Development of inorganic chemistry as a fundamental for the design of new generations of functional materials

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Contents

Abstract. The lines of research in the field of inorganic chemistry that are closely related to the design of novel functional materials are analysed. Special attention is given to areas of inorganic materials chemistry that have been developed most intensely at the Division of Inorganic Chemistry of the Department of Chemistry and at the Department of Materials Science of the Moscow State University over the past decade. The bibliography includes 135 references.

I. Introduction

Much of the actual knowledge which constitutes the basis of modern inorganic chemistry was obtained rather long ago; however, in the second half of the 20th century inorganic chemistry faded into the background of extraordinary achievements in organic chemistry and the chemistry of living systems. The progress in electronic engineering,[1] photonics,[2] sensorics[3] and spintronics,[4] which is impossible without the development of new generations of functional materials, has resulted in a kind of renaissance in inorganic chemistry in the past 10 – 15 years.

An active search for ways of utilisation of virtually all chemical elements systematised as the Periodic Table aimed at the development of novel materials and technologies is under way. The increasing applications of the most recently discovered chemical elements, *e.g.*, rhenium, technetium and francium, to say nothing of plutonium, americium and other actinides, provide illustrative examples.

The transition from chemical elements to materials is extremely complicated, and even the development of methods of combinatorial chemistry[5, 6] does not allow one to master a multitude of combinations of the elements. Just for elements having stable isotopes, the number of such combinations exceeds 7×10^{23}. This increases by many orders of magnitude considering that the

majority of the existing functional materials are developed on the basis of metastable (rather than thermodynamically stable) states of substances which are indefinably numerous for each particular compound with a fixed composition.

Obviously, the method of random enumeration of compositions is inefficient in the design of novel materials, and a significantly more pronounced effect is produced owing to the use of various approaches based, in particular, on the progress in inorganic chemistry. Despite the well-established traditions in the development of inorganic chemistry in Russia, the range of research in the field of inorganic synthesis in our country has recently narrowed considerably due to the limited experimental facilities of many research groups wich have no access to modern high-precision equipment, such as electron microscopes, synchrotron radiation sources, squid magnetometers, high-resolution NMR spectrometers, *etc*. This is all the more distressing taking into account the outstanding contribution of Russian scientists to the development of modern inorganic chemistry. Suffice it to mention the investigations by D I Mendeleev, N S Kurnakov, L A Chugaev and I I Chernyaev and more recent studies by A V Novoselova, I V Tananaev, V I Spitsyn and many others.

At present, the inorganic chemistry of materials is being developed especially intensively at such research centres as the N S Kurnakov Institute of General and Inorganic Chemistry of the RAS (Moscow), the A V Nikolaev Institute of Inorganic Chemistry of the Siberian Branch of the RAS (Novosibirsk), the Institute of Solid State Chemistry of the Urals Branch of the RAS (Ekaterinburg), the I V Grebenshchikov Institute of Silicate Chemistry of the RAS (Saint-Petersburg) as well as by divisions of inorganic chemistry of the largest classical and technical Russian universities including the M V Lomonosov Moscow State University (MSU).

In writing the present review and other reviews published in this issue of the Journal, the authors did not set themselves the task encompassing all the trends in contemporary inorganic chemistry, which is impossible in principle. They have consciously confined the range of scientific problems to those directly related to the design of novel functional materials and appropriate to their own research experience gained at the Division of Inorganic Chemistry of the Department of Chemistry and the Department of Materials Science of MSU over the past 10 – 15 years.

It may be hoped that despite the inevitable subjectivity, the reviews presented in this issue will provide an insight into modern

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inorganic chemistry as a fundamental for the design of new generations of functional materials. The main research trends touched upon in the present review are as follows:

— chemistry of ionic and molecular precursors;

— crystal chemical design of novel inorganic compounds and design of materials based on them;

— inorganic nano- and supramolecular chemistry;

— chemistry of non-stoichiometric compounds;

— chemistry of elements in unusual oxidation states;

— inorganic chemistry of biomaterials and implants;

— inorganic synthesis of functional materials using ultrasonic, hydrothermal and microwave methods.

II. Chemistry of ionic and molecular precursors

The design of materials with a definite range of structure-dependent properties on the basis of chemical compounds (rather than merely the synthesis of chemical compounds) is the ultimate goal for a wide range of inorganic chemists engaged in the development and perfection of functional materials. Such properties depend on the real structure of a material beginning with the structure of the unit cell and ending with the peculiarities of polycrystalline (ceramic) structures with their characteristic defects (dislocations, crystallite boundaries, pores and cracks). Different structural levels are mutually related. The possibility of control over such relationships is considered in reviews [7, 8] within the framework of approaches of non-linear dynamics. The latter can be used for the description of the evolution of physicochemical systems under non-equilibrium conditions determined by specific interactions of these systems with the environment. It has been shown [9] that some factors, among which the unambiguity and reproducibility of the original states of chemical precursors are critical, should be taken into consideration in the optimisation of the reaction zone for the synthesis of materials. The more complex are the systems the more difficult this is to attain. Here, we define the complexity of a system as both its chemical and phase compositions and activities of its precursors determined by their chemical and thermal prehistories, i.e., the effect of 'topochemical memory'.[10]

If a material, which is the target product of chemical and phase conversions, is multicomponent, additional requirements for homogeneity and ability to preserve it upon transition to the target product are imposed on its precursors. It is for this reason that solid-phase synthesis, which seems to be technologically the simplest and has been widely employed previously for the manufacture of magnetic dielectrics and piezoceramics, is fairly ineffective in the preparation of many functional materials. Thus the synthesis of manganese–zinc ferrites with high magnetic permeability was carried out by the reaction:

$$1/3\,MnCO_3 + 2/3\,ZnO + Fe_2O_3 = Mn_{0.33}Zn_{0.67}Fe_2O_4 + 1/3\,CO_2.$$
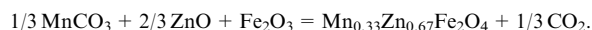
It was found, however, that in many cases the combination of traditional processes, such as mechanical blending, compaction of precursor mixtures and high-temperature annealing ($\sim 1200\,°C$), does not allow preparation of a single-phase product. An increase in temperature results in inevitable losses in volatile zinc oxide and dissociation of iron(III) oxide to form magnetite. These processes significantly deteriorate the composition and properties of the product due to considerable magnetic and dielectric losses, especially at ultrahigh frequencies. Repeated grinding and heating at constant temperatures lead to further contamination of the product with the mill materials, which markedly decreases the magnetic permeability of the target ferrites.

