

SOL - GEL REACTION IS THE BEST WAY FROM ANCIENT INORGANIC CHEMISTRY AND ALCHEMY OF CERAMICS TO MODERN NANOTECHNOLOGY: AN HISTORICAL POINT OF VIEW

V.Ya. SHEVCHENKO

Grebenshchikov Institute of Silicate Chemistry, Russian Academy of
Sciences, St. Petersburg, Russia

Glass and ceramics are being used in the everyday life for thousands years, being a result of industrial development of the 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 are presently produced in the industrial society are listed in Table 1¹.

Generally, the notion of ceramics comprises the totality of all materials based on the non-metallic inorganic compounds produced by baking (firing), whereas glasses commonly imply substances in the amorphous metastable state. Among the artificial materials, which are those produced by special treatment of natural raw materials or having no natural analogs at all, ceramics occupies a special place. The main ceramics and glass technologies, the times of their advent, and the fields of the human activities that had changed drastically under the influence of the emerging new technologies are listed in Table 2². Egyptian faience was the first non-clay material that had been produced in Egypt and in the Middle East as long ago as about 4000 B.C. It consisted of a mixture of fine pound quartz or sand, often with admixture of lime, alkali metal oxides, and cuprate-based dyestuffs. Its optical properties essentially surpassed those of the clay-based ceramics and could not be achieved in the traditional pottery. In the history of the ceramics technology development, it was the first step toward the artificial composition, which had basically changed the methodology of the ceramic materials science for all the following period.

Having originated in the early 30th century B.C., metallurgy involved ceramic materials for the fireclay lining of smelting furnaces, casting moulds and crucibles. Further extension of the variety of metal alloys called for the creation of new refractory materials. Some modern refractories have approximately same composition as the refractories of Ancient Rome and Middle Ages (Fig. 1)³.

TABLE 1 - Production and consumption of the industrial society products.

Materials	Producing from	Production level today, million ton	Raw materials	Products
Wood (natural organic composite)	3 000 000 B.C.	up to 5 000	reproducible, geographically limited	building materials
Ceramics (non-metallic inorganic materials including cements)	10 000 B.C.	10 000	SiO ₂ , Al ₂ O ₃ , CaO, MgO, Fe ₂ O ₃ , etc.; everywhere	porcelain, faience, insulators, refractories, optics, building materials, components for mechanical engineering, etc.
Metals	5 000 B.C.	Iron – up to 500, Other - < 500	ore, geographically uneven	Every 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	electronics

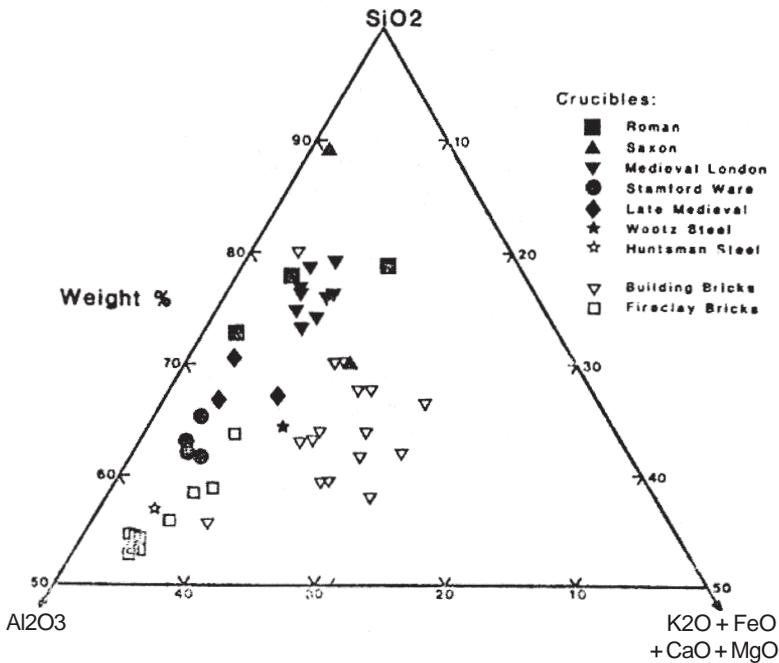


FIGURE 1 - Bulk compositions of crucibles compared with modern fireclay bricks and clay building blocks.

TABLE 2 - Methods of Egyptian faience manufactory by period and site.

Period	Body manufactory	Glaze process	Factory evidence	Faience examined from this sites
Predynastic (4000-3100 BC)	Modeling a core for grinding Surface grinding Free-form modeling (rare)	Experimental period Application (?) (Beck, Petrie) Cementation Efflorescence (?) (Binns)	None	Naqada, Badari, El Amrah, Matmar, Harageh, Abadiya, Gerza
Protodynastic (3100-2686 BC) Old Kingdom (2686-2181 BC) 1st Intermediate (2181-2040 BC)	Modeling Surface grinding Painting with slurry Layering (rare) Forming on a core (rare) Marbleizing (rare) Molding (?)	Efflorescence	None	Hierakonpolis, Saqqara, Abydos, Barmamiya, Mahasna, Qau, Matmar, El Kab, Armant
Middle Kingdom (2133-1786 BC) 2nd Intermediate (1786-1567 BC)	Modeling Molding on a form Forming on a core Marbleizing Layering Painting with a colored quartz slurry Incizing Inlaying Resisting Painting with a pigment wash	Efflorescence (Noble) Cementation (Kiefer and Allibert) Application as a liquid (Reisner)	Kerma Lisht	Abydos, Kerma, El Kab, Haraga, Beni Hasan, Mostagidda
New Kingdom (1568-1085 BC)	Molding on a form Pressing into open-face molds Forming over a core Joining of molded parts with quartz slurry Layering Incizing Inlaying with a quartz slurry Painting with pigment wash Throwing (?)	Efflorescence Application as a liquid Finely powdered glass added to body or inlay to extend color range (Kühne)	Amarna	Amarna, Abydos, Serabit el Khadim, Yahudiya, Lahun, Nebesha, Medinet, Ghurob, Akhmin
Later Periods (1085 BC-30 AD)	All of New Kingdom techniques and Throwing (?)	Efflorescence Application as a liquid	Memphis Naurcratis	Memphis, Abydos, Thebes, Giza, Matmar, Saqqara

Dated back to the times of craftsmen of the Bronze Age, the glass technology survived the technical revolution in the 2nd century B.C. which gave rise to the development of the new industrial technology for mass production of glassware for all social strata of the Roman Empire and spread out overall.

The achievements of the Roman engineers, who created the technology of concretes for building blocks and production of structural elements, are impressive as well (Table 3)⁴. This had led to flourishing of the civil engineering and formation of townships.

Chinese porcelain (celadon) also has the long enough history (Table 4)⁵. Its advent and improvement exerted a perceptible influence on the progress of civilization. Having begun more than 2000 years ago, the investigations in this field proceed up to date owing to the infinite diversity of the chemical processes in multi-component silicate and oxide systems. Chinese porcelain

TABLE 3 - Macroscopic description of selected Roman cement-containing materials.

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

TABLE 4 - Characteristic features of different Chinese celadons.

