Chapter 19
Physico-chemical Analysis of Ceramic Material Systems: From Macro- to Nanostate

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Abstract The historical aspects of ceramic production, as well as the modern approaches to the technical side of ceramic production, especially solgel technology as the path to modern nanotechnologies, are discussed. It is pointed out that the most essential significance of the nanostate for the applied sciences lies in the possibility of merging the inorganic, organic, and biological worlds, thus creating a prodigious number of new materials.

Glass and ceramics have been used in everyday life for thousands of years; they are a result of the industrial development of society. Ceramics is commonly referred to as the first industrial material. Some data on the overall production and consumption of various materials that have been created and that are presently produced in industrial society are listed in Table 19.1 [1].

Generally, ceramics comprises all materials based on the nonmetallic inorganic compounds produced by baking (firing), whereas glasses commonly imply substances in the amorphous metastable state. Among the artificial materials that are produced by the special treatment of natural raw materials or that have no natural analogs, ceramics occupies a special place. The main ceramics and glass technologies, the times of their advent, and the fields of human activity that changed drastically under the influence of the emerging new technologies are listed in Table 19.2 [2]. Egyptian faience was the first nonclay material, which was produced in Egypt and in the Middle East as long ago as about 4000 B.C. It consisted of a mixture of finely pounded quartz or sand, often with an admixture of lime, alkali metal oxides, and cuprate-based dyestuffs. Its optical properties significantly surpassed those of clay-based ceramics and could not be achieved in traditional pottery. In the history of the development of ceramics technology, it was the first step toward an artificial composition, and it fundamentally changed the methodology of ceramic materials science throughout the following time period.

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Table 19.1 Production and consumption of the products of industrial society

Materials	Produced from	Production level today, millions of tons	Raw materials	Products
Wood (natural organic composite)	3,000,000 BC	Up to 5000	Reproducible, geographically limited	Building materials
Ceramics (nonmetallic inorganic materials including cements)	10,000 BC	10,000	SiO_2, Al_2O_3, CaO, MgO, Fe_2O_3, etc., everywhere	Porcelain, faience, insulators, refractories, optics, building materials, components for mechanical engineering, etc.
Metals	5000 BC	Iron, up to 500; other, <500	Ore, geographically uneven	All possible goods
Polymers	~1900	100	Oil	Containers, films, tars, etc.
Artificial composites	~1950	1	Mineral and organic raw materials	Machines and mechanisms
Semiconductors, ferroelectrics, etc.	~1940	0.01	Crystals and structures	Electronic

Metallurgy, which originated in the early thirtieth century B.C., employed ceramic materials for the fireclay lining of smelting furnaces, casting molds, and crucibles. Further extension of the variety of metal alloys called for the creation of new refractory materials. Some modern refractories have approximately the same composition as the refractories of ancient Rome and the *Middle Ages* (Fig. 19.1) [3].

Dating back to the times of the craftsmen of the *Bronze Age*, glass technology survived the technical revolution in the second century B.C. that gave rise to the development of new industrial technology for the mass production of glassware for all social strata of the Roman Empire and that spread out overall.

The achievements of Roman engineers, who created the technology of concrete for building blocks and producing structural elements, are impressive as well (Table 19.3) [4]. This led to the flourishing of civil engineering and the formation of townships. Chinese porcelain (celadon) also has a long history (Table 19.4) [5]. Its advent and improvement exerted a perceptible influence on the progress of civilization. Investigations in this field were begun more than 2000 years ago, and they still proceed today thanks to the infinite diversity of chemical processes in multicomponent silicate and oxide systems. Chinese porcelain was exported to many countries, including Egypt, Syria, and Turkey, where it was a household article of prosperous people. Let us recall a legend about Marco Polo, who brought a small porcelain bottle known as the "*Medici bottle*" when he returned to Venice in 1295. Possibly this was the first Chinese celadon article imported to Europe. Later,

Table 19.2 Methods of Egyptian faience manufacture by period and site

Period	Body manufactory	Glaze process	Factory evidence	Faience examined from these sites
Predynastic (4000–3100 BC)	Modeling a core for grinding	Experimental period	None	Naqada, Badari, El Amrah, Matraar, Harageh, Abadiya, Gerza
	Surface grinding	Application (?) Beck, Petrie)		
	Free-form modeling (rare)	Cementation		
		Efflorescence (?) (Binns)		
Protodynastic (3100–2686 BC)	Modeling Surface grinding Painting with slurry	Efflorescence	None	Hierakonpolis, Saqqara, Abydos, Bammamiya, Mahasna, Qau, Matmar, El Kab, Armant
Old kingdom (2686–2181 BC)	Layering (rare) Forming on a core (rare) Marbleizing (rare)			
I intermediate (2181–2040 BC)	Molding (?)			
Middle kingdom (2133–1786 BC)	Modeling molding on a form Forming on a core	Efflorescence (Noble) cementation (Kiefer and Allibert)	Kerma Lisht	Abydos, Kerma, El Kab, Haraga, Beni Hasan, Mostagidda
II intermediate (1786–1567 BC)	Marbleizing Layering Painting with a colored quartz slurry Incising Inlaying Resisting Painting with a pigment wash	Application as a liquid (Reisner)		
New kingdom (1568–1085 BC)	Molding on a form Pressing into open-face molds	Efflorescence Application as a liquid Finely powdered glass added to body or inlay	Amarna	Amarna, Abydos, Serabit el Khadim,Yahudiya, Lahun, Nebesha, Medinet, Ghurob, Akhmin

(continued)

Table 19.2 (continued)

Period	Body manufactory	Glaze process	Factory evidence	Faience examined from these sites
	Forming over a core Joining of molded parts with quartz slurry Layering Incising Inlaying with a quartz slurry Painting with pigment wash Throwing (?)	to extend color range (Kühne)		
Later periods (1085 BC–30 AD)	All new kingdom techniques and throwing (?)	Efflorescence Application as a liquid	Memphis Naucratis	Memphis, Abydos, Thebes, Giza, Matmar, Saqqara

