
Institute of Ceramics Textbook Series

CERAMIC RAW MATERIALS

Second Revised Edition

by

W E WORRALL

University of Leeds, Leeds, UK



PERGAMON PRESS

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W E WORRALL

MSc, PhD, ARIC

*Senior Lecturer in Ceramics
The Houldsworth School of Applied Science,
The University of Leeds, UK*

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1. Raw Materials

1.1 INTRODUCTION

The oldest ceramic raw material is undoubtedly clay. Clay has been defined as an earth that forms a coherent sticky mass when mixed with water; when wet, this mass is readily mouldable but if dried it becomes hard and brittle and retains its shape. Moreover, if heated to redness, it becomes still harder and is no longer susceptible to the action of water. Such a material clearly lends itself to the making of articles of all shapes.

Clay may take various forms; it is easily recognized as the sticky, tenacious constituent of soil, but it can also occur as rock or slate which, owing to compression, is so hard and compacted that water penetrates it very slowly. Clay is seldom pure, but the substance responsible for its characteristic properties is usually called the "clay mineral" or "clay substance".

Although probably the earliest ceramic articles were made entirely from clay, from very early times additions to it of other materials are known to have been made. At the present time in the pottery industry the chief raw materials used in conjunction with clay are the various fluxes and silica. In the refractories industry, increasing demand for specialized refractories has resulted in products containing little or no clay, such as alumina, magnesite and chrome; such products are also classed as "ceramics" because in general they are shaped whilst wet and then fired in order to be hardened.

In recent years a wide variety of inorganic, non-metallic materials has been developed for the electrical, nuclear power, and engineering industries. In the shaping and processing of these products some form of heat treatment is involved, and they too are regarded as ceramic materials. Examples are: rutile, a form of titanium dioxide used for making ferroelectric materials; steatite or talc, for electrical insulators; alumina, zirconia, thoria and beryllia as refractories and electrical insulators, uranium oxide as a nuclear-fuel element, and nitrides and carbides as abrasives or insulators.

1.2 SILICA

1.2.1 Structure of Crystals

Before being able to understand the properties of silica, we must know something of its structure—that is, the way in which the solid is built up from the atoms of silicon and oxygen. The principles outlined here will help in understanding the structures of the other minerals to be described later.

Most solid substances are crystalline—their component atoms are arranged in a regular array which is called a *lattice*. A lattice is a continuous structure, capable of indefinite extension in at least two dimensions, rather like the pattern on a wallpaper that is repeated again and again. This “repeat pattern” is called a unit cell. Even in a simple lattice such as that of NaCl, however, there are no individual molecules of NaCl as such; no single atom can be said to “belong” entirely to any other atom; it is “shared” between all its neighbours.

The bonding in crystals is of two main types: (a) *electrovalent*, where the atoms have become charged by the gain or loss of electrons, to form ions; in this instance the electrostatic attraction between oppositely-charged ions constitutes the bond; (b) *covalent*, where two or more atoms acquire stability by sharing electrons. Apart from bonds between like atoms, as in N_2 , O_2 , etc., most bonds are neither purely covalent nor purely electrovalent but partake of the character of both. However, for many of the compounds encountered in ceramics, there is sufficient ionic character for the crystals to be regarded as made up of ions. Although the modern theories of bonding based on wave mechanics have enabled us to formulate the electron distribution in compounds more precisely, the ionic model is adequate for our present purpose.

The sign of the electrostatic charge depends on the nature of the atom—in general, “metallic” ions carry a positive charge and non-metallic ions carry a negative charge, equal in magnitude to their valencies; thus in silica the ions are Si^{4+} and O^{2-} . Since the lattice as a whole must be electrically neutral, the sum of the positive charges must equal the sum of the negative charges.

In ionic crystals such as sodium chloride and silica, the various types of ion may be regarded as spheres having definite radii; some examples of ionic radii are given in Table 1.

