

Quartz ceramics have some advantages over other materials which have been considered for use in missile cones. Their dielectric constant at 10^{10} Hz should not vary by more than ±5% between room temperature and the maximum, and the tangent of the dielectric loss angle under these conditions should be less than 0.01. [31]

Of the three materials: quartz ceramic, corundum ceramic, and Pyroceram 9606, a ceramic made from fused quartz satisfies these requirements most fully [31,52].

Furthermore, rocket cones made by slip casting from fused quartz are much cheaper to produce [52] than those made from Pyroceram or Al_2O_3. Their flexural strength increases with temperature (by 33% at 1100°), as compared with a 67% decrease for Al_2O_3 and a 25% decrease for Pyroceram [52]. It has even been suggested [33] that articles can be made more cheaply in quartz ceramics than in fused quartz. Porous quartz insulators are used also in radar installations.

Many fields of application require high thermal stability, constancy of dimensions, low thermal conductivity, and other important properties: quartz ceramics satisfy these requirements fully. Quartz ceramics can be used in the newer technological areas, such as missile and nuclear technology, and also as general purpose refractories.

The devitrification of quartz ceramics at temperatures above 1100° does not exclude the use of these materials at the higher temperatures: the permissible concentration of cristobalite is determined by the specific conditions of use of the article. An important consideration is the duration of the exposure to the maximum temperature. Studies of the suitability of quartz ceramics for thermal shielding systems and for the manufacture of aircraft components have shown that quartz ceramics are the most promising material for these purposes. Among the articles which could be manufactured from quartz ceramics the following are listed: front flanges and nose cones for rockets, antenna fairings, nozzles for rocket engines, etc. In addition to their excellent dielectric properties, quartz ceramics offer a high thermal stability and low thermal conductivity, which make them suitable for these applications [31-33].

A rocket cone 61 cm in diameter and 1.22 m high has been made by slip casting. Its wall thickness was so uniform that no further mechanical operations were needed [36].

When a missile re-enters the denser layers of the atmosphere the temperature rises well above the melting point of quartz, and can reach 2500°. However, since the passage through the dense layers is of short duration, and the material has a high viscosity, the rate of wear of the nose cone is only ~0.025 mm s^{-1}.

The nose cone of the U. S. Titan intercontinental ballistic missile is an example of the use of quartz ceramics in space technology [49].

Quartz foam, which is used as a heat shield, is a very promising material for applications in aerospace technology [43,44]. In order to increase its mechanical strength, quartz foam is impregnated with organic resins [44].

Heat shields are also used for the nose cones of rockets in order to give reliable protection to the electronic systems against heat and radiation during passage through the dense layers of the atmosphere [29]. Rare-earth elements or their oxides are added to the fused quartz. The most favoured is gadolinium, or the other rare-earth elements with similar properties (La, Ce, Pr, Nd, Eu, Tb, Er, etc.). The concentration of the additive is kept between 0.1 and 10%. and this determines many of the properties of the shield. When nuclear radiation is present gadolinium is to be preferred, because it has the property of absorbing radiation. Without the addition of rare-earth elements, infrared radiation and heat are readily transmitted from the outer surface of the quartz layer to the inner regions when the nose cone is subjected to heating. However, the rare-earth elements cause absorption and back radiation from the outer layers of the nose cone.

In order to assess the properties of quartz ceramics, their ablation properties have been evaluated with an electric arc whose temperature was stabilised with air or water [32]. The specimen used for the test was cylindrical, with one hemispherical end. The rate of ablation was assessed by monitoring the rate of decrease in the length of the specimen whilst the arc discharge was applied. The experimental results and the working parameters of the test are summarised in Table 4.

Foamed quartz ceramics make high-grade reflectors of infrared radiation. This is because the outer layer of the quartz foam reaches a high temperature almost as soon as the lamps are energised and generates energy which is absorbed as infrared radiation. Furthermore, the underlying layers of the quartz foam greatly obstruct the transmission of infrared rays.

TABLE 4. Ablation data for quartz ceramics, obtained by plasma torch spraying.

Type of arc	Air stabilised	Water stabilised
Power, kW	100	60
Specimen diameter, mm	12.7	19
Gas velocity	Mach 2.5	100–1000 m s^{-1}
Duration of test, s	25	20
Ablation, cm	1.2	0.78
Rate of ablation, cm s^{-1}	0.048	0.039

Quartz ceramics are used in the manufacture of electrical insulators and of fairings for radar aerials. Ceramic insulators of any shape can be made by slip casting. After firing, these are impregnated with a synthetic resin or lacquer to eliminate the porosity.

Fig. 12 shows the temperature variation of electrical resistance of ceramic specimens, both with and without silicone varnish impregnation, as well as tan α and ϵ.