? Hypothesis about this fact or method

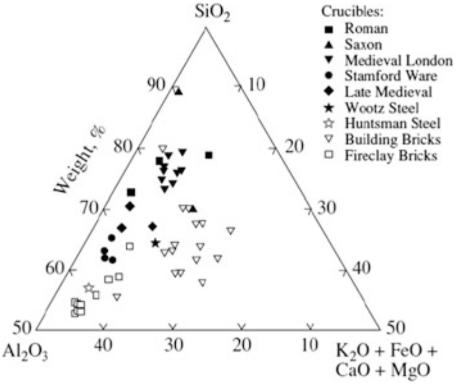


Fig. 19.1 Bulk compositions of crucibles compared with modern fireclay bricks and clay building blocks [3]

the import of celadon grew continuously and increased up to the eighteenth century. Meanwhile, persistent attempts by European craftsmen and researchers to reproduce the porcelain composition did not cease. It was not until as late as 1708 that the famous German alchemists *Chirnhaus*, *Pabst*, and *Böttger* from Meissen succeeded in obtaining firm white porcelain of a quality comparable to that of Chinese items. It is worthwhile to commend the role of *King Augustus of Saxony*, who lavishly sponsored not only the investigations of chemists but also the construction of a porcelain works that was enormous for that time. This fundamentally changed the economy of Saxony. France and England followed Saxony's example and thereby became prosperous exporters of porcelain (Fig. 19.2) [6].

Table 19.3 Macroscopic description of selected Roman cement-containing materials

Sample	Mortar matrix	Aggregate
Concrete wall Hadrian's tomb	Coherent, carbonated >20% (including ash <0.5 mm)	1. Trachytic tuff, rounded, vesicular to dense, 5–10 mm <70% 2. Volcanic ash, <1 mm, <10%
Rome ∼139 AD Concrete wall Terme Caracalla	Coherent, carbonated >30% (including ash <0.5 mm)	1. Trachytic tuff, rounded 5–15 mm 2. Volcanic ash, <1 mm, >10%
Rome ∼212 AD Concrete Forum	Mod. coherent to crumbly, carbonated >20% (including ash <0.5 mm)	1. Trachytic tuff, rounded angular, dense to vesicular, <5 mm, <60%
Rome ∼60 AD Concrete wall Theater	Coherent, carbonated >20% (including ash <0.5 mm)	2. Leucite, feldspar, augite crystals <1 mm, >20%
		1. Trachytic tuff, rounded to angular, vesicular, 5–15 mm, >60%2 2. Leucite, augite crystals up to 1 mm, >10%
Ostia 200–300 AD		3. Volcanic ash, <1 mm, <10%

Table 19.4 Characteristic features of different Chinese celadons

Yue wares	Eastern Han-Tang dynasty 25–907 AD	The bodies are light gray in color, the body section is dense and vitrifiable, the glaze color is mugwort-leaf green, the surface is much brighter and with some small cracks, and the glaze thickness is thinner (∼0.1–0.2 mm)
Fengsi's grave green ware	North dynasties 386–581 AD	The body is gray–white in color, the body section is dense and vitrifiable, the glaze color is green with a slight yellow cast, and the glaze layer is thicker (∼0.25 mm)
Jiabi ware	Sui dynasty 581–618 AD	The body is gray–yellow in color, and the section is not sufficiently vitrified, but the glaze color appears green
Yixing ware	Tang dynasty 618–907 AD	The body appears deep gray in color, some little pores can be seen, the glaze color appears greenish yellow, and its thickness is ∼0.2 mm
Yaozhou ware	North Song 960–1126 AD	The body is gray–white in color and is very dense, the glaze is olive green and bright, clear with much smaller cracks, and its carving pattern decoration especially is very fine
Ru ware	North Song 960–1126 AD	It is one of the five famous kilns of the North Song dynasty, but its body is not sufficiently vitrified, with a light gray color; the glaze is bright and clear with a greenish color, and the glaze thickness is ∼0.6 mm
Linru ware	North Song 960–1126 AD	Although it was located in the same area as the Ru kiln site, their stiles are different. Its body is very dense

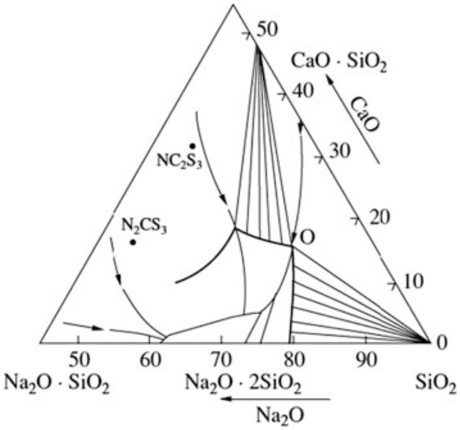


Fig. 19.2 Equilibrium phase diagram for the system Na_2O–CaO–SiO_2 illustrating the location of a typical French softpaste porcelain [6]

It can be seen from the presented data that practically all the mentioned technologies are based on the dissolution (hydration) and subsequent drying (firing) of a mixture of natural raw materials consisting mainly of metal oxides with additives of some other oxide mixtures for coloring and glazing purposes. Suitable compositions were selected for hundreds of years from the mineral raw materials in the nearest area and, of course, without any chemical analysis. Practically all of the minerals were assessed organoleptically.

A new stage in the development of these technologies came in the *Middle Ages*, when the Age of Alchemy began.

The old alchemy was not only deception and delusion. Proceeding from ancient notions of the unity of matter and basing their work on *Aristotl*e's doctrine of four basic elements (fire, air, water, and earth), the alchemists tried to separate, from the infinite diversity of substances, each elemental matter as the embodiment of some "basic" property or quality. For instance, according to their doctrines, mercury was assumed to correspond to the metallic luster property, sulfur to inflammability, and salt to indestructibility.