The problem of reproducibility and enhancement of functional properties of solid-phase synthetic products can be overcome by combining the solid-phase synthesis and thermolysis. In this case, mechanical mixtures or co-precipitated salts of various oxoacids [11] including sulfates, carbonates, nitrates, oxalates, acetates, citrates, formates and stearates are used as chemical precursors. The use of salt solid solutions obtained under equilibrium or non-equilibrium conditions was next step forward. It has

been found [12, 13] that schoenite-type salts of the general formula $M^{2+}A^+(RO_4)_2 \cdot 6\,H_2O$ (M = Mg, Mn, Ni, Co, Fe, Cu, Zn; A is an alkali metal or NH_4; R = S, Se, Te, Cr) or alum-type salts $A^+M^{3+}(SO_4)_2 \cdot H_2O$ (where A is an alkali element or NH_4; M = Fe, Cr, Co) are the most convenient for equilibrium crystallisation.

The ability to form continuous solid solutions at any ratios of the reaction components and good solubility in water, which decreases drastically upon cooling, were used as a basis for the development of original methods for the preparation of highly homogenous isomorphic salt mixtures. These methods are based on isoconcentration evaporation of the solvent or isoconcentration elimination of micro-oversaturation of the solution.

The practical implementation of these processes has become possible due to extensive studies [12] of equilibrium diagrams of ternary (salt 1–salt 2–water) and more complex systems and determination of thermodynamic distribution coefficients of salt components between co-existing liquid and solid phases aimed at selecting the conditions for equilibrium crystallisation of salt solid solutions the cationic compositions of which are identical to those of the ferrites to be synthesised. The transition from the salt precursor to the target product occurs upon thermolysis using a reaction of the type:

$$(Ni_{1/3}Fe_{2/3})SO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O =$$
$$= 1/3\,NiFe_2O_4 + 2\,SO_2 + 2\,NH_3 + 3/2\,O_2 + 7\,H_2O.$$
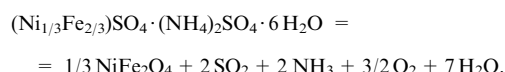
The conditions of this reaction predetermine, to a large extent, the feasibility of preparation of a polycrystalline material with a preset ceramic structure and structure-dependent properties.

The cryochemical method may be regarded as a versatile procedure for the preparation of salt-like multicomponent precursors. The cryochemical technology [13–15] is based on a balanced combination of heating and cooling processes, the latter being used to prevent the uncontrollable changes in intermediate and target products (Fig. 1). Rapid freezing (e.g., in liquid nitrogen) of solutions containing metal salts as constituents of materials to be synthesised and dispersed in the form of mono- or polydispersed drops is a crucial step in the cryochemical technology. Frozen
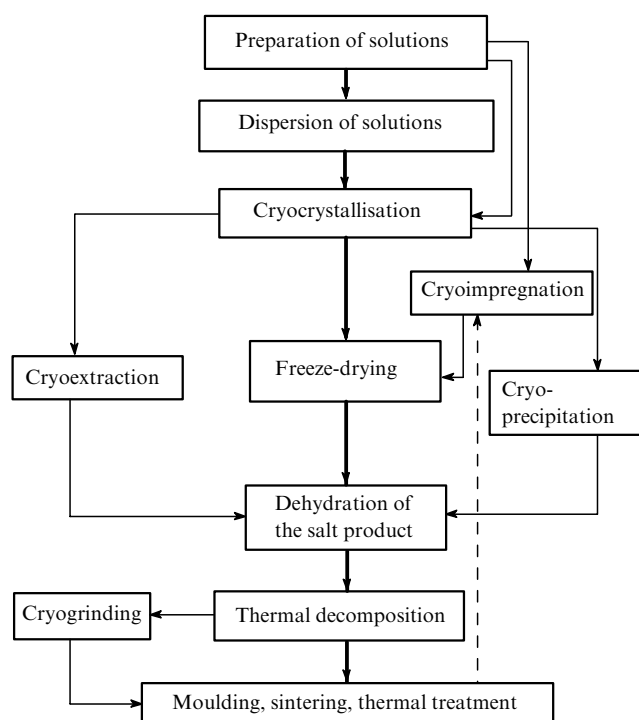

Figure 1. Processes of cryochemical technology.

solutions of salts in the form of cryogranules are usually subject to freeze-drying; its optimum conditions provide the preparation of highly homogenous salt precursors. The rate of cryocrystallisation exceeds that of solid phase formation by several orders of magnitude when other known non-equilibrium methods (*e.g.*, solvent replacement by desalting from aqueous solutions with non-aqueous solvents, such as acetone, ethanol or methanol) are used for the preparation of salt precursors.

The wide application of cryochemical technology was preceded by fundamental investigations of cryocrystallisation, freeze-drying, cryoprecipitation, cryoextraction, cryodispersion and some original cryocalorimetric procedures.[13-16] The cryochemical synthesis of salt precursors underlies the preparation of various functional materials (Fig. 2). Dispersed powders prepared by thermal decomposition of salt precursors are distinguished by microplasticity, high reactivity and sintering ability in addition to their chemical homogeneities.

The so-called topochemical memory, *i.e.*, the ability of solid-phase chemical conversion products to store ('to remember') information about their origin and to transfer it upon subsequent topochemical reactions, is a characteristic feature of salt-like ionic precursors. A real structure, which is usually formed under non-equilibrium conditions and affects significantly the properties of functional materials obtained as polycrystalline ceramics, seems to be the most probable candidate for 'storing' and 'delivering' information in solids.[10]

Studies related to the chemistry of molecular precursors are extremely important for the design of thin-film materials by molecular deposition. In order to solve the global problem of the increase in the density of information recording in silicon chips, it is necessary to replace the 'natural' oxide (SiO_2) by oxides with higher dielectric constants. The most probable candidates are HfO_2, ZrO_2 and Ln_2O_3. Preparation of films of such oxides on the surface of silicon by MOCVD (Metal-Organic Chemical Vapour Deposition) requires development of molecular precursors possessing high volatilities and relative thermal stabilities as well as abilities to undergo hydrolysis, pyrohydrolysis or other decomposition reactions leading to the formation of amorphous oxides on the surface of silica. The main idea realised at the Laboratory of Coordination Chemistry of MSU[17] consists of the use of novel molecular precursors based on metal complexes with complete saturation of the coordination sphere with ligands that form relatively weak donor–acceptor bonds. Saturation (and, as a consequence, volatility) was provided by the introduction of an additional neutral ligand (*e.g.*, phenanthroline); charged ligands were chosen on the basis of quantum-chemical calculations of the energies of the metal–ligand bonds.