Table 1. Ionic Radii of some Common Elements

Element	Symbol of ion	Valency	Ionic Radius (Å)*	Usual co-ordination number(s)
Boron	B ³⁺	3	0.20	3, (4)
Beryllium	Be ²⁺	2	0.31	4
Silicon	Si ⁴⁺	4	0.41	4
Aluminium	Al ³⁺	3	0.50	4, (5), 6
Magnesium	Mg ²⁺	2	0.65	6
Sodium	Na ⁺	1	0.95	6, (8)
Titanium	Ti ⁴⁺	4	0.68	4, 6
Zirconium	Zr ⁴⁺	4	0.80	6, (8)
Calcium	Ca ²⁺	2	0.99	(7), 8, (9)
Potassium	K ⁺	1	1.33	(6), (7), 8, (9), (10), 12
Iron: ferrous	Fe ²⁺	2	0.75	6
ferric	Fe ³⁺	3	0.60	4, 6
Oxygen	O ²⁻	—2	1.40	—
Fluorine	F ⁻	—1	1.36	—
Sulphur	S ²⁻	—2	1.84	—
Chlorine	Cl ⁻	—1	1.81	—

* Å = 1 Ångstrom Unit = 10⁻¹⁰ m. () signifies less common co-ordination numbers.

It will be clear from this table that the negative ions (anions) are in general larger than the positive ions (cations). Consequently the type of lattice largely depends on the packing of the anions. Another important feature of the lattice is that, for maximum stability, each ion tends to surround itself with the greatest possible number of oppositely-charged ions, so that all are in contact; this number is known as its co-ordination number. The maximum number of neighbouring ions are in contact. Since Si⁴⁺ is a small ion, the maximum number of O²⁻ ions that can surround it, all being in contact, is four. We say therefore that the *co-ordination number* of silicon with respect to oxygen is four. This arrangement is shown in perspective in Figure 1.

Each type of ion, depending on its size, has a characteristic co-ordination number with respect to oxygen; co-ordination numbers for some of the commoner cations with respect to oxygen are given in Table 1.

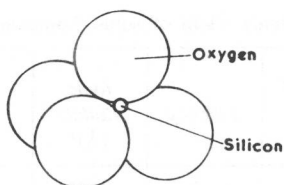


Fig. 1.—Packing of silicon and oxygen atoms in silica and the silicates.

The arrangement of four O^{2-} ions around one Si^{4+} ion is characteristic of all compounds containing silicon and oxygen. If we imagine the centres of the four oxygen ions to be joined by straight lines, as in Figure 2, the resulting geometrical figure is known as a tetrahedron, with a triangular base and three triangular sides meeting at an apex; the Si^{4+} ion is situated at the centre of this tetrahedron. Often it is convenient to speak of this (SiO_4) unit as a “silica tetrahedron”.

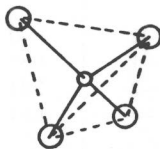


Fig. 2.—A silicon-oxygen tetrahedron.

We can work out the “valency requirements” as follows. Each Si^{4+} ion, of course, has four “valency bonds”, and may be imagined to “share” these four valency bonds between the four surrounding O^{2-} ions, giving one “valency share” (+1) to each. (Figure 3).

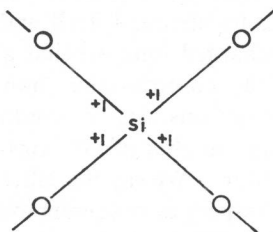


Fig. 3.—Distribution of charges in the silicon-oxygen tetrahedron.

In this way the valency requirements of Si^{4+} are satisfied, but the oxygen valencies in this (SiO_4) group are only partially satisfied, because whereas each O^{2-} requires two valency shares, it receives only one. In order therefore to satisfy the free oxygen

valencies, the (SiO_4) group requires other ions. In silica (SiO_2) these free valencies are satisfied because the tetrahedra join to one another in such a way that each O^{2-} ion is effectively joined to two Si^{4+} ions. Consequently the valency requirements of both Si^{4+} and O^{2-} are satisfied, and the net formula is then not (SiO_4) but SiO_2 . There are several ways in which the tetrahedra can be joined, and it is therefore not surprising that there are three principal crystalline forms of silica—quartz, cristobalite and tridymite—each having the formula SiO_2 , but differing in the way the silica tetrahedra are arranged.