Alchemists observed a continuous disappearance of one substance and the appearance of another substance in its place. They saw how lead originated from litharge and mercury originated from cinnabar, neither of which look like metals at all. They had no reason to think that obtaining gold from lead is less possible. Their thinking was directed toward a search for the mystic "*philosopher's stone*," the possession of which allowed one to control all the transmutations of substances and to convert ordinary metals into gold, as well as to eliminate all evil diseases occurring from "evil elements."

Alchemy was closely woven with astrology and kabbalistic study. Alchemists were quite sure that all the substances being obtained, especially metals, and their transmutative abilities are in mysterious relationships with various forces and elements hidden in nature. Mercury was assumed to symbolize femininity, and sulfur, masculinity. The Sun corresponded to gold, the Moon to silver; Venus meant copper; Mars, iron; Jupiter, tin; Saturn, lead; and Mercury, quicksilver.

The knowledge of alchemists was imparted in the darkness of secluded laboratories, among bizarre retorts, dried herbage, skeletons, and parchment books covered with mysterious signs and symbols borrowed from various Orient cults strangely mixed with the Christian religion. Dragons, snakes, ravens, and peacocks symbolized various substances and properties. Such "chemical" signs as planet symbols designating various metals were still in use in *Lomonosov*'s time (Tables 19.5 and 19.6) [7].

Tireless searching for the "philosopher's stone" required the alchemists to test everything that can be seen on the Earth's surface, found hidden in its bowels, or produced by flora and fauna. They made many observations and wonderful discoveries. They obtained sulfuric, nitric, and hydrochloric acids; potash; caustic; and iron vitriol. They brought into laboratory practice chemical furnaces, steels, filtrating, precipitation, and crystallization. But they worked at random and on the off chance.

The Age of Alchemy was concluded by the laying of the foundations of modern chemistry. This is colloidal chemistry, whose principles were first formulated by Ebelmen [8] and Graham [9] in the middle of the nineteenth century.

It will suffice to point out that, for instance, the absence of crystal forms, the presence of jellylike solid masses, the transition into solutions, and the setting up from those are, incidentally, the attributes of live organisms and, at the same time, characteristic features of colloids. Therefore, the study of colloids, especially those that originate from inert matter, is obviously the subject of highest importance for studying organisms. The general concept relating to this subject was formulated by *Graham*. Though the transition of silica into soluble and insoluble or jellylike states was known much earlier (for example, see [8]), he is renowned for his

Table 19.5 Working log of M.V. Lomonosov, 1751 (precipitation of colloidal gold)

(1) Solut. Θ in 🜆cum ∋✕multa aqua diluta praecipitata alcall animato dedit tincturam rubram coloris granati, quae per noctem subsedit in pulverem rubrum, ipsa flava facta
(2) Eadem solutio diluta pariter, primo cum calce Stannl eluta et in 🜆eadem soluta affunderetur, turbabatur quidem et albes-cebat ad momentum, sed praecipitatum nullum promittebat at affuso alcali animato, statim viridis evasit pellucida 1-mo, tandem turbida et opaca. per noctem subsedit ⌣ tum liquor supra erat viridis
(3) Eadem liquore Stanni turbida flava
(4) Eadem ⌣ solutione cinerum clavellatorum turbida iactescens subflava
(5) Eadem ⌣ ta Wismuto in ⦶fixo soluto. Nullae quidem turbae, sed solutio ad prasinam accedebat
(6) Eadem ⌣ ta Zinco in ϕ fixo soluto. Solutio statum evasit flavens turbida. Calida aqua erat
(7) Eadem ta solutione ♂ is in ϕ fixo. Nullae fere mutationes

Table 19.6 Working log of M.V. Lomonosov, 1751 (precious glaze of fine quartz and clays from Gzhel and Moscow)

	Massa ad vasa murrhea	Encaustum	Color encausti
1	∇Gzel. ex filtro p. I, cryst. subt. p. II		
2	----------p.I---------------------- p.III		
3	----------p.I---------------------- p.IV		
4	----------p.I*--------------------- p.II		
5	----------p.I---------------------- p.III		
--		1	♃ +
6	----------p.IV-------------p.IV------------	2	♃ +
7	∇ Gzel. inspiss p. I, cryst. subt. p. II		
8	-----------p.I---------------------- p.VI	8	♃ +
9	-----------p.I---------------------- p.IV		♃
10	-----------p.I, cryst. rud. p. II		
11	-----------p.I-------------rudior p. III	9	
12	-----------p.I---------------------- p.IV		
13	p I, cryst. Subtilissimae p. IV		
14	∇Mosqu. insp. p. I, cryst. subt. p. I3	3	♃ ++
15	-----------p.I---------------------- p.VI	4	♃
16	-----------p.I---------------------- p.IV		
17	-----------p.I, cryst. gross. p. II		
18	-----------p.I---------------------- p.VI		

generalization of such phenomena and for revealing the general rules that underlie such transitions. Thus, within the last decade, the origin of all research into organic substances forming the contents of animal bodies and plants was newly established. In this respect, silica (as well as alumina, tungsten hydrate, and so forth), with its easily occurring metamorphoses, will forever remain a typical subject for its simplicity and huge prevalence in nature.

Let us cite an excerpt from Mendeleev's work [10]. It does not seem plausible that the absence of crystallization should be considered the indication of colloids, because there are a lot of crystalline substances yet between them (hematocrystalline of proteins and tridymite of silica) and especially because there is only a quantitative rather than a qualitative difference between one and another. The difference between silica and quartz, which have specific weights of 2.2 and 2.6, respectively, does not at all mean that the former should be considered colloid and the latter should be considered crystalloid; it possibly means only that one of them is less polymerized. The difference between colloids and crystalloids should be rather sought only in the fact that the particles of the former have almost equal attraction in various directions, while those of the latter differ in attraction [10].

From the purely chemical point of view, colloids are of interest in various respects, which it would not be amiss to mention once again: All the colloids seem to be substances of complex composition; the particles are heavy in weight; they are large in size (alumina), and hence, they do not penetrate through membranes; they can be easily subjected to modifications of their chemical and physical properties; and they do not have an exact value of a chemical potential. All of the features mentioned above encourage special chemical interest in colloids.