Complexes with organic ligands were also successfully used for the solution of yet another vital task, *viz.*, preparation of thermoprotective (barrier) coatings for gas-turbine unit blades. It was shown[18] that deposition of coatings from vapours of β-diketonates of appropriate metals using ZrO_2 (Y_2O_3) is the most
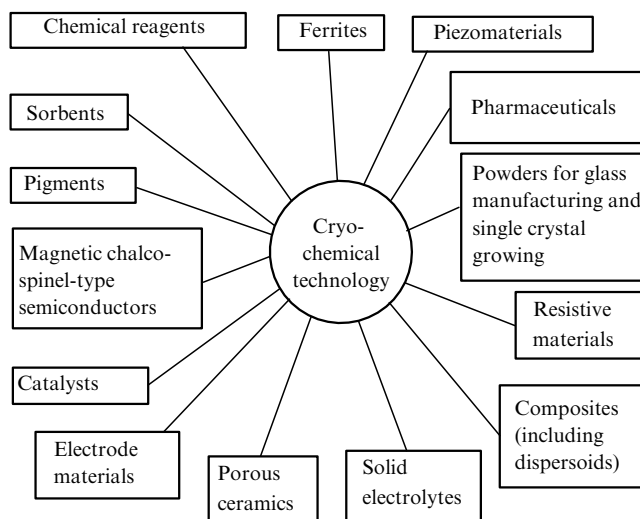

Figure 2. The main products prepared by cryochemical technology.

efficient approach which allows radical reduction of the production cost owing to the use of inexpensive acetylacetonates. As for the problem of insufficient volatility of polymeric $Y(acac)_3$, it is solved by co-evaporation with volatile $Zr(acac)_4$, its small portions being fed gradually into the evaporator. The well-known synergistic effect is observed, *i.e.*, joint evaporation is more complete than separate.

A series of novel REE mixed-ligand complexes including Tb(III) complexes with some aromatic acid derivatives to be used as luminescent materials for an organic light emitting diode (OLED) have been synthesised. An OLED represents a multilayer unit constructed using planar technology. The material of the working layer should not only possess bright electroluminescence, but also be temperature-resistant (since OLED is spontaneously heated during operation) and form smooth films upon deposition on the surface of the substrate, *i.e.*, be readily soluble in organic solvents, to moisten the surface of the anodic layer and be resistant to cracking. Such luminescent materials are prepared by mixed-ligand complex formation using neutral ligands.

Spectral characteristics of the terbium salicylate complex $Tb(sal)_3 \cdot H_2O$ with triphenylphosphine (TPPO) obtained by the reaction

$$Tb(sal)_3 \cdot H_2O + TPPO \xrightarrow{EtOH-C_6H_6} Tb(sal)_3 \cdot (TPPO)_2$$
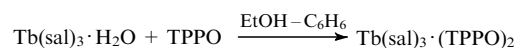
are shown in Fig. 3 as an example.

Terbium salicylate is stable at temperatures up to 120 °C, whereas the complex $Tb(sal)_3 \cdot (TPPO)_2$ retains stability up to
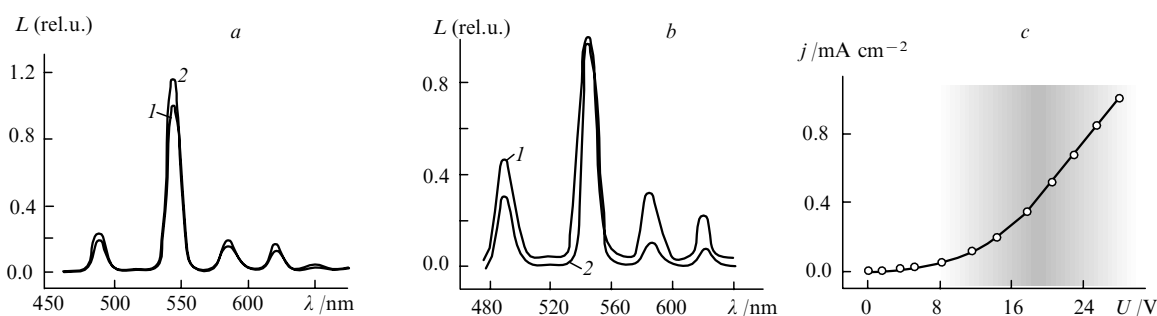
Figure 3. Spectral characteristics of $Tb(sal)_3 \cdot H_2O$, $Tb(sal)_3 \cdot (TPPO)_2$ (*a*) and OLED based on $Tb(sal)_3 \cdot (TPPO)_2$ (*b, c*). (*a*) Luminescence spectra of $Tb(sal)_3 \cdot H_2O$ (*1*) and $Tb(sal)_3 \cdot (TPPO)_2$ (*2*); (*b*) photo- (*1*) and electroluminescence (*2*) spectra of OLED; (*c*) voltammetric characteristics of OLED (the luminescence zone is shown in grey).

200 °C, the surface roughness of the former being 66 nm, that of the latter being 9 nm.

One of the latest successful investigations related to molecular precursors was carried out by Romanov *et al.*[19] These authors have synthesised a mixed-ligand complex niobium isopropoxide – dipivaloylmethanate and used it, along with dipivaloylmethanate potassium *tert*-butoxide, for the preparation, by the MOCVD method, of epitaxial films of potassium niobate $KNbO_3$ characterised by extremely high values of non-linear optical and piezo-electric constants.

III. Crystal chemical design of novel inorganic compounds and preparation of materials based on them

Antipov and co-workers[20] have developed a concept of inter-growth structures and used it in a search for novel oxide materials. This was achieved through the use of structural design which had proved to be efficient in the preparation of novel high-temperature superconductors based on complex copper oxides. The latter contain structures derived from perovskite (ABO_3) or a perov-skite-like fragment as one of the structural components of inter-growth structures. The prediction and synthesis of novel superconductors were carried out by selecting various intergrowth structures. Such a synthesis is, to a certain extent, similar to that of organic compounds; however, its realisation demands an analysis of infinite two-dimensional layers forming structural units rather than of isolated groups of atoms as in the case of organic molecules.