1.2.2 Structure of Quartz

In quartz the Si—O—Si bonds joining neighbouring tetrahedra are not straight but bent round to form spiral chains (Figure 4). Starting with any Si^{4+} ion, a spiral can be traced in one definite direction, depending on the crystal (in this instance the direction is anti-clockwise). The whole structure consists of many such

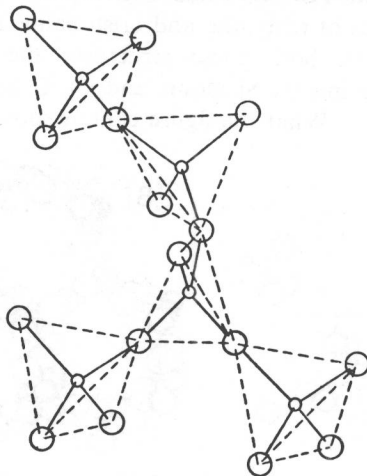


Fig. 4.—Arrangement of silica tetrahedra in quartz.

spiral chains, joined by common Si^{4+} ions, shown in perspective in Figure 5. Note that, in these and subsequent atomic models, the distances between atoms have been exaggerated and the ionic radii are not to scale. This has been done to show the valency bonds clearly; in a scale model with all the atoms in contact the bonds would be difficult to discern.

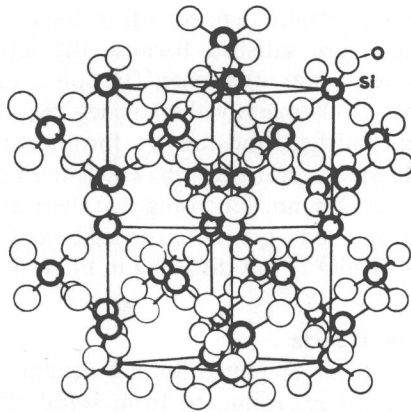


Fig. 5.—The structure of β -quartz. (Atoms nearer to the reader drawn in heavy outline).

1.2.3 Structures of Tridymite and Cristobalite

The structures of tridymite and cristobalite are perhaps easier to understand. In both these structures the silica tetrahedra form rings containing six Si atoms and six O atoms, as shown in Figure 6, A and B. What the figure cannot show is that in neither

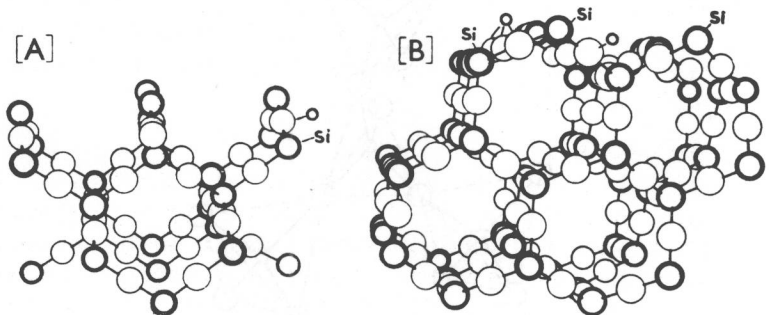


Fig. 6.—The structures of : A. Tridymite. B. Cristobalite.

the tridymite nor the cristobalite structure are the rings flat; they are somewhat distorted and so the Si atoms are not all in the same plane. This distortion is more marked in cristobalite than in tridymite. The difference between the two is best appreciated by considering how the oxygen atoms are arranged. Figure 7A shows how two silica tetrahedra are linked in tridymite. Note that the lowest three oxygen atoms form the triangular base of the lower

tetrahedron. The second tetrahedron is inverted, with its base uppermost, and is joined to the first through a common oxygen atom forming the apex. Now observe that the three basal oxygen atoms of the upper tetrahedron fall directly below corresponding oxygen atoms in the base of the lower tetrahedron; this arrangement of the oxygen repeats throughout the structure and is characteristic of tridymite.