Let us consider, for instance, pyroxene or augite. Its composition can be expressed by the formula $CaMgSi_2O_6$; i.e., it corresponds to hydrate H_2SiO_3, namely the bisilicate. It is very similar in various respects to another mineral referred to as lithium spoudumene, which has the composition $Li_6Al_8Si_{15}O_{45}$. Both minerals belong to the monoclinic system; the angles between the axes are 73° and 69°; the angles of prism inclining are 87°5′ and 87°; the specific weight of pyroxene is 3.4 and that of spoudumene is 3.18. Having reduced the formulas of both minerals to the equivalent content of silicon, one sees the following difference:

Lithium spoudumene	$Li_{12}Al_{16}Si_{30}O_{90}$
or	$(Li_2O)_6(Al_2O_3)_8 30SiO_2$;
Augite	$Ca_{15}Mg_{15}Si_{30}O_{90}$ or $(CaO)_{15}(MgO)_{15}30SiO_2$.

This means that all the difference is in the fact that the sum of magnesia and lime $(MgO)_{15} + (CaO)_{15} = 1440$ is substituted by the sum of lithium oxide and alumina $(Li_2O)_6 + (Al_2O_3)_8 = 1002.4$, and such sums are equal in a chemical sense because magnesium and calcium are intermediate between lithium and aluminum with due account of all the relations and in terms of oxidation forms and alkali power. Thus, the first sum may be substituted for the second sum.

Let us consider another purely empirical example. Augite from *Saal* contains 54.86 SiO_2, 0.21 Al_2O_3, 0.44 FeO, 0.42 MnO, 16.49 MgO, and 23.57 CaO. Similar augite from *Vesuvium* contains 50.90 SiO_2, 5.37 Al_2O_3, 6.25 FeO, 14.43 MgO, and 22.96 CaO. The first one contains more silica, lime, and magnesia, while the second one, on the contrary, contains more alumina and iron protoxide. However, the sums may be equal to each other in the chemical sense.

It is necessary to mention briefly another kind of widely used silica compounds, namely cements (concretes). Ordinary lime and its mixture with sand, called in practice mortar or whitewash, is washed away by water, at least in the freshly prepared state. After some time, water destructs the cement formed by ordinary lime. However, some lime grades yield mortars that are not washed away by water and that are hardened under water. Generally, this is not characteristic of a mixture of lime with sand. Obviously, such hardening under water depends on the chemical composition of the mixture, which, in turn, depends on the origin of the source materials. Such lime grades are referred to as hydraulic lime or hydraulic cements. Incidentally, in technical terms, one should distinguish the proper hydraulic lime, which brings about mortar hardening under water, and cements, which usually make the mortar capable of hardening when mixed with lime. The hydraulic properties of lime are governed by admixtures of silica and alumina compounds. This is best proved in the method of artificial cement preparation. Lime should be taken mixed with clay ($\sim 25\%$), and the mixture should be subjected to some firing, so that the batch is not sintered but it loses the carbonic acid water that was contained in the clay. Such a batch, ground if it previously was homogeneous, forms a cement that hardens under water. The hardening process possibly involves the formation of chemical bonds between lime, silica, alumina, and water.

The theory and modern methodology of the solgel processes have been developing since the 1930s [11–13]. It is worthwhile to give modern definitions of sol and gel.

Sol (a colloidal solution) is a liquid colloidal system with particles of the dispersed phase (micelles) moving freely and independently of each other in Brownian motion. Sols with an aqueous dispersed environment are referred to as hydrosols, and those with an organic environment, as organosols.

Gel (from the Latin word *gelo*—to thicken) is a dispersed system with a liquid dispersed environment, in which the particles of the dispersed phase form a spatial network. Gels possess some solid-state attributes, i.e., form preservation ability, strength, and plasticity. Typical gels are formed, for instance, by sticking together the particles of sols, and they resemble jellylike sediments. By drying the gels, fragile microporous solids are produced, which are referred to as aerogels (silica gel, alumogel, etc.).

The generalized chemical formulas of solgel processes can be represented as follows:

The scheme of the general solgel process is shown in Figs. 19.3, 19.4, 19.5 and 19.6.

The solgel reaction is one of the best methods for preparing powders for technical ceramics among the methods from ancient inorganic chemistry and alchemy of ceramics that paved the way for modern nanotechnology (Figs. 19.7 and 19.8).

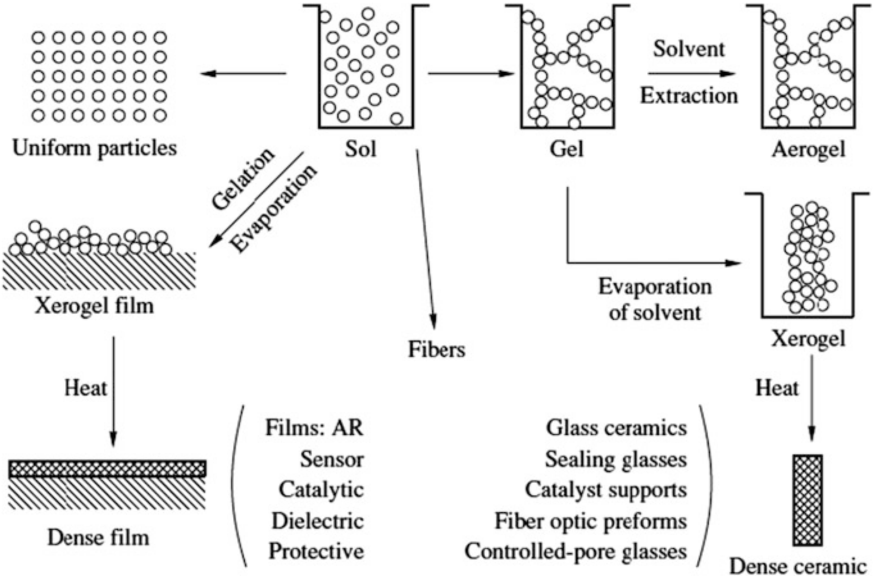
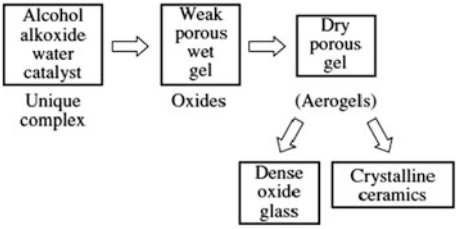