The geometric commensurability of structurally different fragments in the plane *ab* is a prerequisite for the formation of intergrowth structures. By varying the cationic compositions of the units and the formal degree of oxidation of copper ions, one can vary the geometrical sizes of the units and obtain the desired compounds using an appropriate synthetic procedure. In predict-ing the compositions of intergrowth structures, attention should be given to crystal chemical characteristics of the cations, their chemical similarities and electron neutrality of the elementary cell as a whole. The choice of a synthetic procedure is determined by the chemical peculiarities of the starting compounds and the degree of oxidation of the cations in the target structure.

This approach was used for the preparation of more than 100 novel complex copper oxides among which about 30 oxides possess superconducting properties.[21]

The search for novel superconductors was carried out among compounds comprising an anion-deficient perovskite-like struc-ture, *viz.*, $A_n(Cu,M)_nO_{3n-\delta}$, and a series of novel oxides was obtained. The 'structural substitution' approach was also used in the synthesis of novel compounds where prototypes with a layer sequence corresponding to the formula $(CuO_2)(M\square)(CuO_2)$ served as the basis of the structure. In the structures of novel compounds, this fragment was rearranged into the sequence $(CuO_2)(A_2O_2)(CuO_2)$ the (A_2O_2) block in which has the structure of fluorite.

Crystal chemical simulation has made it possible to predict the existence and to synthesise a new family of superconductors, *viz.*, $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ with record values of T_c. The transition temperatures for superconduction of the phases $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ depend on the content of oxygen (δ) and the number of CuO_2 layers (n). A progressive increase in T_c on going from the first member of the homologous family (97 K) to the second (127 K) and third (135 K) members is followed by its decrease for the fourth (127 K), fifth (110 K) and sixth (107 K) members. The T_c value for $HgBa_2Ca_2Cu_3O_{8+\delta}$ at 23.5 GPa was found to be equal to 157 K. The possibility, in principle, of a transition into the superconducting state at $T_c = 150 - 160$ K at atmospheric pressure has been demonstrated for compounds with the $Cu-O$ distances corresponding to those in the $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ complexes under external pressure.

The fact that the anionic sublattice may contain fluorine atoms along with oxygen atoms significantly expands the area of a search for Cu-containing oxofluoride superconductors. Xenon difluor-ide, which was employed for the first time as a mild fluorinating agent by Abakumov,[22] has a number of advantages over tradi-tional fluorine sources. First, XeF_2 is solid at room temperature, which permits its precise quantification to attain a required level of fluorination and desired copper oxidation state; second, XeF_2 is less aggressive than gaseous fluorine, which excludes the use of sophisticated equipment and, third, no reaction products that could contaminate the target material are formed from XeF_2. Altogether, more than twenty novel cuprates including superconductors, such as $YBa_2Cu_3O_6F_2$ ($T_c = 94$ K) and $Y_2Ba_4Cu_7O_{14}F_2$ ($T_c = 62$ K), have been synthesised. Special mention should be made of the synthesis of $HgBa_2Ca_2Cu_3O_8F_{0.32}$; here, the introduction of fluorine caused anisotropic chemical compression and a record-high elevation of T_c (138 K).

The method of structural design was successfully used for the simulation of structures of novel complex manganites that some-times possess colossal magnetoresistance.[23]

Epitaxial stabilisation of unstable oxide phases in the form of thin films developed by Kaul *et al.*[24] is a new in principle approach to the design of novel materials. Based on the results of thermody-namic simulation, direct syntheses of the novel phases RBO_3 (R = REE; B = Ni, Co, Mn, Fe, In) have been carried out. Some of them are ferroelectrics ($RFeO_3$ and $RMnO_3$); in others ($RNiO_3$, $RCoO_3$), a transition 'metal – insulator' is possible; ($R_3Fe_5O_{12}$) is a magnetic material. It was found that epitaxial stabilisation can successfully be used in the technology of preparation of thin-film materials for microelectronics. This technology was used as a basis for realisation of the local epitaxy principle during photolitho-graphic formation of planar heterostructures.

A detailed study of epitaxial ratios of various structural types has made it possible to significantly expand the potential of heteroepitaxy. This method was used,[24] in particular, for the design of nanodomain epitaxial structures based on REE man-ganites characterised by high tunnel magnetoresistance values. It was shown that nanodomain epitaxial structures are formed as a result of self-organisation of a system that is crystallised at the nanolevel. Provided the energetically identical heteroepitaxial approaches exist, these structures can be used as a basis for the manufacture of inexpensive, highly sensitive magnetic field sen-sors.

The fundamental physicochemical problems related to the design of HTSC materials based on nonstoichiometric phases $R_{1+x}Ba_{2-x}Cu_3O_z$ with predetermined compositions, homogene-ities and structures conferring desired structure-dependent prop-erties, are considered in recent reviews.[25, 26] TTT diagrams (Time – Temperature – Transformation) have been developed for the first time and the efficiency of their use in the design of HTSC materials has been demonstrated based on the results of system-atic studies of temperature- and time-dependent changes in these phases.

The properties of manganites manifesting colossal magneto-resistance, which make them promising components of various magnetic sensors and novel magnetic information-recording devi-ces, depend critically on structural parameters. Compositions with extremely high sensitivities to the magnetic field, light and other factors including changes in the isotopic composition have been obtained for the first time.[27, 28] Optimisation of chemical compositions of manganites was carried out with due regard to the results of physical simulation of electron transfer processes. The phases $(La_{1-x}Pr_x)_{0.7}CaO_3MnO_3$ in the form of ceramics and thin epitaxial films have been studied in detail. It was found that unusually high sensitivities of electric resistances of critical com-positions to the light and electric and magnetic fields are related to the competition between the metallic and charge-ordered states. The material synthesised by Babushkina *et al.*[28] ($x = 0.75$) manifests an anomalously high isotope effect upon the substitu-tion of ^{18}O for ^{16}O and a transition from the metal-type con-

ductivity to a dielectric state. The magnetoresistances of film materials depend on elastic stresses generated upon their epitaxial fusion with the substrate. Critical compositions of the system $R_{1-x}Sr_xMnO_3$ are characterised by extremely high magneto-striction concomitant with a strong magnetocalorific effect. Such phases present considerable interest for the design of magnetic and mechanical sensors and Freon-free refrigerating plants having high coefficients of efficiency.