Specimen	Period	Characteristic Features
Yue wares	Eastern Han-Tang Dynasty 25-907 A.D.	The bodies are light-gray in color and the body section is dense and vitrifiable, the glaze color is mugwort leaf green, and the surface is much brighter and with some small cracks, the glaze thickness is thinner (~ 0.1-0.2 mm).
Fengsi's grave green ware	North Dynasties 386-581 A.D.	The body is gray-white in color, the body section is dense and vitrifiable, the glaze color is green with slight yellow, the glaze layer is thicker (~ 0.25 mm).
Jiabi ware	Sui Dynasty 581-618 A.D.	The body is gray-yellow in color and the section is not sufficiently vitrified, but the glaze color appears green.
Anyang ware	Sui Dynasty 581-618 A.D.	Body appears gray-white in color, section is not very dense, the glaze color is greenish with slight yellow, and the glaze thickness is ~ 0.2-0.3 mm.
Yixing ware	Tang Dynasty 618-907 A.D.	Body appears deep gray in color, and some little pores can be seen, the glaze color appears greenish yellow, its thickness is ~ 0.2 mm.
Jing ware	Five Dynasties 907-960 A.D.	Body is light gray in color and dense, the glaze color is greenish and its surface is brighter, and its thickness is ~ 0.1-0.2 mm.
Yaozhou ware	North Song 960-1126 A.D.	The body is gray-white in color and is very dense, the glaze is olive green and bright, clear with much smaller cracks, its carving pattern decoration especially is very fine.
Ru ware	North Song 960-1126 A.D.	It is one of the five famous kilns in North Song dynasty, but its body is not sufficiently vitrified with light gray color, the glaze is bright, clear with a sky-green color, the glaze thickness is ~ 0.6 mm.
Linru ware	North Song 960-1126 A.D.	Although it was located in the same area as the Ru kiln site, their stiles are different. Its body is very dense.

was exported to many countries: Egypt, Syria, Turkey, etc., 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 "Medici bottle" when he returned to Venice in 1295. Possibly this was the first Chinese celadon article imported to Europe. Later the import of celadon grew continuously, increasing up to the 18th century. Persistent attempts of the European craftsmen and researchers to reproduce the porcelain composition did not cease meanwhile. It was as late as in 1708 that the famous German alchemists Chirnhaus, Pabst and Böttger from Meissen succeeded in obtaining firm white porcelain of the quality comparable to that of Chinese items. It is worth 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 really huge for that time. This had cardinally changed the economics of Saxony. France and England followed Saxony's example, thereby having become prosperous exporters of porcelain (Fig. 2)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 mostly of metal oxides with additives of some other oxide mixtures for coloring and glazing purposes. Suitable compositions were being selected for hundreds of years from the mineral raw materials in the nearest area and, of course, without any chemical analysis. Practically all the minerals were assessed organoleptically.

The 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 the deception and delusion. Proceeding from the ancient notions of the matter unity and basing on the Aristotle's doctrine of four basic elements (fire, air, water, and earth), the alchemists tried to separate from the infinite diversity of substances the elemental matters becoming as though the embodiment of some "basic" property or quality. For instance, according to their doctrines, mercury was assumed to be corresponding to the metallic luster property, sulfur to inflammability, and salt to indestructibility.

Alchemists observed a continuous disappearance of one substance and appearance of another substance on its place. They saw how lead originated from litharge and mercury originated from cinnabar, which do not look like metals at all. They had no reasons to think that obtaining gold from lead is less possible. Their thought was directed towards search for the mystic "philosopher's stone", possessing of which allowed one to control all the transmutations of substances and to convert ordinary metals into gold, as well as to eliminate all the evil disease occurring from "evil elements".

Alchemy was closely woven with astrology and kabalistic study.

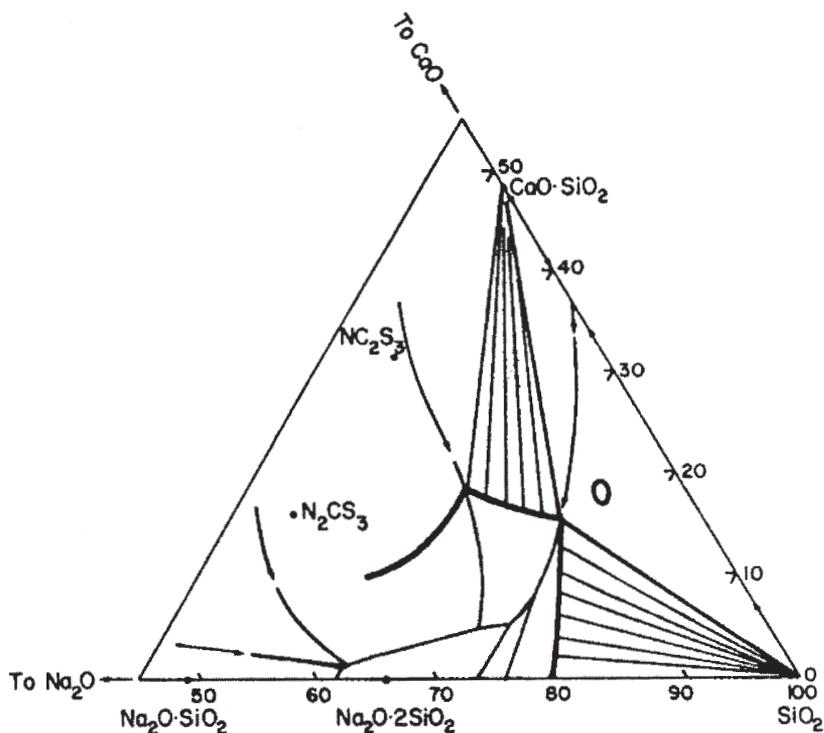


FIGURE 2 - Equilibrium phase diagram for the system $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$, illustrating the location of a typical French soft-paste porcelain.

Alchemists were quite sure that all the substances being obtained, especially metals, and their transmutation ability are in mysterious relation with various forces and elements hidden in the Nature. Mercury was assumed to symbolize the femininity, and sulfur the masculinity. The Sun corresponded to gold, the Moon to silver, the Venus meant copper, the Mars – iron, the Jupiter – tin, the Saturn – lead, and the Mercury – quicksilver.

Alchemists' knowledge was imparted in darkness of secluded laboratories, among the bizarre retorts, dried herbage, skeletons, parchment books covered with mysterious signs and symbols borrowed from various orient cults strangely mixed with 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 5, 6)⁷.

Tireless searching for the "philosopher's stone" enforced the alchemists to test everything that can be seen on the Earth surface, hidden in bowels, and produced by flora or fauna. They have made a lot of observations and

TABLE 5 - Working log of M.V. Lomonosov, 1751 (precious glaze of fine quartz and clays from Gzhel and Moscow).

	Massa ad vasa murrhea Проба 1-я	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	2+ +
6	———— p. VI ————— p. IV	2	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 — rudlor p. III	9	2
12	———— p. I ————— p. IV		
13	———— p. I, cryst. subtilissimae p. IV		
14	▽ Mosqu. insp. p. I, cryst. subt. p. I	3	2+ + +
15	———— p. I ————— p. III	4	2
16	———— p. I ————— p. IV		
17	———— p. I, cryst. gross. p. II		
18	———— p. I ————— p. III		

wonderful discoveries. They have obtained the 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 off-chance.

The Age of Alchemy was concluded by laying the foundation of modern chemistry. Colloidal chemistry is its part, whose principles have been first formulated by J. Ebelmen⁸ and T. Graham⁹ in the middle of the 19th century.

Suffice it to point out that, for instance, the absence of crystal forms, the presence of jelly-like solid masses, transition into solutions and setting up

TABLE 6 - Working log of M.V. Lomonosov, 1751 (precipitation of colloidal gold).

1) Solut. \odot in ∇ cum \otimes multa aqua diluta praecipitata alcali animato dedit tincturam rubram coloris granati, quae per noctem subsedit in pulverem rubrum, ipsa flava facta.