Fig. 19.3 Overview of the solgel process [11]

Fig. 19.4 Simplified overview of the first generation of the solgel process [12]



The nanostate problem is not new for materials science. *Zsigmondy* and *Svedberg* were the first scientists to be awarded *Nobel Prizes* (in 1925 and 1926, respectively) for important achievements in the chemistry of dispersed (nano) systems. To date, more than ten chemists have won *Nobel Prizes* for different aspects of research into the nanostate. The contribution of chemists in solving the nanostate problem is more essential than that of physicists. Along with scientists working in the field of inorganic chemistry, those involved in organic chemistry and biochemistry should be highlighted. Over the past seventy or eighty years, chemists have synthesized hundreds of fundamentally different kinds of nanoobjects, including particles, materials, and structures. These include centaur particles, coacervates, tactoids, phasoids, allophanes, giant icosahedral clusters, fullerenes, fumaroids, and nanotubes. It is important to note that all this diversity of forms exists within a limited size range (nanosizes) or consists of nanosized structural elements. Entering the nanoscale domain resulted in the discovery of many new

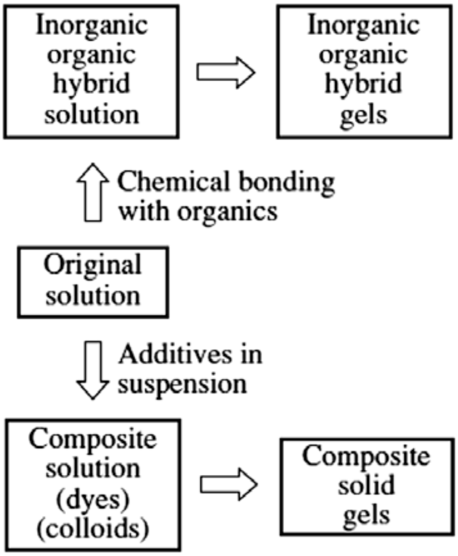


Fig. 19.5 Simplified overview of the second generation of the solgel process [12]

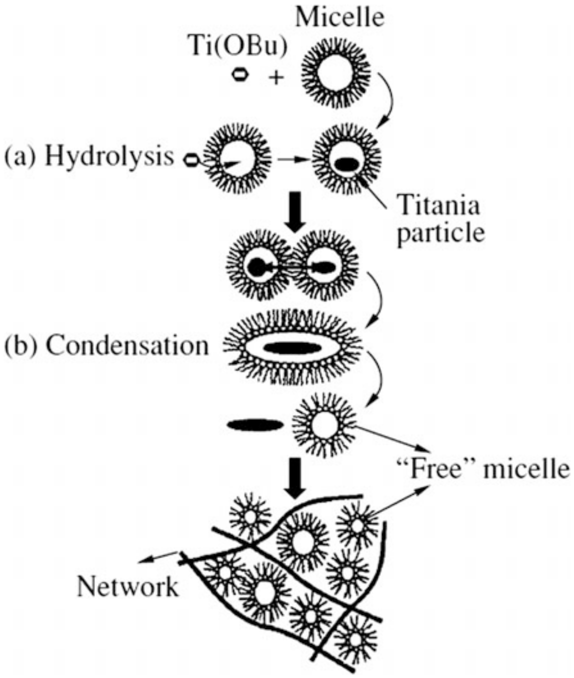


Fig. 19.6 Scheme of the solgel process in reverse micelles [13]

Liquid-phase methods	**Gas-phase methods**
Precipitation (coprecipitation)	Rapid melt solidifying
Sol–gel process	Spraying pyrolysis
Homogeneous precipitation	Plasmochemical synthesis
Controlled pyrolysis of alcoholates	Laser beam technique
Emulsion polymerization	Cryochemical method
Hydrothermal synthesis	Hydrolysis in vapor phase

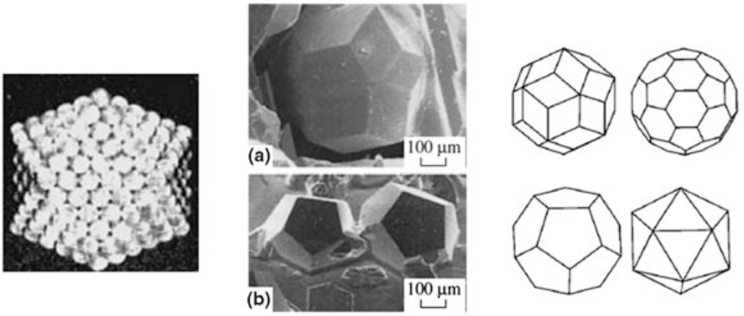
Fig. 19.7 Chemical methods of preparation of powders for technical ceramics

Vapor–vapor	**Vapor–liquid**	**Vapor–solid**	**Liquid–solid**	**Solid–solid**
Plasmochemical synthesis	Spraying pyrolysis	Carbothermal reduction	Precipitation & co-precipitation	SHS
Oxidantion in flame	Hydrolysis in gas phase	Nitridization of silicon	Hydrothermal synthesis	Solid phase reactions
Laser beam technique		Salts decomposition	**Sol–gel process**	

Fig. 19.8 Powder synthesis methods

structure types in inorganic chemistry that do not comply with the unshakeable macroworld laws of classical (generalized) crystallography [14–19] (Fig. 19.9). For example, screw axes of the fractional order are allowed [20] (Fig. 19.10).