Needless to say, the ideology of the construction of functional materials is not confined to a crystal chemical design of novel inorganic compounds. Suffice it to remember the system of physicochemical principles formulated by the author of the present review rather long ago [29] and successfully used for the optimisation of properties of many functional materials, such as ferrites, magnetic semiconductors based on chalcospinels, elec-tronic-ionic conductors of the oxide bronze type, complex silver chalcogenides and lanthanoidates, ceramic electrolytes with uni-polar conductivities with respect to anions, cations and hydrogen as well as piezoceramic materials and flexible piezocomposites based on them.[30] This system comprises the following principles:

periodicity (properties of compounds of elements arranged according to the increase in their atomic numbers change periodi-cally);

physicochemical analysis (principles of continuity, conformity and compatibility of components of an equilibrium system);

limitation of the number of independent parameters of states (among the multitude of parameters of state that characterise an equilibrium system comprising material-forming solid phases, only very few are independent according to the Gibbs' phase rule);

disordering and variability of composition (diverse defects are formed in crystalline lattices of solids at any temperature different from the absolute zero, while any solid-phase compounds with non-molecular types of bonds have variable compositions);

complication of composition (properties of a system change as a result of its chemical, structural and phase complication);

homogeneity (properties of solid-phase materials are sensitive to the degree of their homogeneities at both micro- and macro-levels);

equivalence of disorder sources (under equilibrium conditions, materials acquire specific defects which ensure a maximum increase in the entropy at minimum energy expenditures);

similarity of responses to physicochemical effects (necessary changes in the properties of materials can be achieved under the influence of various physicochemical factors);

nonequivalence of volume and surface;

metastable diversity (the number of non-equilibrium states of materials is indefinitely large; these states can be kinetically stable in solid phases).

The aforementioned principles constitute the system which defines possible approaches to the solution of material-science problems from the point of view of a chemist. Initially, no preference to these principles can be given, they represent a specific set of alternatives. However, when a specific problem is concerned, a decisive (key) principle is isolated from the system for a particular step by analysis of physicochemical conditions and used for the solution of problems aimed at the practical realisation of this principle. The next step towards the solution of the entire problem entails return to the system of principles, isolation and realisation of the next alternative, and so on.

IV. Inorganic nano- and supramolecular chemistry

In 2000, a national programme for investigations and develop-ments in the field of nanotechnologies which has the name 'The National Nanotechnology Initiative' was set up in the USA. In the 2001 budget, the financing for its realisation constituted $500 M, i.e., significantly larger than, for example, the sum allocated for investigations in the field of high-temperature superconductivity immediately after its discovery in 1986. This is not surprising, however, since it is with nanotechnology that the next industrial

revolution is associated. Amazingly, many research groups in Russia manage to carry on successful research in the field of nanomaterials and nanotechnologies with financial support which is three orders of magnitude smaller than that in the USA.

The interest in nanomaterials is associated with their unusual physical properties which are not characteristic of bulk materials. For example, a decrease in the size of semiconductor particles below a certain critical level can lead to the change in the width of a band gap, the generation of a second harmonic and dimensional quantisation of energy levels. At the same time, it is known that the predisposition of free nanoparticles to aggregation restricts their practical application. In this context, the development of methods for preparation of nanocomposites, i.e., nanoparticles incorporated into an inert matrix, which protects the particles from environmental factors and thus prevents their aggregation, appears to be of crucial importance.

A promising method of matrix isolation of nanoparticles is based on chemical modification of lamellar double hydroxides (LDH)[31] with the general formula $M_{1-x}^{2+}M_x^3(OH)_2[(X^{n-})_{x/n} \cdot m\,H_2O]$. These compounds are made up of positively charged hydroxide layers $M_{1-x}^{2+}M_x(OH)_2^{x+}$ and interstitial anions X^{n-}. The method for the synthesis of nanocomposites is related to the chemical modification of these anions. The reaction zone is surrounded by hydroxide layers, so the conditions for the syn-thesis of the nanophase are similar to those observed in a two-dimensional nanoreactor.

The unique characteristics of lamellar double hydroxides open up broad opportunities for the design of nanocomposite materials based on them. Magnetic (based on metallic iron, cobalt and nickel) and semiconducting (based on MS, M = Pb, Zn, Cd) nanomaterials prepared from anion- and cation-substituted hydrotalcite, $Mg_{1-x}Al_x(OH)_2[(CO_3)_{x/2} \cdot m\,H_2O]$, using the above-mentioned method were the subjects of investigation.[32-35] Some of the factors influencing the structures and properties of nanocomposites synthesised have been established. Thus the dependences of the composition, size distribution, morphology and anisotropy of the nanostructures on the structure and composition of LDH used as a lamellar matrix were revealed. Conditions for chemical modification of substituted LDH also have a pronounced effect on the composition and structure of the nanophase formed inside the matrix.

In addition to LDH, a family of silica-based mesoporous molecular sieves has been recommended as a template for the synthesis of nanocomposite materials with a nanophase endowed with predetermined properties.[36] The structure of silica is charac-terised by the presence of a highly ordered system of pores with the diameters ranging from 20 to 100 Å. It is of note that such specific features of the aforementioned mesoporous materials as uniform size distribution of pores, extremely high specific surface (~ 1000 m^2 g^{-1}) and broad variability of a pore size, make them especially attractive for investigators. By virtue of its ordered structure, mesoporous SiO_2 can be used as a template in the synthesis of metal and semiconductor nanoparticles as well as polyaniline and carbon fibres.

Currently, the main attention of specialists in inorganic supra-molecular chemistry is focused on the design of supramolecular ensembles manifesting specific properties. Of considerable interest are ideally ordered ensembles, their structure being determined by the structure of the backbone of the 'host' (receptor), while the functional properties are determined by the nature of the 'guest' (substrate). The diversity of physical properties is due to structural peculiarities of the 'guest' structures including magnetic ordering of d^1-, d^3- and d^9-centres, spin transitions in d^6-centres, electron transitions with valence fluctuations and dynamic effects.

The properties related to dynamic effects are employed in the design of novel thermoelectrical materials. Semiconducting clath-rates provide an example of compounds that are studied to this end.[37] The crystalline structure of a clathrate includes the back-bone of the 'host' with 'guest' atoms with the coordination numbers of 20 and 24 in its cavities. The 'guest' atoms are not

bound to the 'host' backbone by covalent bonds and oscillate inside the cage with frequencies ensuring effective scattering of heat-conducting phonons. This results in a very low heat conductivity (as in the case of glasses). At the same time, the covalently bound backbone ensures high concentrations and mobilities of charge carriers, which accounts for high electroconductivity. A combination of these two features makes clathrates promising compounds for the design of effective thermoelectric materials. It has been found [38] that abnormal magnetisation and thermal capacities of tin-containing clathrates observed at ~ 250 K are not associated with ordinary phase transitions. These data point to the possibility, in principle, of independent optimisation of electro- and heat-conducting properties determined by the structure of the backbone and the dynamics of guest molecules, respectively.