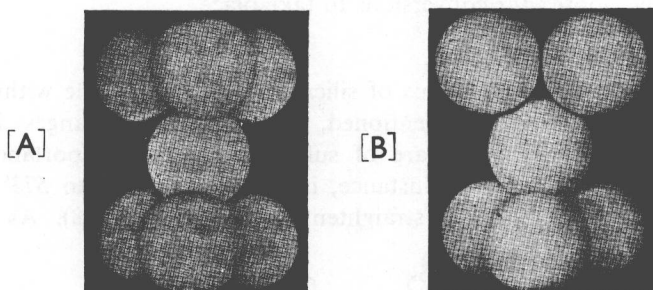


Fig. 7.—Packing of oxygen atoms in : A. Tridymite. B. Cristobalite.

Figure 7B shows the arrangement of the oxygen atoms in cristobalite and it is clear that the basal oxygen atoms of the respective tetrahedra no longer correspond; it is as if one of the tetrahedra of Figure 7A had been twisted through 60° with respect to the other. This arrangement is characteristic of the oxygen atoms in cristobalite.

1.2.4 Conversions

The structures of the three forms of silica differ considerably, and it is not easy to convert one to another. Any such conversion involves the breaking of Si-O bonds—in other words, separating the tetrahedra and then joining them again differently. Nevertheless, if quartz is heated above 1470°C for a considerable time, it is gradually converted to cristobalite. Furthermore, if cristobalite is heated in the range 870°C to 1470°C , it is gradually converted to tridymite. Both these reactions can be speeded up by catalysts or mineralizers—e.g. lime assists the conversion of quartz (or tridymite) to cristobalite. These conversions may be represented by the equation:



these high-temperature forms of silica can only with great difficulty

be reconverted to quartz, consequently in the equation the conversion of quartz to tridymite is represented by a single arrow. This conversion being apparently irreversible, it is surprising that quartz is much more common in Nature than the other forms; cristobalite and tridymite are, of course, formed artificially, e.g. in the manufacture of silica bricks. All three forms are relatively stable at room temperature; only at 870°C and above are the Si-O bonds sufficiently "loose" for conversions to take place.

1.2.5 Inversions

Although the three forms of silica are relatively stable within the temperature ranges mentioned, certain minor changes in structure do occur, which are of sufficient practical importance to deserve attention. For instance, if quartz is heated to 573°C or over, the Si-O-Si bonds straighten somewhat (Figure 8). As a

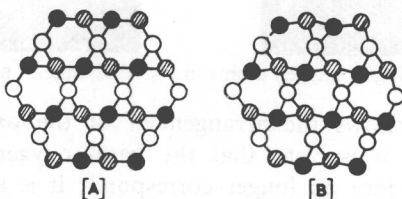
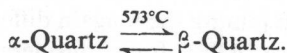
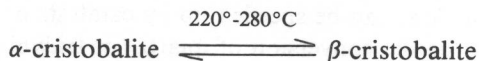


Fig. 8.—Arrangement of silicon atoms in : A. β -quartz. B. α -quartz. (Reproduced from "Structural Inorganic Chemistry", by kind permission of A. F. Wells and the Clarendon Press, Oxford).

result, the atoms become less closely packed and a marked expansion occurs. The modification that exists at room temperature is known as α -quartz and that above 573°C is known as β -quartz, and the transition from one to the other can be represented by the equation:



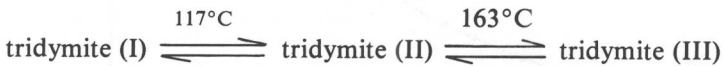
Similarly, if cristobalite is heated at 220°-280°C, it is converted to the β -form:



Whilst the inversion temperature of quartz does not appear to vary appreciably, that of cristobalite has been found to depend on its previous history and may vary, as indicated, over a range of temperature. This variation is believed to be caused by differences

in the degree of perfection of the crystal structure.

Tridymite also undergoes a series of inversions, the number and type of which vary from one specimen to another. Because the number of modifications is greater than with quartz or cristobalite, Roman numerals are now used to distinguish them and have replaced the older α - β notation. Thus, a typical specimen of tridymite undergoes the following inversions:



Some specimens of tridymite have been reported to exhibit as many as five inversions. In contrast to conversions, the inversions referred to above occur rapidly and are reversible.