2) Eadem solutio diluta pariter, primo cum calce Stanni eluta et in ∇ eadem soluta affunderetur, turbabatur quidem et albescebat ad momentum, sed praecipitatum nullum promittebat at affuso alcali animato, statim viridis evasit pellucida 1-mo, tandem turbida et opaca. per noctem subsedit \cup tum liquor supra erat viridis.

3) Eadem liquore Stanni turbida flava.

4) Eadem solutione cinerum clavellatorum turbida lactescens subflava.*

5) Eadem \cup ta Wismuto in \oplus fixo soluto. Nullae quidem turbae, sed solutio ad prasinam accedebat.

6) Eadem^b \cup ta Zinco in \oplus fixo soluto. Solutio statim evasit flavens turbida. Calida aqua erat.

7) Eadem \cup ta solutione σ is in \oplus fixo. Nullae fere mutationes.

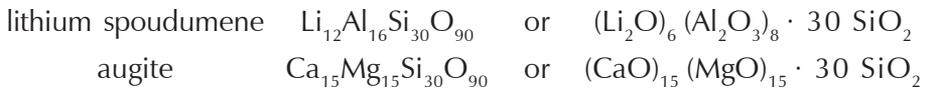
from those are incidentally the attributes of live organisms and, at the same time, characteristic features of colloids. Therefore, the study of colloids, especially those which originate not from a live matter, is obviously the subject of highest importance for studying organisms. The general concept relating to this subject has been formulated by T. Graham. Though the transition of silica into soluble and insoluble or jelly-like state was known much earlier (for example, see ref. 8), he is renowned for the generalization of phenomena of such kind and for revealing the general rules that underlie such kind of transitions. Thus, within the last decade, the new origin of the whole research into organic substances forming the contents of animal bodies and plants was established. In this respect, silica (as well as alumina, tungsten hydrate, and so forth) with its so easily occurring metamorphoses will remain forever as a typical subject of its simplicity and the huge prevalence in the Nature.

Let us quote an excerpt from D.I. Mendeleev's work¹⁰. 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, trydymite of silica), and

especially because there is only quantitative rather than qualitative difference between one another. The difference between silica and quartz, having specific weights of 2.2 and 2.6, respectively, not at all does mean that the former should be colloid and the latter should be crystalloid, but 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 and those of the latter differ in attraction¹⁰.

From the purely chemical point of view, colloids are of interest in various respects, which would not come amiss to be mentioned once again as follows: all the colloids seem to be the substances of complex composition; the particles are heavyweight; they have large size (alumina), hence they do not penetrate through membranes; they can be easily subjected to modifying their chemical and physical properties; they do not have an exact value of the chemical potential. All said above arouses special chemical interest to colloids.

Let us consider, for instance, pyroxene or augite. Its composition can be expressed by formula $\text{CaMgSi}_2\text{O}_6$, i.e., it corresponds to hydrate H_2SiO_3 , namely, the bisilicate. It is very similar in various respects to other mineral referred to as lithium spoudumene, which has the composition $\text{Li}_6\text{Al}_8\text{Si}_{15}\text{O}_{45}$. Both minerals belong to the monoclinic system, the angles between axes are 73° and 69° , the angles of prism inclining are $87^\circ 5'$ 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 difference:



It means that all the difference is that the sum of magnesia and lime $(\text{MgO})_{15} + (\text{CaO})_{15} = 1440$ is substituted by the sum of lithium oxide and alumina $(\text{Li}_2\text{O})_6 + (\text{Al}_2\text{O}_3)_8 = 1002.4$, and such sums are equal in 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 the alkali power. Thus, the first sum may be substituted by 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, 23.57 CaO. Similar augite from Vesuvium contains 50.90 SiO_2 , 5.37 Al_2O_3 , 6.25 FeO, 14.43 MgO, 22.96 CaO. The first one contains more silica, lime and magnesia, and 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.

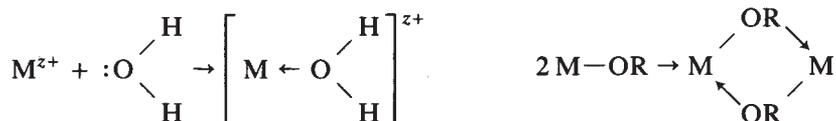
It is necessary to mention briefly another kind of widely used silica compounds, namely, cements (concretes). Ordinary lime and its mixture prepared with sand, called in practice as mortar or whitewash, are washed away by water, at least in the freshly prepared state. After some time, water destructs the cement formed by the ordinary lime. However, some lime grades yield the mortars which are not washed away by water and 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 renders mortar hardening under water, and cements, which usually make the mortar capable of hardening when being mixed with lime. The hydraulic properties of lime are governed by the admixtures of silica and alumina compounds. This is best proved in the method of artificial cement preparation. Lime should be taken mixed with clay (~25%), the mixture should be subjected to some firing, so that the batch is not sintered but loses the carbonic acid water that was contained in clay. Such a batch, being ground if it previously was homogeneous, just forms cement which hardens under water. The hardening process possibly involves the formation of chemical bonding between lime, silica, alumina, and water.

The theory and modern methodology of the sol-gel processes have been developing since the 1930s¹¹⁻¹³. It is worthwhile to give modern definitions of the sol and gel.

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

Gel (from *latin* gelo - thicken) is a dispersed system with liquid dispersed environment, in which the particles of the dispersed phase form the spatial network. Gels possess some of the 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 look as jelly-like sediments. By drying the gels fragile microporous solids are produced, which are referred to as aerogels (silicagel, alumogel, etc.).

Generalized chemical formulas of the sol-gel processes can be represented as follows.



The scheme of the sol-gel process in general view is shown in Figs. 3-6.

Sol-gel reaction is one of the best methods to prepare the powders for technical ceramics. It is the best way from ancient inorganic chemistry and alchemy of ceramics to modern nanotechnology (Figs. 7, 8).

The nanostate problem is not new for the materials science. Probably, R. Zsigmondy and T. Svedberg were the first scientists who were awarded with the Nobel Prizes in 1925 and 1926, respectively, for the important achievements in the chemistry of dispersed (nano-) systems. More than ten chemists have won up to date the Nobel Prizes for different aspects of the research into nanostate. The contribution of chemists in solving the nanostate

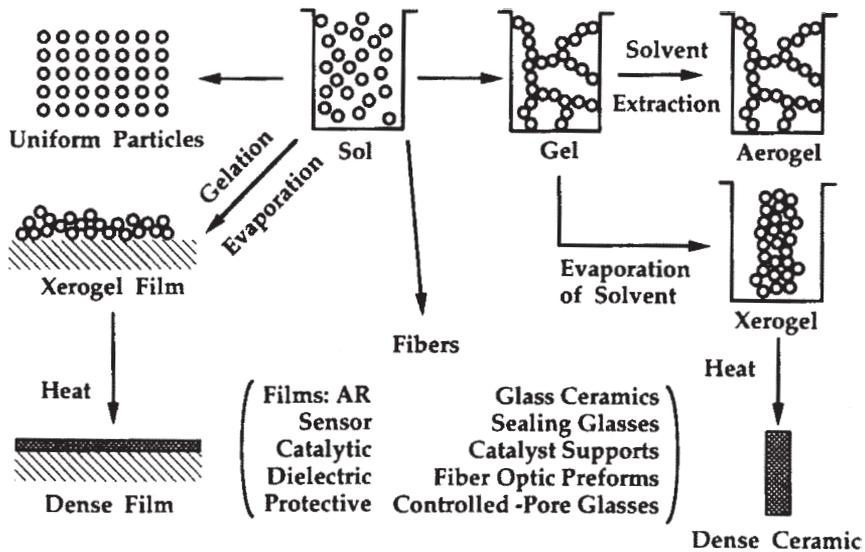


FIGURE 3 - Overview of the sol-gel process.