A new trend in inorganic supramolecular chemistry is related to controlled self-assembly of ordered supramolecular ensembles under conditions of high-temperature reactions where reaction systems are complex and heterophasic and are not subject to analysis. Such processes are based on the mutual adjustment of the 'host' and the 'guest' where the 'guest' is a template for the formation of a definite topology and geometry of the 'host' backbone and it itself changes its parameters in accordance with the 'host' requirements. It has been found [39] that weak 'guest – host' interactions are decisive in such self-assembly. Being limited by van der Waals forces, these interactions control the reciprocal arrangement of the 'guests' and the particles forming the 'host' backbone in the first step. If the 'guest' and the 'host' match each other, the formation of ideally ordered supramolecular ensembles takes place where hosts are recognised by 'guests' of various compositions and occupy their predetermined specific sites. As an illustration, Fig. 4 shows the structure [Hg₆P₄](TiCl₆)Cl formed as a result of self-assembly of $TiCl_6^{3-}$ and Cl^- in the cavities of the backbone of $[Hg_6P_4]^{4+}$.
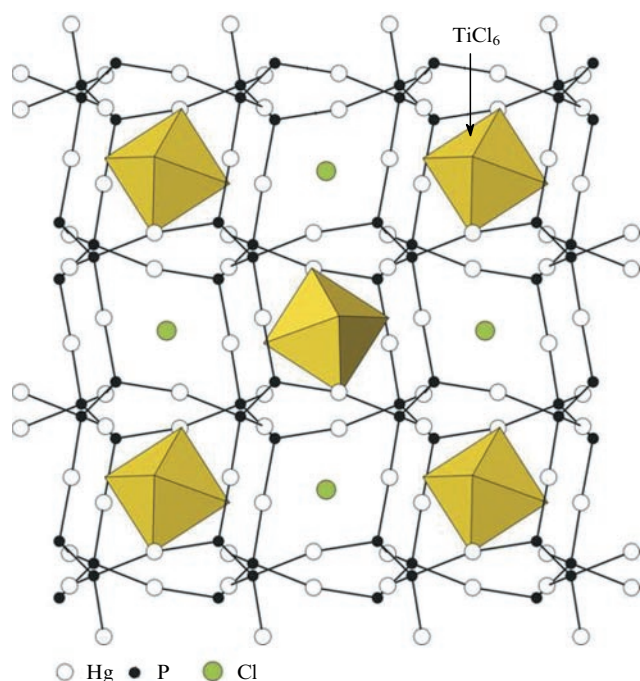

TiCl₆

○ Hg   ● P   ● Cl

Figure 4. The structure of [Hg₆P₄](TiCl₆)C1 prepared by high-temperature synthesis.
The structure was formed by self-assembly of TiC_6^{3-} and Cl^- in the cavity of a three-dimensional cage of $[Hg_6P_4]^{4+}$.
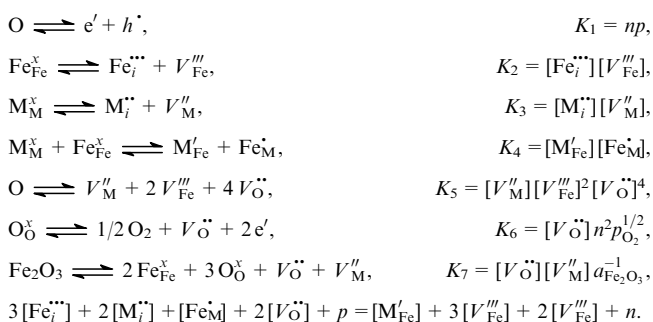
V. Chemistry of compounds with variable compositions

The formation of chemical compounds with variable compositions, which have the name 'berthollides', was discovered over 100 years ago by N S Kurnakov who studied silicate and metallic systems. Later, it was found that compositional variability is an intrinsic property of inorganic solid-phase compounds with ionic bonds predominating. Depending on the nature of the elements constituting inorganic compounds, the area of their existence is either very broad (*e.g.*, titanium and iron monoxides) or, *vice versa*, extremely narrow (*e.g.*, alkali metal halides, zinc, lead and cadmium chalcogenides). In any case, a deviation from stoichiometry is a critical factor in the formation of binary and more complex crystals.

Using statistical thermodynamics methods, Schottky and Wagner [40] have established a correlation between the defects of crystal lattices of inorganic compounds and their non-stoichiometries and proved the inevitable existence of the latter in any ionic crystal. Minor deviations from stoichiometry are usually described within the framework of disordering models with formation of non-interacting vacancy-type point defects, incorporated atoms or antistructural defects. Defect formation is accompanied by pronounced changes in electrical, magnetic, optical, thermal and mechanical properties of solid-phase compounds; therefore, an analysis of their non-stoichiometries is one of the most important directions in inorganic chemistry of solids.[41]

The development of methods for coulometric titration in reversible electrochemical circuits with solid electrolytes possessing ionic (anionic or cationic) conductivity [42] has led to considerable progress in the study of non-stoichiometry, in particular of compounds manifesting a narrow range of homogeneity. Quasichemical models of defect formation in inorganic compounds were successfully employed for the description of functional properties of semiconductors and ferrites. For example, the results of studies of non-stoichiometry as a function of oxygen pressure and temperature using a quasichemical approximation have provided a clue to the solution of problems related to directed doping of ferrites.[43]