1.2.6 Other Forms of Silica

Although in recent years, certain new high-pressure forms of silica have been discovered, it is sufficient here to mention only the following more common forms:—

Silica Gel

When solutions of sodium silicate are acidified, silica is precipitated as a gelatinous mass, which can then be extracted and dried. The resulting silica gel, as it is called, has no definite structure and is non-crystalline. The structural units of silica gel are still silica tetrahedra but they are joined together at random and not according to a "pattern".

Vitreous Silica

When quartz, cristobalite or tridymite is heated above 1710°C (the fusion point) and then cooled rapidly, again the silica tetrahedra do not have time to arrange themselves in a definite order, and so they link in a random fashion to form a glass (more accurately a "super-cooled" liquid) which, like silica gel, is also amorphous. It is therefore not strictly correct to call it "fused quartz", as is commonly done.

1.2.7 Physical Properties

Pure quartz occurs as transparent, hexagonal crystals, and at 20°C has a specific gravity of 2.65.

Under the microscope, in thin sections of fired siliceous material tridymite usually appears as wedge-shaped crystals; occasionally it has been found in volcanic lava. In tridymite the atoms are packed less densely than in quartz, and therefore the

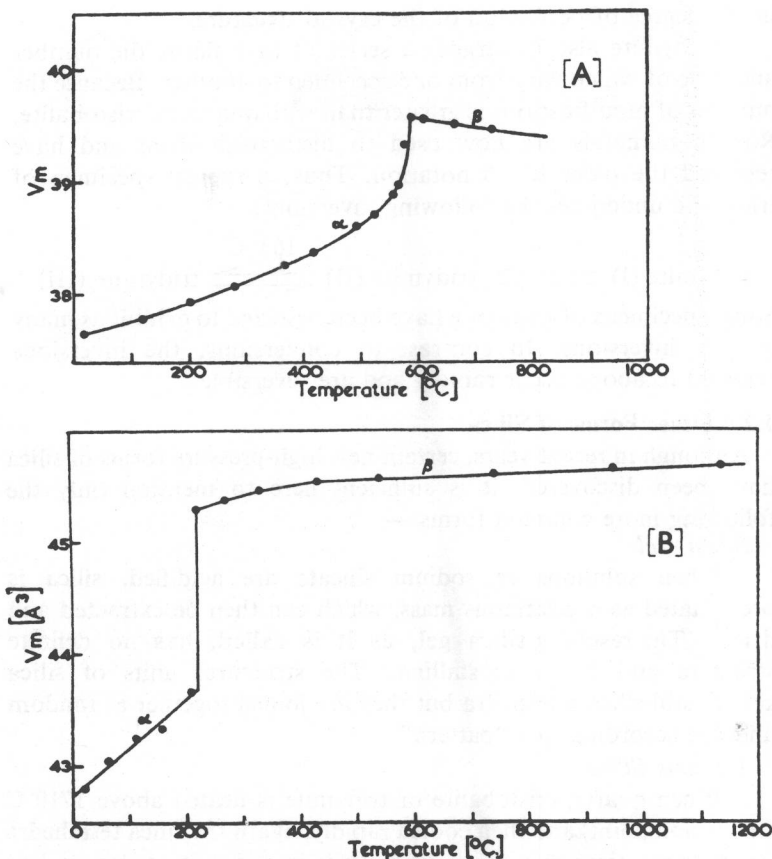


Fig. 9.—Thermal expansion of : A. Quartz B. Cristobalite.

specific gravity of tridymite is lower—2.27 at 20°C.

Cristobalite, like tridymite, is rarely found in Nature, but under the microscope in thin sections of certain ceramics it is frequently observed as a mass of small crystals. In cristobalite the packing of the atoms is also less dense than in quartz, the specific gravity of cristobalite at 20°C being 2.33.

The variation in the coefficient of thermal expansion of quartz and cristobalite with temperature reveals very strikingly the α - β inversions, and is best seen by plotting the percentage volume expansion for each mineral against the temperature (Figure 9). Owing to the difficulty of obtaining pure tridymite its expansion