Nanoparticles are characterized by quite different structural elements, such as one-, two-, and three-dimensional and fractal fragments and their various combinations. This brings up the following question: What is the cause of this diversity of structures in the nanoworld? The answer to this question can be found in the quantum nature of nanostates and in the specific statistical laws dominating the nanoworld. Owing to the developed surface, nanosystems are far from equilibrium.



Structure of adenovirus particle

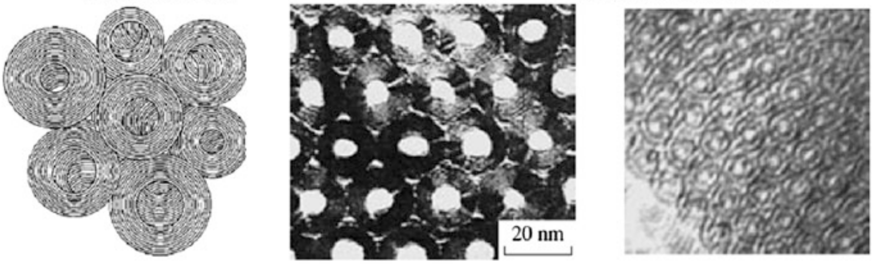
Scanning electron micrographs of (a) triacontahedron of Zn–Mg–Sc quasicrystal, (b) dodecahedron of Zn–Mg–Ti quasicrystal

Typical nanosized fragments with five fold symmetry axes

Bernal, Carlisle, 1968

T. Ishimasa *et al.*, 2004

V.Ya. Shevchenko *et al.*, 2003



Structure of chrysotile

Bundles of fibers of cylindrical serpentine chrysotile

Bundles of double-walled carbon nanotubes

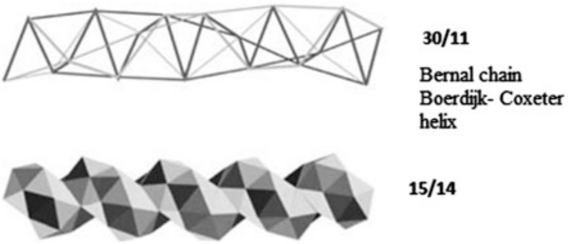
Bragg, Claringbull, 1965

V.Ya. Shevchenko *et al.*, 2004

J.-F. Colomer *et al.*, 2004

Fig. 19.9 Nanosize particles and structures that do not correspond to classical (generalized) crystallography [14–19]

Fig. 19.10 Fractional order axes



Atomic sites in the vicinity of the surface differ geometrically and physically from those in the bulk of the crystal. The composition of a surface layer does not correspond to the stoichiometric composition of the chemical compound. The structural modulation can extend over a depth of several monatomic layers. These effects suggest the existence of nonindependent surface phases and their pseudomorphic conjugation with the internal region of the particle.

The abatement of the restrictions of regular translational symmetry leads to the appearance of icosahedral packings with pentagonal symmetry for the inorganic particles. *Centaur* nanoparticles with coherent interfaces between various structure fragments of "incompatible" symmetry are also being realized [21]. To imagine how this happens, one can use the artistic outlines that wend their way into the fantastic (and now real) world of metamorphoses developed by the outstanding Dutch graphic artist Escher [22]. In his woodcut "*Metamorphoses*," one can see the gradually changing symmetry by step-by-step translation (Fig. 19.11).

The multivariance of nanostructures and nanoparticle states determines the accidental nature of their formation and implies the time dependence of the system parameters. To analyze the nanostate theoretically, one has to overcome the difficulties of its conceptual character. It is important that they are known. The *Wadsley–Andersson* paradigm implies, for example, that disordered arrays of blocks of ordered structures may be joined as in simple compounds (e.g., by corner or edge sharing) [23–25] (Fig. 19.12). Our "*centaur*" paradigm implies coherent joining and cross-linking of various fragments within the framework of the curved space formalism [14, 15, 26] (Fig. 19.13).