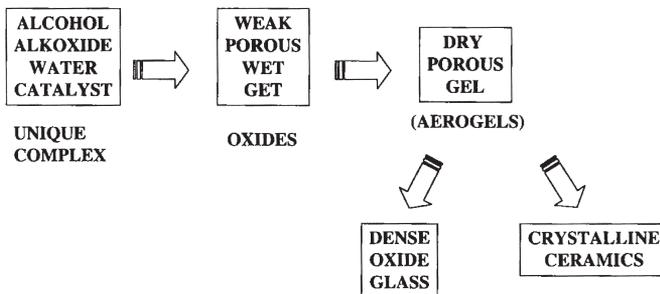


FIGURE 4 - Simplified overview of the 1st generation of the sol-gel process.

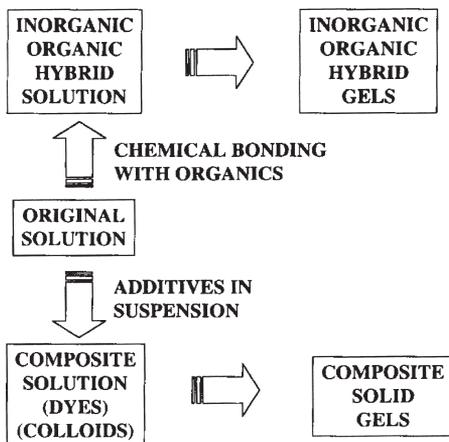


FIGURE 5 - Simplified overview of the 2nd generation of the sol-gel process.

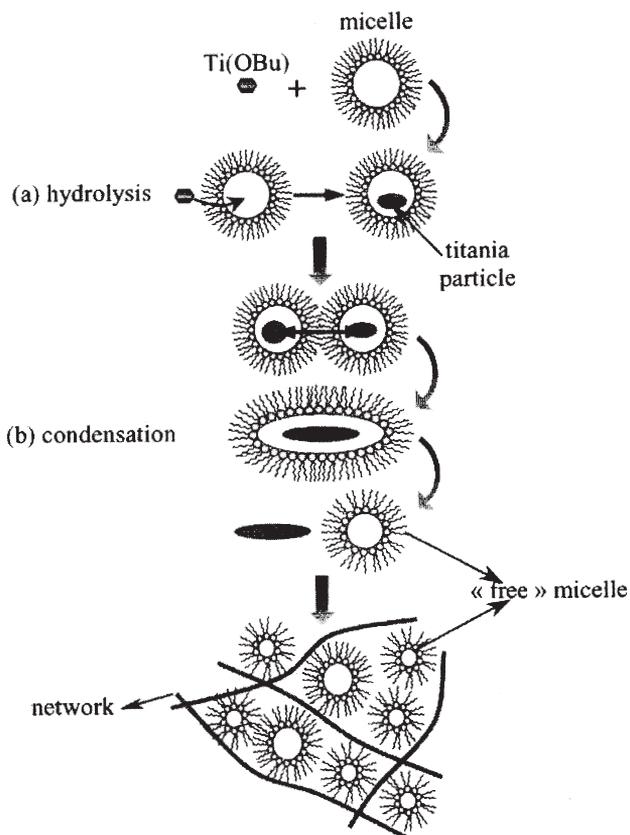


FIGURE 6 - Scheme of sol-gel process in reverse micelles.

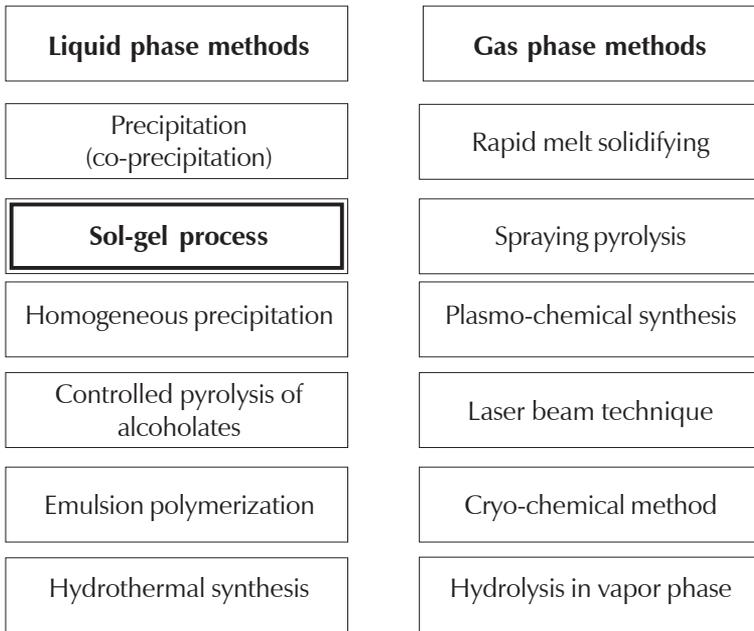


FIGURE 7 - Chemical methods of preparation of powders for technical ceramics.