To test the possibility of using quartz ceramics as insulators in high-temperature nuclear reactors, a series of quartz rods was cast and fired at 1380° for 48 h in order to form cristobalite [19,33]. Another batch of rods, earmarked for studying the influence of neutron irradiation on the strength of quartz ceramics, was fired at 1260° for 1 h.

The quartz ceramic specimens were irradiated in an experimental reactor with a neutron flux of energy 816 mV r. Complete collapse of the cristobalite structure to the amorphous state was observed at a dose of about 4×10^{20} neutrons cm^{-2} s^{-1}. No permanent changes in flexural strength were noted in any of the irradiated specimens.

Fused quartz does not undergo changes under the influence of nuclear radiation, and has a small capture cross-section for thermal neutrons: this is why the material is used for containers in experiments involving radiation.

Irradiation with a dose of $\sim 2 \times 10^{20}$ neutrons cm^{-2} s^{-1} has little effect on the strength of quartz ceramics, which varies within the range ±10%.

The possibility of using a ceramic made from fused quartz in the atomic energy industry as a medium for fuel elements in the SiO_2–UO_2 system has been investigated. It

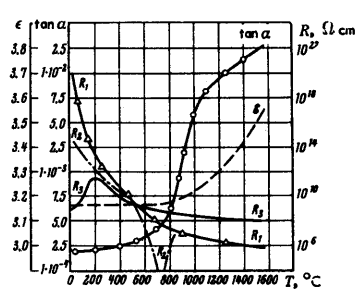


Fig. 12. Temperature dependence of the electrical resistance of quartz glass (R_1), impregnated (R_2), and non-impregnated (R_3) quartz ceramics, of the tangent of the dielectric loss angle (tan α), and of the dielectric constant (ϵ) of quartz ceramics.

was shown that these materials satisfactorily retain the gaseous fission products and are highly stable towards the breakdown caused by the recoil of fission products[19]. Quartz bodies prepared by casting and quartz foam should find widespread use as materials for thermal insulation in nuclear reactors.

The following applications may be quoted as examples of the use of quartz ceramics as refractories: dies for hot pressing, fixtures for rigidly welding cellular constructions of stainless steel, pipes for conveying molten aluminium, etc.

One of the applications of quartz ceramics is the monolithic lining of boilers: high-grade refractories were previously used for this purpose, but their life was limited to three months by temperature drops and by mechanical vibrations[33], whereas linings of quartz ceramic give service for upwards of two years. Another example of the use of quartz ceramics is in the lining of roasting kilns. Panels 122 × 152 × 15 cm in size were cast from a mass made from fused quartz, and used in the kiln assembly after being dried but in the unfired condition. The performance after one year's use of the kiln was satisfactory, although the temperature drop from the hot to the cold side of the blocks was of the order of 1000°.

Ceramic foam has been used for lining crucible furnaces for melting aluminium, with a resulting fuel saving of 50–60% as compared with the conventional refractory lining[33].

Quartz ceramics can be successfully applied to the production of casting moulds for repeated use[20,21]. To investigate the effect of devitrification, an iron melt was cast into a mould made of quartz ceramic (from fused quartz) and allowed to solidify completely. After 12 such cycles, no sign of crystallisation was observed in the material. It was also found that if the first cycle did not induce the onset of devitrification, the subsequent cycles also failed to bring it about.

TABLE 5. Properties of quartz glass, quartz ceramic, and foamed quartz ceramic.

Parameters	Quartz glass	Quartz ceramic	Foamed quartz ceramic
Density at 20°, g cm^{-3}	2.21	1.82–2.15	0.4–0.7
Overall porosity, %	0	1–20	50–60
Limiting strength at 20°, kg cm^{-2}			
crushing	5000–10 000	2500–5000	500–700
flexural	700–800	200–600	14–35
tensile	230–400	140–210	—
Limiting strength under impact bending, kg cm^{-2}	0.85–1.0	0.8–1.8	—
Thermal expansion coefficient, deg^{-1}, × 10^6	0.54	0.54	0.54
Thermal conductivity, kcal h^{-1} deg^{-1}			
at 0°	1.0–1.2	0.5	0.1
at 1200°	—	0.8	0.5
Specific heat, cal g^{-1} deg^{-1}, × 10^3 at 0°	200	200	—
Softening temperature under a load of 2 kg cm^{-2}, °C	1250	1250	1250
Dielectric constant			
at 20°	3.7	3.2–3.6	—
at 1000°	—	3.3–3.7	—
Tangent of the dielectric loss angle in the frequency range 30 kHz–10 MHz			
at 20°	6×10^{-4}	2×10^{-4}	
at 800°	6.7×10^{-4}	6×10^{-4}	
at 1200°	8×10^{-2}	8×10^{-2}	
Total linear shrinkage after drying and firing, %		1–6	1–6
Microscopic absorption cross-section for thermal neutrons at 2200 m s^{-1}	—	0.26	—
Macroscopic absorption cross-section for thermal neutrons at 2200 m s^{-1}	—	0.057	—
Relative slowing down	—	1.29	—

In another experiment one size of a quartz ceramic block was exposed to a high furnace temperature whilst the other side remained cold: the hot side crystallised at 1090°, but the crystallised regions were firmly bound by the uncrystallised substrate, as shown by a vibration test[31].