Defect formation in ferrospinels MFe₂O₄ can be described by the following system of equations:

$$O \rightleftharpoons e' + h^{\bullet}, \qquad\qquad\qquad K_1 = np,$$

$$Fe_{Fe}^x \rightleftharpoons Fe_i^{\bullet\bullet\bullet} + V_{Fe}''', \qquad\qquad K_2 = [Fe_i^{\bullet\bullet\bullet}][V_{Fe}'''],$$

$$M_M^x \rightleftharpoons M_i^{\bullet\bullet} + V_M'', \qquad\qquad K_3 = [M_i^{\bullet\bullet}][V_M''],$$

$$M_M^x + Fe_{Fe}^x \rightleftharpoons M_{Fe}' + Fe_M^{\bullet}, \qquad K_4 = [M_{Fe}'][Fe_M^{\bullet}],$$

$$O \rightleftharpoons V_M'' + 2 V_{Fe}''' + 4 V_O^{\bullet\bullet}, \qquad K_5 = [V_M''][V_{Fe}''']^2[V_O^{\bullet\bullet}]^4,$$

$$O_O^x \rightleftharpoons 1/2\, O_2 + V_O^{\bullet\bullet} + 2 e', \qquad K_6 = [V_O^{\bullet\bullet}]n^2 p_{O_2}^{1/2},$$

$$Fe_2O_3 \rightleftharpoons 2 Fe_{Fe}^x + 3 O_O^x + V_O^{\bullet\bullet} + V_M'', \qquad K_7 = [V_O^{\bullet\bullet}][V_M'']a_{Fe_2O_3}^{-1},$$

$$3[Fe_i^{\bullet\bullet\bullet}] + 2[M_i^{\bullet\bullet}] + [Fe_M^{\bullet}] + 2[V_O^{\bullet\bullet}] + p = [M_{Fe}'] + 3[V_{Fe}'''] + 2[V_{Fe}''] + n.$$

In addition to activity ($a_{Fe_2O_3}$), temperature (T) and partial oxygen pressure (p_{O_2}), the role of variables is played by the concentrations of all possible types of point defects, *viz*., $[M_i^{\bullet\bullet}]$, $[Fe_i^{\bullet\bullet\bullet}]$, $[M_{Fe}']$, $[Fe_M^{\bullet}]$, $[V_O^{\bullet\bullet}]$, $[V_M'']$, $[V_{Fe}''']$, n, p, which can be calculated as functions of the parameters of state. Whilst the quasichemical approach is not strictly accurate, its practical utility leaves no doubt.

Figure 5 shows a defect formation diagram plotted in the coordinates $\log[i] - f(\log p_{O_2})$ at constant values of T and $a_{Fe_2O_3}$, where $[i]$ is the concentration of the defects of the *i*th type. From the diagram it follows that changes in thermal treatment and sintering regimes of ferrites can underlie the transitions from electron to hole conductivity and the predominance of ionic conductivity for compositions close to stoichiometric.
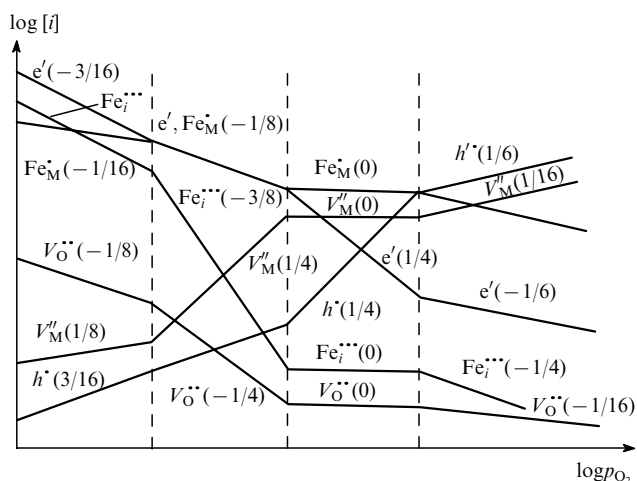
Figure 5. A diagram of defect formation in a crystal lattice of a ferrospinel at constant temperature and constant activity of Fe_2O_3.
The individual segments of the dependences show the predominant defects; the numbers in parentheses indicate the slopes.

Passage to inorganic compounds with more pronounced non-stoichiometries casts doubts on the existence of a strict correlation between the non-stoichiometry index and the concentration of predominant point defects as is implied by the quasichemical approximation.

Changes in the structures of binary or more complex crystals as a result of increasing non-stoichiometries have a different origin. Sometimes, they are related to the formation of associates, the simplest being bivacancies, to a spatial ordering of super-structure-type defects and finally to annihilation of point defects accompanied by changes in the types of bonds of coordination polyhedra and formation of the so-called crystallographic-shift structures of the type of homologous series: M_nO_{3n-1} where $n = 8$, 9, 10, 11, 12 and 14. However, the concept of discrete compositional changes resulting necessarily from rearrangements of coordination polyhedra upon crystallographic shift (CS) is questionable.

According to Anderson,[44] there exist many systems possessing infinitely adaptable structures, *i.e.*, the phases that maintain a high level of structural organisation despite continuous composition changes by virtue of changes in the repetition frequencies of CS planes or orientation of the latter with the preservation of fragments of the matrix structure rather than involvement of point defects. The former process is discrete and gives rise to the formation of various homologues of the same series, while the latter is continuous. Their combination ensures the continuity of compositional changes within the same order. An infinitely adaptable structure was found, for example, in phases with variable compositions of $Y(OF)_{2.13-2.22}$, solid solutions $(TiO_2-Cr_2O_3)$ and cerium–cadmium alloys.

The imperfections of structural patterns, *e.g.*, coherent inter-growth of sites with different orientations of CS planes, are predominant defects in the case of non-stoichiometric phases with a high level of structural organisation. These defects, which are commonly referred to as Wadsley defects, strongly affect the properties of solid phases and their behaviour under the action of various chemical and physical agents.

It is clear that the compositions and structures of non-stoichiometric compounds do not always correspond to the equilibrium conditions of their formation. On the contrary, very often the conditions of synthesis, thermal treatment and existence of such compounds are far from equilibrium and the net result is determined by the rates of processes involved. For example, nickel monoxide prepared by thermolysis of nickel nitrate at moderate heating temperatures may contain excess oxygen up to the composition $NiO_{1.5}$, whereas nickel monoxide synthesised in air

under equilibrium conditions has the composition NiO_{1-x}, where $x = f(T, p_{O_2})$. At 1373 K and $p_{O_2} = 2 \times 10^{-9}$ atm, the value of x is equal to 1.8×10^{-8}.

Undoubtedly, the fundamental principles of chemistry of non-stoichiometric compounds considered above are valid for any newly produced functional materials, be they superconducting cuprates, manganites with superhigh magnetic resistance or cerates manifesting high proton conductivity. At the same time, any of these materials have specific features of their own and demand analysis of their non-stoichiometries as in the case of semiconducting or ferrite systems.

The design of superconducting materials able to maintain high levels of critical currents in strong magnetic fields has become possible owing to the passage from yttrium–barium cuprate $YBa_2Cu_3O_z$ with strict cationic stoichiometry to neodymium–barium cuprate $Nd_{1-x}Ba_{2-x}Cu_3O_z$ with a broad range of homogeneity for both oxygen and cations. It was found also that a change in the cationic composition within the homogeneity zone is accompanied by evolution of the structure from 123 *via* 336 to the superstructure 213.[45] The use of a TTT diagram, which characterises the behaviour of a metastable, slowly evolvable system, is necessary because of an extremely low rate of cationic ordering in neodymium–barium cuprates.