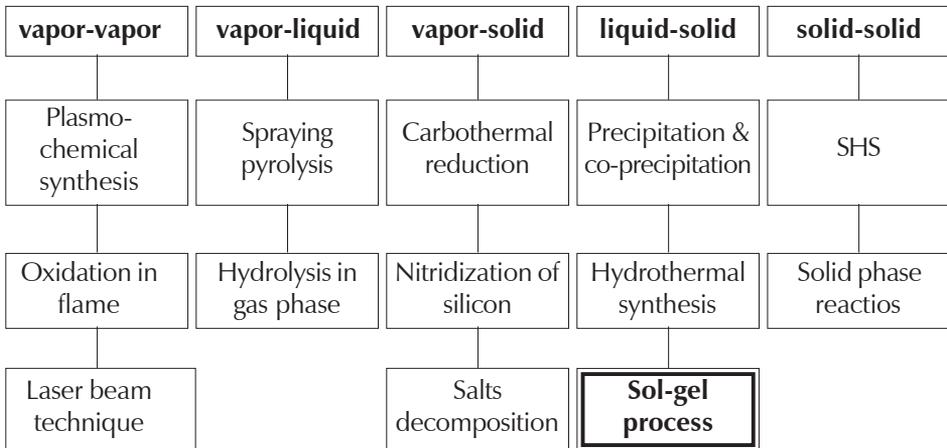
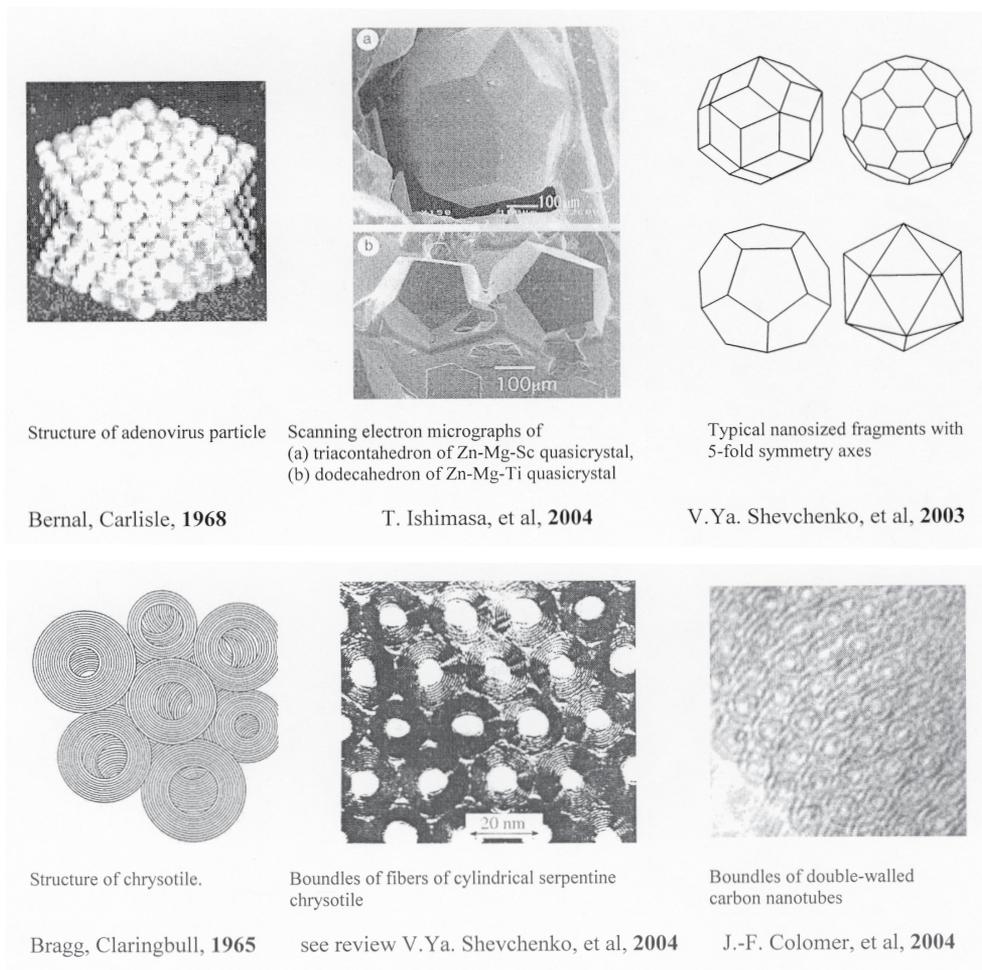


FIGURE 8 - Powders synthesis methods.

problem is more essential than that of physicists. Along with scientists working in the fields of inorganic chemistry, those involved in organic chemistry and biochemistry should be highlighted. For 7-8 decades chemists synthesized hundreds of essentially different kinds of nanoobjects, such as particles,



Structure of adenovirus particle

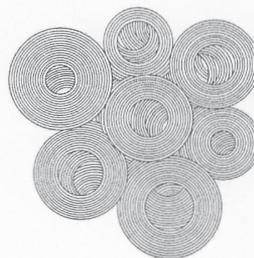
Bernal, Carlisle, 1968

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

T. Ishimasa, et al, 2004

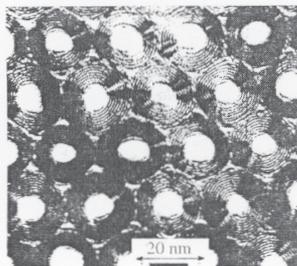
Typical nanosized fragments with
5-fold symmetry axes

V.Ya. Shevchenko, et al, 2003

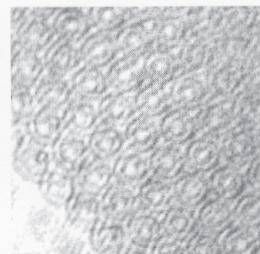


Structure of chrysotile.

Bragg, Claringbull, 1965

Bundles of fibers of cylindrical serpentine
chrysotile

see review V.Ya. Shevchenko, et al, 2004

Bundles of double-walled
carbon nanotubes

J.-F. Colomer, et al, 2004

FIGURE 9 - Nanosized particles and structures do not corresponding the classical (generalized) crystallography.

materials, structures. These are centaur-particles, coacervates, tactoids, phasoids, allophanes, giant icosahedral clusters, fullerenes, fumaroids, nanotubes, etc. It is important that all the diversity of forms exist within the limited size range (nanosizes) or consist of nanosized structural elements. Entering the nanoscale domain allowed the discovery of many new structure types in the inorganic chemistry, which do not comply with the unshakeable macroworld laws of the classical (generalized) crystallography¹⁴⁻¹⁹ (Fig. 9). For example, the screw axes of the fractional order are allowed²⁰ (Fig. 10).

Nanoparticles are characterized by quite different structural elements, such as one-, two-, and three-dimensional, and fractal fragments and their

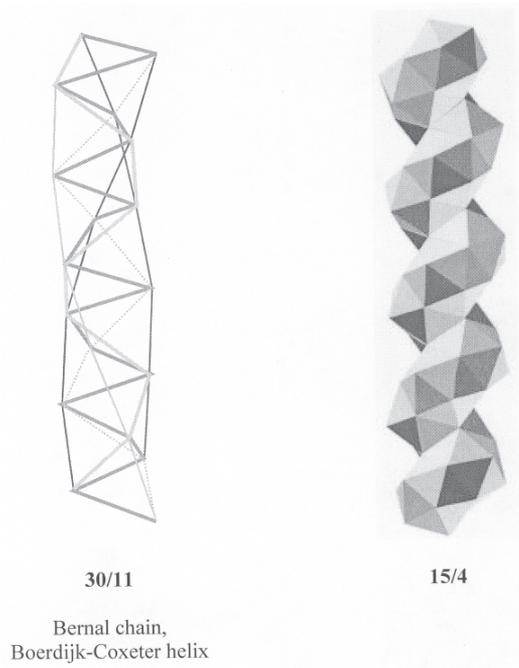


FIGURE 10 - Fractional order axes.

various combinations. This brings up the question: What is the cause for this diversity of structures in the nanoworld? The answer to this question can be found in the quantum nature of nanostates and specific statistical laws dominating in the nanoworld. Owing to the developed surface, the nanosystems are far from equilibrium. 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 monoatomic layers. These effects suggest the existence of nonindependent surface phases and their pseudomorphic conjugation with the internal region of the particle.

Abatement of the restrictions of regular translational symmetry leads to the appearance of the icosahedral packings having pentagonal symmetry for inorganic particles. The centaur-nanoparticles with coherent interfaces between various structure fragments of “incompatible” symmetry are also being realized²¹. To imagine how it happens, one uses the artistic outlines wending oneself to the fantastic (and now real) world of metamorphoses developed by the outstanding Dutch graphic artist Maurice Escher²². On his woodcut “Metamorphoses” one can see the gradually changing symmetry by