The main properties of quartz glass, quartz ceramics, and quartz ceramic foam are listed in Table 5.

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Quartz ceramics can be manufactured by slip casting, slip foaming, hot pressing, semi-dry pressing, and various other methods from fused quartz, synthetic amorphous silica, and quartz sand.

Devitrification of the articles, which occurs at the maximum firing temperatures, can impair the thermal stability if it reaches appreciable proportions; however, by choosing the most appropriate firing schedules, the formation of cristobalite can be avoided or limited to low amounts.

The property of quartz ceramics which distinguishes them from other types of ceramic is their low coefficient of thermal expansion and their unusually high thermal stability. Compared with quartz glass, quartz ceramics have a significantly lower thermal conductivity (especially at high temperatures), and they do not break up as a result of cristobalite formation.

Quartz ceramics may find wide applications in the heat-resisting members of missiles, in nuclear technology, in the chemical and metallurgical industry, and as general purpose refractories.

Some specific features of the production of quartz ceramics must be pointed out. Devitrification during sintering is a complicating factor in the production of a densely sintered ceramic. It is therefore desirable to start from specially prepared fused quartz, which has a lesser tendency to form cristobalite (gas melting, avoidance of impurities conducive to crystallisation, etc.). It is important to maximise the density of the stock in order to assist sintering. Increasing the density of the ceramic can improve the physical and electrical properties of these materials very considerably.

Doping the quartz with rare-earth elements offers interesting possibilities because these elements can improve many of the properties of quartz.

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Department of General Silicate Technology
Mendeleev Moscow Institute of Chemical Technology

U. D. C. 541.6 : 541.24

STUDIES OF POLYMER SOLUTIONS CARRIED OUT IN POLAND

E. Turska

The field of studies on polymer solutions is very extensive and covers a wide range of varied problems. Such studies may be carried out with various aims in view — to define the properties of the solutions, or to characterise the macromolecules themselves from the properties of the solutions. Because of the variety of problems raised it is not possible to cover completely all work on the study of polymer solutions.

In order that the material presented shall be treated as fully as possible we shall consider only two questions, namely the determination of molecular weight and the study of polydispersity. We shall also examine some interesting papers on the hydrodynamics of solutions, and certain others.

In Polish literature on molecular weight determination, problems of practical importance arouse greatest interest. These papers generally describe experimental studies. The number of theoretical papers on this problem is much smaller.

Most attention has been paid to viscometric studies, and second place, as far as number of papers is concerned, is taken by work on procedures using the ultracentrifuge.

Papers on the determination and calculation of average molecular weight by osmometric and cryoscopic methods and from terminal groups are fairly numerous. There are fewer papers on light scattering by polymer solutions, and they have begun to appear only recently. There are also some papers which discuss the possible use of procedures which have not yet found such extensive application as those noted earlier.

The viscometric method, which requires simple apparatus, is the most convenient method for determining the molecular weight of polymers. It is becoming the most commonly used method of control in industry. The interest of Polish authors in this method is determined to a considerable extent by the practical approach.

Among the large number of papers in this field, mention may be made of the comparatively early determinations, the first to appear in the scientific literature, of the viscometric relationships for polyethylene terephthalate[1]. Tursa and Skwarski determined the molecular weights of a number of low-polymer polyterephthalate fractions by a cryoscopic method and, with the aid of viscometric data, they calculated the constants of the Mark–Houwink equation for the system studied.

Among recent work, mention may be made of a paper by Nadziakiewicz and Jedlińska[2] of the Lodz Synthetic Fibres Institute, devoted to methods of determining the degree of polymerisation of cellulose in solvents in which it does not undergo degradation under the influence of atmospheric oxygen. On the basis of published data and their own studies, they concluded that ethylenediaminecadmium hydroxide has a number of advantages as a solvent for cellulose. Overcoming difficulties in the procedure, associated with the low solubility of some forms of cellulose, the authors confirmed that the viscosity of the solution is linearly dependent on the degree of polymerisation in the range studied, and derived the viscometric equation.

Several other papers[3,4] have been devoted to studies of the dependence of the viscosity of solutions of cellulose in other solvents on the degree of polymerisation.

The viscosity of solutions of other polymers was studied by Kryszewski[5], Skwarski[6], Orszagh[7], Łaszkiewicz[8], and others.

Problems new to the scientific literature in this field were raised by Połowiński[9,10] of the Physical Chemistry of Polymers Faculty in Lodz Polytechnical Institute. Poło-