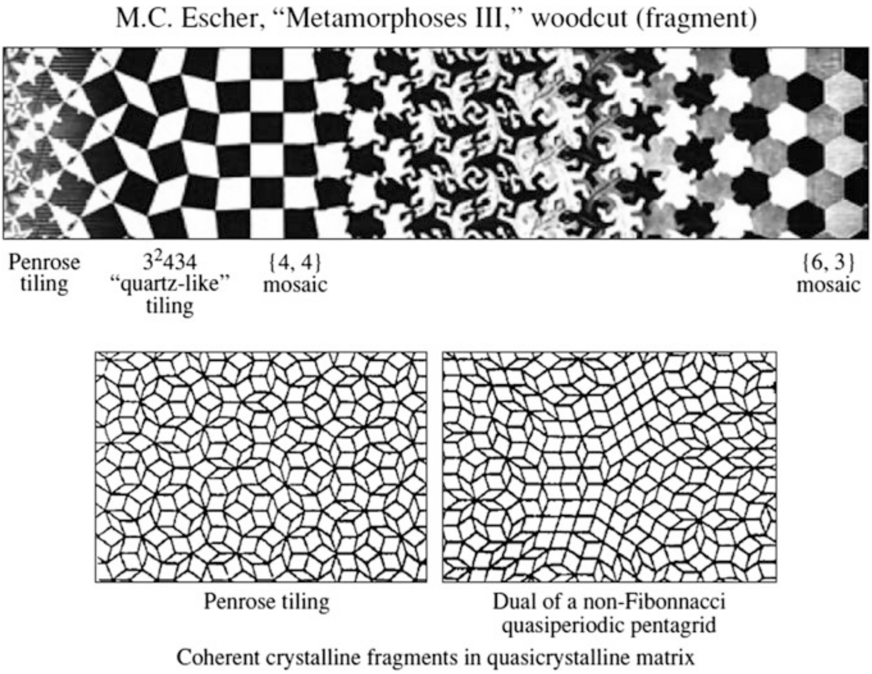


Fig. 19.11 Metamorphoses

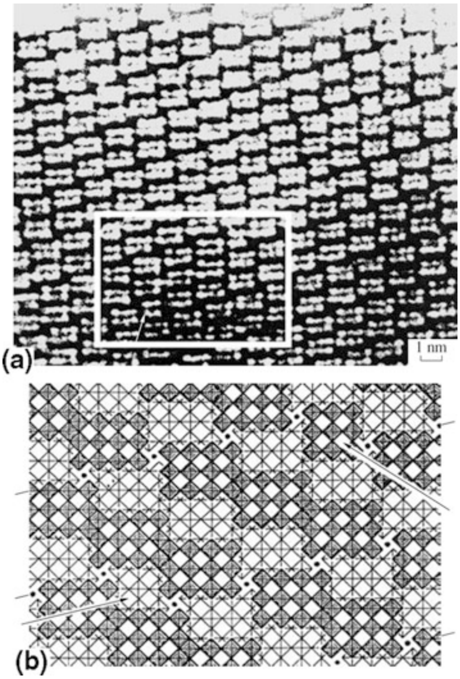
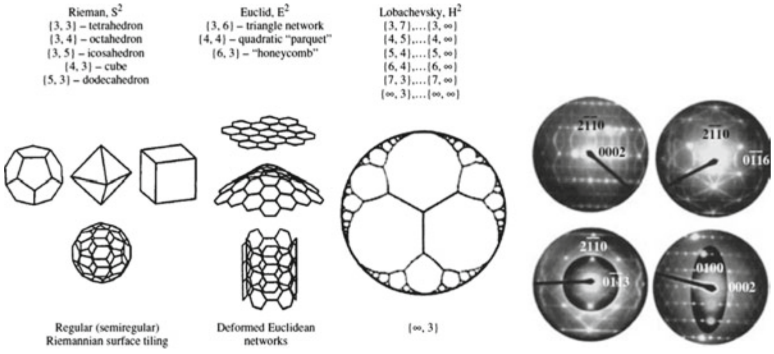


Fig. 19.12 Block structure of $TiO_2 \cdot 7Nb_2O_5$ (*arrows* indicate the presence of isolated 3 × 3 blocks in the matrix of 4 × 3 blocks) [25]



Characteristic curved (hyperbolic) diffuse intensity distribution for SiO_2-tridymite [26].

Fig. 19.13 Curved space formalism

The *Nobel Prize* winner *Feynman* said in 1959 that "there is plenty of room at the bottom," pointing out that, in the range of small sizes, there is much of interest. Many people suppose this comment to be the starting point of the ***Nano Age***. It does not hold true all the same.

Another *Nobel Prize* winner, *Prigogine*, said in 1977 that "we know now where the door is to this room."

The methods of high-resolution transmission electron microscopy and femtosecond spectroscopy have been being developed during the last 20 years for the investigation of chemical and physical processes. They make it possible to investigate the nanostate with open eyes and to determine many of its properties, which permits the next step to be made, that is, to move on to nanotechnologies. Let us assert that the door to Feynman's room is now open. (But there is surprisingly no light therein).

It was shown for the first time in [27] that structurally inhomogeneous zirconia nanoparticles consisting of interpenetrating fragments of different symmetries obey orientation relationships that are "incompatible" in terms of classical crystallography. We refer to the regularly oriented joining of structural fragments of various symmetries for which the rigorous requirements of classical crystallography are violated as centaur particles (nanostructures with coherent interfaces). This means that the interface between fragments does not need to be a plane, the orientation relationship does not need to be rational, the joining fragments are not necessarily crystalline fragments, etc.

From an analysis of the selected area electron diffraction patterns (SAED) and direct observations of structurally inhomogeneous ZrO_2 particles by high-resolution transmission electron microscopy (HTREM) [27], we have ascertained that structural inhomogeneity is the fundamental feature of the nanostate. There are a lot of experimental results confirming this principle for various materials. For example, the oriented noncrystallographic joining of the cubic and icosahedral phases in metallic alloys was observed in [28], whereby the interface was found to not be a plane and the rigorous orientation relationship was established to be irrational in both cubic and icosahedral indexing systems.

The local diffraction patterns from an individual nanoparticle represent the result of putting together two or more arrays of diffraction spots, namely the convolution of the corresponding reciprocal space mappings. Such nanoparticles are basically nonclassic. At the same time, the explanation of diffraction patterns is usually based on classical crystallography. Such a consideration reduces the description of the phenomenon to a simple superposition of diffraction patterns of two or more classical crystal phases. This basically contradicts the definition of the centaur nanoparticle as a single whole.

The spatial transitions from a region of some local symmetry to another region of a different symmetry can be considered as an example of the metamorphoses illustrated by the well-known woodcut by Escher (Fig. 19.11). The metamorphoses in a structure consisting of intergrowing fragments with various symmetries cannot be described by any Fedorov group. In Escher's graphic work, it is possible to distinguish the following fragments: one of the modifications of two-dimensional Penrose tiling, $\{3^2434\}$ tiling, various modifications of the regular *Euclidean mosaic* $\{4, 4\}$, various modifications of the mosaic $\{6, 3\}$, and transition layers. A nanoparticle with similar structure can be treated as a regular joining of the icosahedral, cubic, and hexagonal phases by coherent, but not plane, interfaces.

The depicted structure is built up of clusters, and it is possible to pinpoint the center for each of them. This structure can be interpreted as a set of points, which together form a base loaded with clusters (layers) so that the transition from one base point to another ensures cross-linking of the corresponding layers. Such an interpretation corresponds to the most simplified definition of the stratificated space as a special structure in terms of algebraic geometry, which is the mathematical basis of the “local” approach [29]. Within the framework of the local approach, the condensed structure (not necessarily crystalline) is considered to be built up from a set of special generating clusters, whereby the cross-linking rules are defined by the clusters themselves and by the space topology. The local approach is the basis of the generalized crystallography of the condensed state, which involves the formalism of an algebraic geometry that is more general than Euclidean geometry and includes classical crystallography as the limiting case.