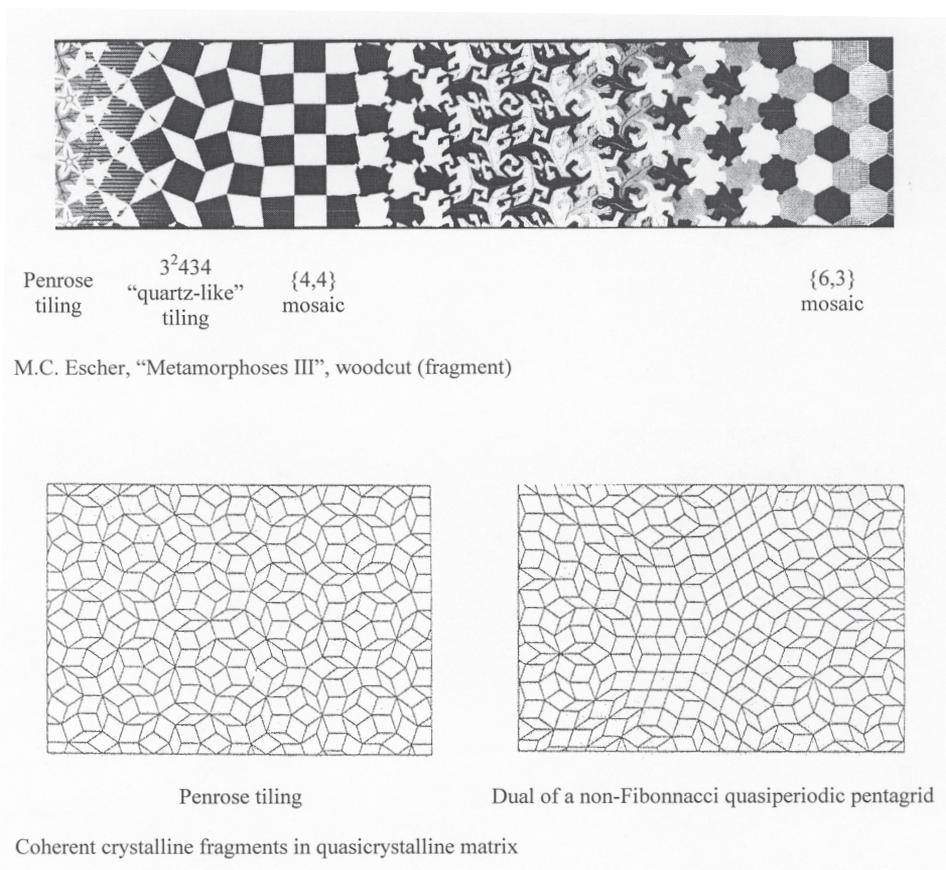
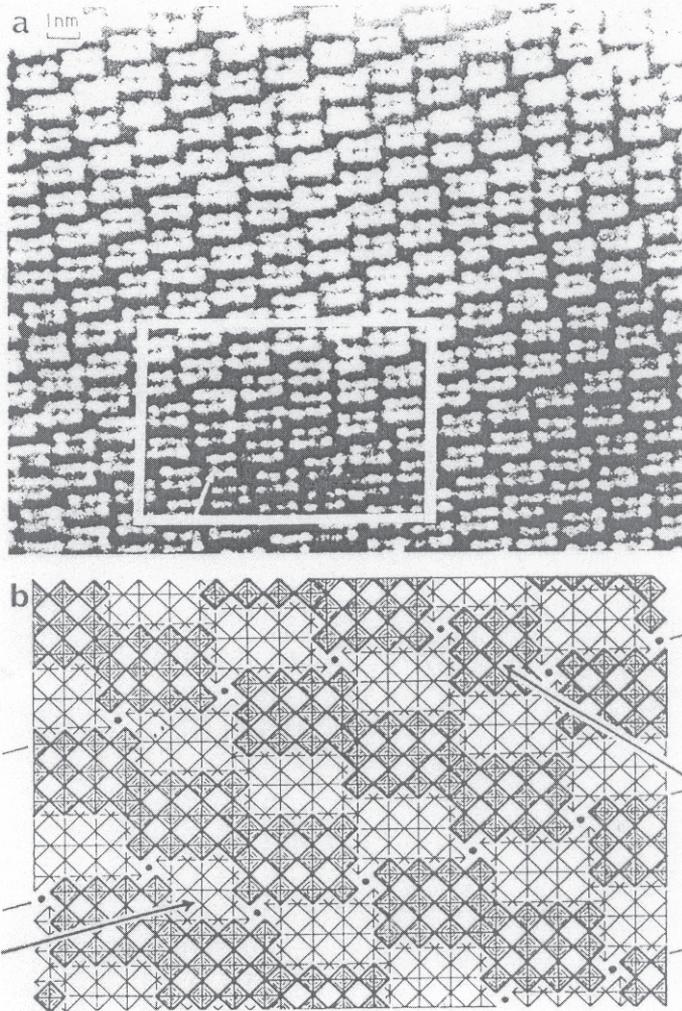


FIGURE 11 - Metamorphoses.

step-by-step translation (Fig. 11).

Multivariance of the nanostructures and nanoparticle states determines the accidental nature of their formation. It implies the time-dependence of the system parameters. To analyze the nanostate theoretically, one has to overcome the difficulties of the 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. 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. 13).

The Nobel Prize winner R. Feinman 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 it to be the start point of the Nano Age. It does not hold true all the same.



Block structure of $\text{TiO}_2 \cdot 7 \text{Nb}_2\text{O}_5$
 (arrows indicate the presence of isolated 3x3 blocks in the matrix of 4x3 blocks)

FIGURE 12 - Wadsley-Andersson paradigm. Disordered arrays of blocks of ordered structure joined as in simple compounds (e.g. by corner- or edge-sharing).

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

The methods of High-Resolution Transmission Electron Microscopy and Femtosecond Spectroscopy are being developed for investigation of chemical and physical processes during the last 20 years. This makes it possible to inve-

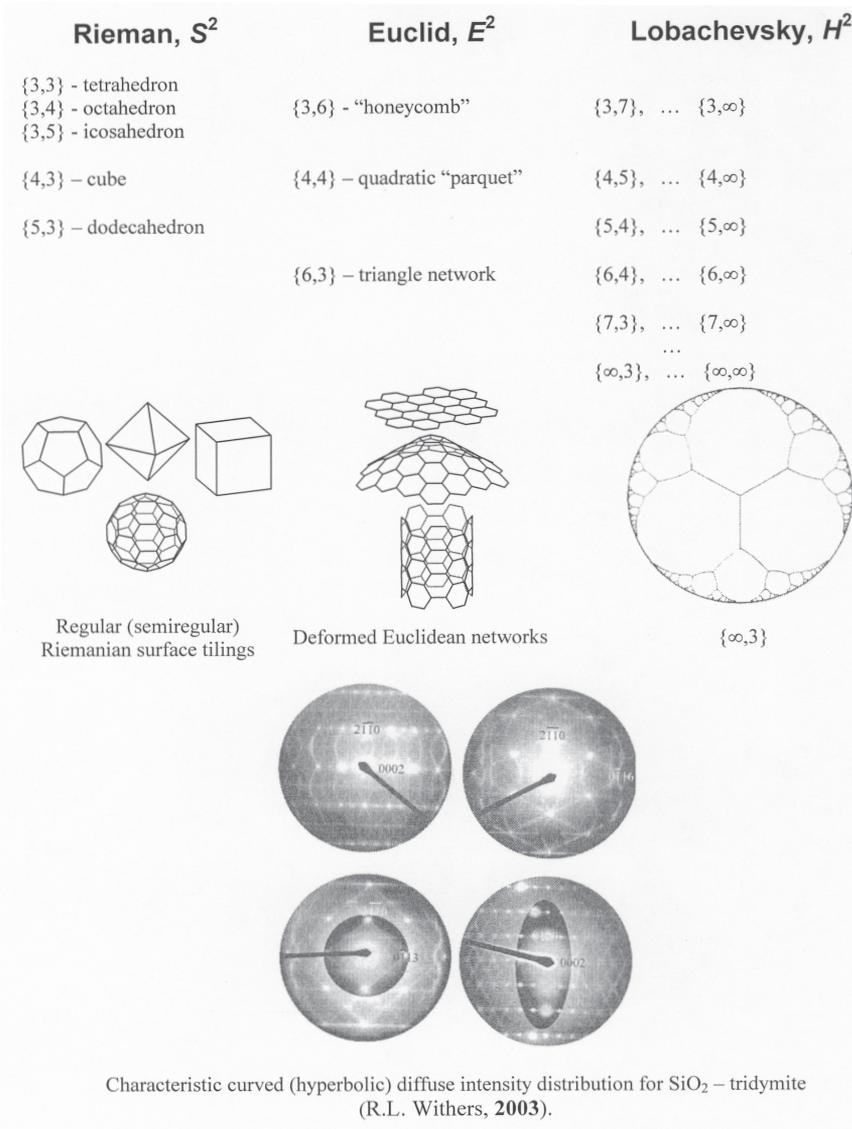


FIGURE 13

stigate the nanostate with open eyes and to determine many of their properties, which permits the next step to be made, that is, to go over to the nanotechnologies. Let us assert that the door to the Feinman's room is now open. (But there is surprisingly no light therein).

It has been shown for the first time in ref. 27 that the structurally inhomogeneous zirconia nanoparticles consisting of the interpenetrating fragments of different symmetry obey the orientation relationships, which

are “incompatible” in terms of the classical crystallography. We refer to regular oriented joining of the 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, joining fragments are not necessarily crystal-like fragments, etc.

From analysis of the Selected Area Electron Diffraction patterns (SAED) and direct observation of the structurally inhomogeneous ZrO_2 particles by the High-Resolution Transmission Electron Microscopy (HTREM)²⁷, we have ascertained that the structural inhomogeneity represents the fundamental feature of the nanostate. There are a lot of experimental results confirming this principle for various materials. For example, the oriented non-crystallographic joining of the cubic and icosahedral phases in metallic alloys was observed in ref. 28, whereby the interface was found out to be not a plane and rigorous orientation relationship was established to be irrational in both cubic and icosahedral indexing systems as well.

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 non-classic. At the same time, the explanation of diffraction patterns is usually based on the 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 metamorphoses illustrated by the well-known Escher’s woodcut (Fig. 11). The metamorphoses in a structure consisting of the intergrowing fragments with various symmetries cannot be described by any Fedorov group. In the Escher’s graphic work, it is possible to depicture the following fragments: one of 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 having similar structure can be treated as regular joining of the icosahedral, cubic, and hexagonal phases by coherent, but not plane, interfaces.

The depicted structure is built up with clusters, whereby it is possible to point the center for each of them. This structure can be interpreted as a set of points, which altogether forms the 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” approach²⁹. 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 represents the basis of the generalized crystallography of the condensed state, which involves the formalism of the algebraic geometry that is more general than the Euclidean geometry, including the classical crystallography as the limiting case.

Dodecahedron represents the regular map $\{5,3\}$ on a sphere (3 pentagons come together in each vertex), Fig. 14. Decacycle represents its Petrie polygon (consequence of the graph edges, for which each two rather than three neighboring edges belong to the common side). Six decacycles embracing all the 30 edges and the 20 vertexes are isomorphic to the $\{10,3\}_5$ map (the map closes into itself after 5 steps along the Petrie polygon) representing the tiling of the non-oriented (like the Möbius strip) surface. The $\{10,3\}_5$ map is allomorphic to the $\{10,3\}'_5$ map arising after the 2π -disclination. Both are the 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 the coherent interfaces between crystalline and quasicrystalline fragments is shown in the Fig. 14. Thus, crystalline, diamond-like, gas-hydrate, quasicrystalline and other structural fragments can be joined together without dangling bonds and ruining the local symmetry.

So, what one does now mean by nanotechnologies? Formally, its elements are subjects having characteristic size R at least in one direction 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 being as large as $> 1 \mu\text{m}$ in one or two dimensions. Due to various reasons (purely geometrical and physical), along with size decreasing the characteristic times of various processes occurring in the system decrease as well and the potential processing speed increases. It is very important for electronics and computing. The really achieved processing speed for typical computers is presently about 1 ns (10^{-9} s) per elementary operation, but it may be still

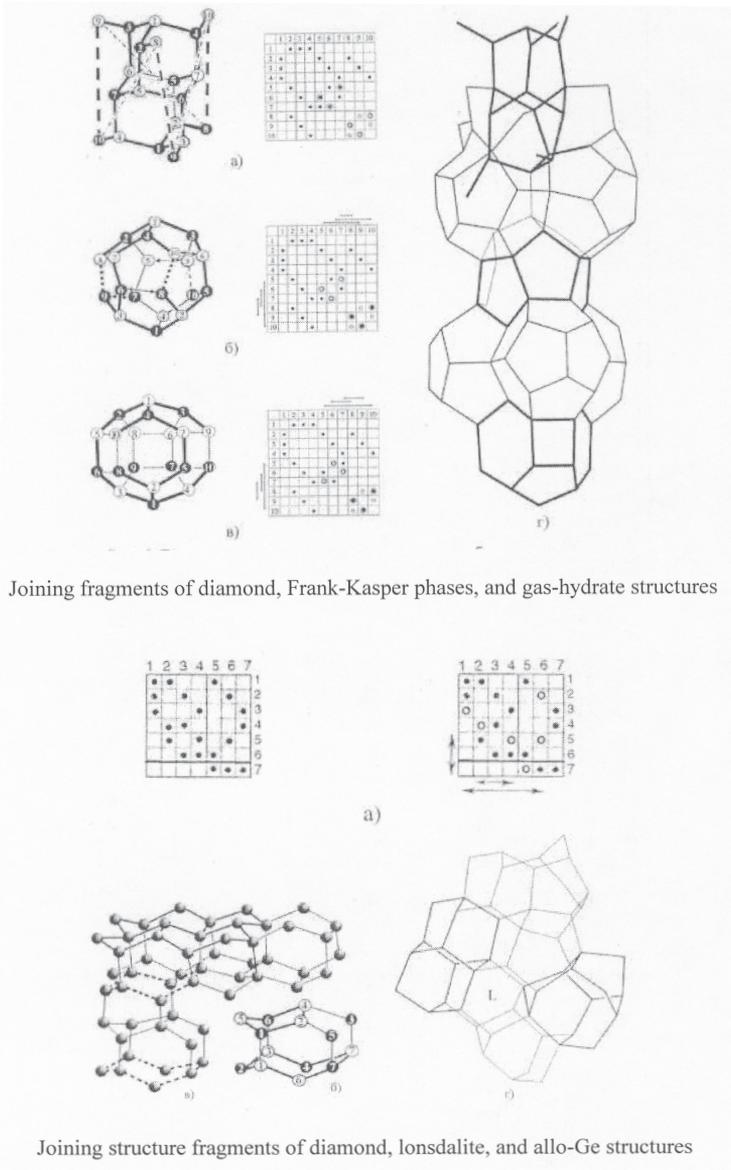


FIGURE 14 - Stratified space geometry.

shorter for some nanostructures.

It would be naïve to suppose that the nanosized objects and related processes were not used before the Age of Nanotechnologies. Biochemical reactions of macromolecules, of which all the 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”, first being developed spontaneously without proper understanding, cannot lay a reliable foundation in the future. Consequently, the basic research aimed at the development of new technological processes and products is of highest significance. May be, the nanotechnologies will supersede some of obsolete and ineffective technologies, but their most important part 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 *meso*-hierarchical matter structure (*mesos*, Greek – 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 be created thereby, being able to change radically the life of all the human society. At the same time, there will be no need in spending raw materials, energy, and transport resources; industrial waste and pollution of the environment will be diminishing; the human labor will be more intellectual and healthy.