A dodecahedron represents the regular map $\{5, 3\}$ on a sphere (three pentagons join at each vertex) (Fig. 19.14). A decacycle represents a *Petrie polygon* (a consequence of the graph edges, for each of which two rather than three neighboring edges belong to a common side). Six decacycles embracing all 30 edges and 20 vertexes are isomorphic to the $\{10, 3\}_5$ map (the map closes into itself after five steps along the Petrie polygon) representing the tiling of the nonoriented (like the Mobius strip) surface. The $\{10, 3\}_5$ map is allomorphic to the $\{10, 3\}_5'$ map arising after the 2π disclination. Both are substructures of the incidence graph of the famous Desargues configuration in the projective geometry. All of these pure geometrical configurations correspond to the frequently occurring generating clusters in regular and defect crystals, structures of gas hydrates, *Frank–Kasper phases*, *quasicrystals*, etc.

Thereby, the mechanisms of the structural transitions between various structures can be described and predicted.

The model of a nanostructure with coherent interfaces between crystalline and quasicrystalline fragments is shown in Fig. 19.14. Thus, crystalline, diamond-like,

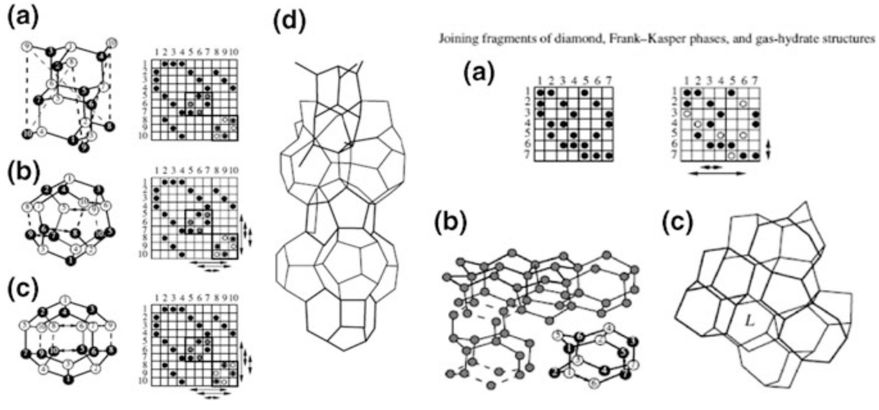


Fig. 19.14 Stratified space geometry

gas hydrate, quasicrystalline, and other structural fragments can be joined together without dangling bonds and without ruining the local symmetry.

So, what does one now mean by nanotechnologies? Formally, its elements are subjects with a characteristic size R in at least one direction that is comparable to 1 nm. Actually, the scope of the subjects and phenomena under discussion is much broader—from single atoms ($R < 0.1$ nm) to their agglomerates and organic molecules containing more than 10^9 atoms and that are as large as >1 μm in one or two dimensions. For various reasons (purely geometrical and physical), along with the decreasing size, the characteristic times of various processes occurring in the system decrease as well, and the potential processing speed increases. This is very important for electronics and computing. The achievable processing speed for typical computers is presently about *1* ns (10^{-9} s) per elementary operation, but it may be still shorter for some nanostructures.

It would be naive to suppose that nanosized objects and related processes were not used before the *Age of Nanotechnologies*. Biochemical reactions of macromolecules, of which all animate nature consists; photographic image processing; catalysis in the chemical industry; fermentation processes in wine, cheese, and baking; and many other processes proceed at a nanolevel scale. The “intuitive nanotechnology” that was first developed spontaneously without proper understanding cannot lay a reliable foundation for the future. Consequently, basic research that aimed at the development of new technological processes and products is of highest significance. Perhaps nanotechnologies will supersede some obsolete and ineffective technologies, but their most important application lies in new areas where traditional methods are basically inapplicable.

In between the macrolevel field on the one hand, in which the well-developed continual theories and computational methods of engineering run perfectly, and the quantum mechanical atomic level on the other hand, there is the huge and not yet settled vast field of mesahierarchical matter structure (mesos, from the Greek for middle, intermediate). At this level run important biochemical processes involving macromolecules of DNA, RNA, proteins, ferments, subcell structures, etc., which call for more profound understanding. Unprecedented products and technologies can thereby be created, which will be able to radically change life in human society. At the same time, there will be no need to spend raw materials, energy, and transport resources; industrial waste and pollution of the environment will diminish; and human labor will be more intellectual and healthy.

In other words, nanotechnology is a new strategy. Instead of the “top-down” technology (processing of components and finished products from intermediate ones by removing the superfluous parts), “bottom-up” technology (wasteless molecular design and self-assembling of products from elementary bricks of nature —atoms and molecules) will emerge as predominant.

The physical basis of such a new paradigm in technology is the knowledge of each type of atoms in *Mendeleev’s* atomic table. Due to the action of interatomic forces, stable atomic configurations and associates can be formed. The smaller the particle and the lower the temperature, the more intensely its quantum properties are manifested. The sudden change of a particle’s properties with respect to those of the macroscopic particles of the same substance occurs, as a rule, well ahead of the approach to the quantum limits (at $R_c \leq 10 \ldots 100$ nm). This critical size may be dependent on the particular properties (mechanical, electrical, magnetic, chemical, etc.) of the substance.

The migration of atoms over the particle's surface occurs much faster than in its volume (especially at elevated temperatures). The attractive forces between them result in the self-organization and self-assembly of islandlike, columnlike, and other structures on the surface, which is commonly used for the creation of ordered heterostructures. The specific quantum size effects may arise at fairly small sizes and at low temperatures, which may be used in electronics, optics, and computer engineering. Vivid examples of such phenomena include quantum dots, wires, and rings.

Due to the strong dependence of the properties of the substance on the number of atoms in a cluster and, consequently, on the cluster size, the latter is sometimes even referred to as the third coordinate of *Mendeleev's* table.

The future of the nanosciences is not at all in the fact that nanoelectronics will supersede microelectronics, or that nanochemistry and nanobiology will emerge as subfields of the corresponding disciplines. The most essential significance of the nanostate for the applied sciences is the possibility of merging the inorganic, organic, and biological worlds, thus creating a prodigious number of new materials.

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