In other words, the 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) there will predominantly emerge the “bottom-up” technology (wasteless molecular design and self-assembling of products from elementary bricks of the Nature – atoms and molecules).

The physical basis of such a new paradigm in technology is the knowledge of each sort of atoms of the Mendeleev table. Due to the action of interatomic forces, the 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 the particle properties with respect to those of the macroscopic particles of the same substance occurs, as a rule, well ahead of approaching the quantum limits (at $R_c \leq 10 \dots 100$ nm). This critical size may be dependent on the particular properties (mechanical, electrical, magnetic, chemical, etc.) of the one and the same substance.

Migration of atoms over the particle surface occurs much faster than in its volume (especially at the elevated temperatures). The attraction forces between them result in the self-organization and self-assembling of island-like, column-like and other structures on the surface, which is commonly used for the creation of ordered heterostructures. The specific quantum size

effects may arise from fairly small sizes and at low temperatures, which may be used in electronics, optics, and computer engineering. The vivid examples of such phenomena are quantum dots, wires, rings, and so forth.

Due to the strong dependence of the substance properties on the number of atoms in a cluster and, consequently, on the cluster size, the latter is sometimes even referred to as the 3rd coordinate of the Mendeleev table.

The future of the nanosciences is not at all in the fact that the nanoelectronics will supersede the microelectronics, or nanochemistry and nanobiology will emerge as sub-fields of corresponding disciplines. The most essential significance of the nanostate for applied sciences is the possibility of merging of the inorganic, organic, and biological worlds together, resulting in the creation of the new prodigious materials.

REFERENCES

1. V.Ya. Shevchenko, *Introduction to Technical Ceramics*, Moscow, Nauka, 1993 (in Russian).
2. P. Vandiver, W. Kingery, Egyptian faience: the first high-tech ceramic, in *High-Technology Ceramics: Past, Present and Future*, Amer. Cer. Soc., inc., 1986, pp. 19-34.
3. I. Freestone, M. Tite, Refractories in the ancient and preindustrial world, *ibid*, pp. 35-65.
4. H.N. Lechtman, L.W. Hobbs, Roman concrete and the Roman architectural revolution, *ibid*, pp. 81-128.
5. Li Gao-Zhen, Gao Ling-Xiang, Development of Chinese celadon and its influences, *ibid*, pp. 129-152.
6. W. Kingery, The development of the European porcelain, *ibid*, pp. 153-180.
7. M. Lomonosov, Working log 1751, in *M. Lomonosov, Research in Physics and Chemistry*, ed. by Acad. Sci. USSR, 1951 (in Russian), p. 372.
8. J.J. Ebelmen, *Ann.*, 57, 331 (1846).
9. T. Graham, *J. Chem. Soc.*, 17, 318 (1864).
10. D.I. Mendeleev, *Khim. Zhur. Soc. i Eng.* (in Russian), 4, 65 (1860).
11. C.J. Brinker, G.W. Sherer, *The Physics and Chemistry of Sol-Gel Processing*, Academic Press, 1990.
12. J.D. Mackenzie, Sol-gel research achievements since 1981 and prospects for future, *J. Sol-Gel Sci. Technol.* 26, 23-27 (2003).
13. M. Marchi, R.M. Megri, S.A. Bilmes, Photophysical methods for the study of sol-gel transition and structure of titania gels, *J. Sol-Gel Sci. Technol.* 26, 131-135 (2003).

14. V.Ya. Shevchenko, A.E. Madison, V.E. Shudegov, Fragmentariness and metamorphoses of nanostructures, *Glass Phys. Chem.* 29, 583-588 (2003).
15. V.Ya. Shevchenko, A.E. Madison, V.E. Shudegov, The structural diversity of the nanoworld, *Glass Phys. Chem.* 29, 577-582 (2003).
16. J.D. Bernal, C.H. Carlisle, Range of generalized crystallography, *Kristallografiya*, 13, 5, 927-951 (1968).
17. T. Ishimasa, Y. Kaneko, H. Kaneko, New group of stable icosahedral quasicrystals: structural properties and formation conditions, *J. Non-Cryst. Sol.*, 334-335, 1-7 (2004).
18. W. Bragg, G.F. Claringbull, *Crystal Structures of Minerals*, London, Bell, 1965.
19. J.-F. Colomer, L. Henrard, G. van Tendeloo, A. Lucas, P. Lambin, Study of the packing of double-walled carbon nanotubes onto boundless by transmission electron microscopy and electron diffraction, *J. Mater. Sci.*, 14, 4, 603-606 (2004).
20. J.F. Sadoc, N. Rivier, Boerdijk-Coxeter helix and biological helices, *Eur. Phys. J.*, B12, 309-318 (1999).
21. J.E.S Socolar, P.J. Steinhardt, Quasicrystals. II. Unit-cell configurations, *Phys. Rev. B*, B34, 2, 617-647 (1986).
22. M.C. Escher, *The Complete Graphic Work*, ed. J.L. Locher, London, Thames and Hudson, 2000.
23. S. Anderson, A.D. Wadsley, *Nature (London)*, 211, 581-583 (1966).
24. G. Férey, C. Mellot-Draznieks, T. Loiseau, Real, virtual and not yet discovered porous structures using scale chemistry and / or simulation. A tribute to Sten Andersson, *Solid St. Sci.*, 5, 1, 79-94 (2003).
25. L.A. Bendersky, F.W. Gayle, Electron diffraction using Transmission Electron Microscopy, *J. Res. Natl. Inst. Stand. Technol.*, 106, 6, 997-1012 (2001).
26. R.L. Withers, An analytical solution for the zero frequency hyperbolic RUM modes of distortion of SiO_2 - tridymite, *Solid St. Sci.*, 5, 1, 115-123 (2003).
27. V.Ya. Shevchenko, O.L. Khasanov, A.E. Madison, J.Y. Lee, Investigation of the structure of zirconia nanoparticles by High-Resolution Transmission Electron Microscopy, *Glass Phys. Chem.* 28, 322-325 (2002).
28. Alok Singh, A.P. Tsai, On the cubic W phase and its relationship to the icosahedral phase in Mg-Zn-Y alloys, *Scripta Mater.*, 49, 2, 143-148 (2003).
29. M.I. Samoylovich, V.Ya. Shevchenko, A.L. Talis, Structural diversity of the nanoworld and the algebraic geometry constructions, in: *Nanotechnologies and fotonic crystals*, Kaluga-Moscow, "Technomash"-Publishing, pp. 174-194 (in Russian).

Discussion

Comments by K. HABERKO: This just a comment: the key problem in the application of nanoparticles is to avoid their agglomeration. From this point of view, in the case of hydrothermally crystallized zirconia particles it proved much better not to dry water suspensions but to mould them by filter pressing. Using this technique and 8 nm Y-TZP particles, we were able to obtain nearly theoretically dense polycrystals at sintering temperatures as low as 1150 °C.

Comments by Y. TRETRYAKOV: I have no doubt that sol-gel technology has definite perspectives for nanomaterials preparation, but to my mind this perspective will become more promising upon combination of sol-gel processes with cryochemical processes like cryocrystallization, cryoprecipitation and freeze-drying. It gives a chance to control water removal and to avoid nondesirable agglomeration. It's quite wrong to keep in mind that cryochemical processes are very limited in size, as industry deals successfully with huge amounts of products (from sublimated coffee to sublimated vegetables like potatoes).