VI. Chemistry of elements in unusual oxidation states

The design of novel functional materials based on chemical elements in unusual oxidation states is a nontrivial process, at least because the unusual oxidation state is equivalent to the instability of a particular state of an element. Hence, the phenom-enon of the appearance of one or another unusual oxidation state of a chemical element is insufficient from the practical point of view, one should also be sure that the lifetime of a chemical element in an unusual oxidation state is commensurate with the period of functioning of the material containing this element. A significant contribution to the chemistry of elements in unusual oxidation states has been made by researchers of the Institute of Chemical Physics of the RAS and the Department of Chemistry of the MSU. The former have succeeded in obtaining Np(VII), Pu(VII), Am(VII), Cm(VI), Cm(V) (see Ref. 46) and a series of actinides and lanthanides in lower oxidation states,[47] the latter have demonstrated the possibility of existence of Tm(IV) and found that the tetrad effect characteristic of lanthanides and actinides is more significant for 'distant' lanthanides than for 'near' lanthanides in solid compounds.[48]

At first, the values of extremely high oxidation states for transition metals of Groups 3–11 of the Periodic System correlate with the group number, but then this correlation is absent, which is determined by the electronic structure or, more precisely, by disturbances in the fine balance between binding and loosening forces in atomic orbitals and increasing instabilities of the corresponding compounds in their extremal oxidation states.

'Matrix' systems formed upon crystallisation from homogeneous media (solutions, melts), co-precipitation or solid-phase synthesis present the greatest interest for specialists in materials sciences. Matrix systems containing Fe(IV), Fe(V), Fe(VI) and Co(VI) were prepared by reactions of binary oxides with dopant oxides.[49]

An alternative approach consists of the so-called constitutional substitution where the doping ion occupies the host metal positions of the matrix; the properties of which predetermine the oxidation state of the doping ion. Thus Fe(V) is stabilised in vanadium pentaoxide; this oxidation state unusual for iron is formed upon dissolution of trivalent iron oxide in a melt of vanadium pentaoxide. However, the formation of Fe(V) could be observed only after quenching of the samples into metallic mercury.

The formation of matrix systems under conditions of oxidative synthesis (sintering of Group 3–11 metal oxides with alkali

metal peroxides) revealed certain peculiarities of the final products which are determined by the properties of the matrix metal and the mechanisms of reactions. Thus it was found that the final products prepared with the use of molybdate and tungstate matrices contained extrinsic magnetics, *i.e.*, Mo(V)- and W(V)-containing exchangeable clusters of the ferro- and antiferromagnetic type. The initial steps of the reactions may involve the formation of bronze-type derivatives, trace amounts of which are partly stabilised in final products and elicit the corresponding magnetic responses.[50]

Yet another line of research related to the synthesis of bismuth derivatives in lower oxidation states has been described.[51] The authors have succeeded in preparation of homonuclear polycations of the types Bi_5^{3+}, Bi_8^{5+} and Bi_9^{5+}. A fragment of the crystal structure and the main structural elements of compound $Bi_{10}Nb_3Cl_{18}$ synthesised upon heating of a $Bi-BiCl_3-NbCl_5$ mixture to 550 °C are shown in Fig. 6. In the structure of this compound, the polycations Bi_9^{5+} are surrounded by octahedral counteranions $NbCl_6^{2-}$ containing Nb(IV). Usually, it is $NbCl_6^-$ ions containing Nb(V) that are more stable.

The crystal structure of compound Ni_8Bi_8SI synthesised by Baranov *et al.*[52, 53] contains unusual bimetallic infinitely one-dimensional cationic columns of $[Ni_8Bi_8SI]_\infty^+$ which are made up of square nickel antiprisms surrounded by a sheath of bismuth atoms (Fig. 7). In this compound, nickel and bismuth atoms exist in unusually low oxidation states, which are responsible for the formation of such an unusual system of metallic bonds between the metal atoms. This structure can be regarded as consisting of a set of 'molecular' metal wires (a thread of nickel antiprisms) enclosed in an insulating matrix (a sheath of bismuth atoms). According to its physical properties, this compound represents a one-dimensional metallic conductor and a Pauli paramagnet.

VII. Chemistry of inorganic biomaterials

Natural ageing of biomaterials, the building elements of any living organism, shortens their lifetime. What is most surprising is that ageing problems are inherent in such strong, at first glance,
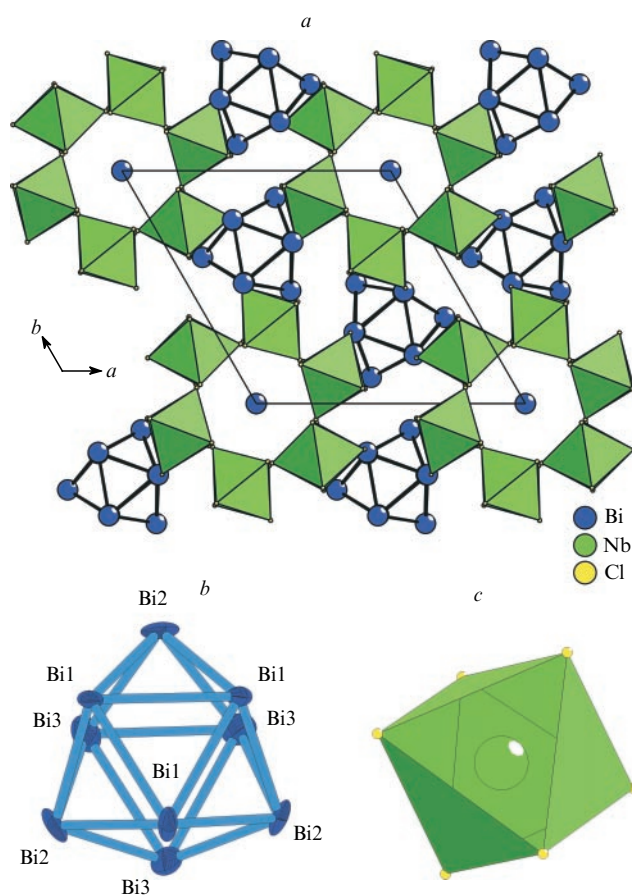

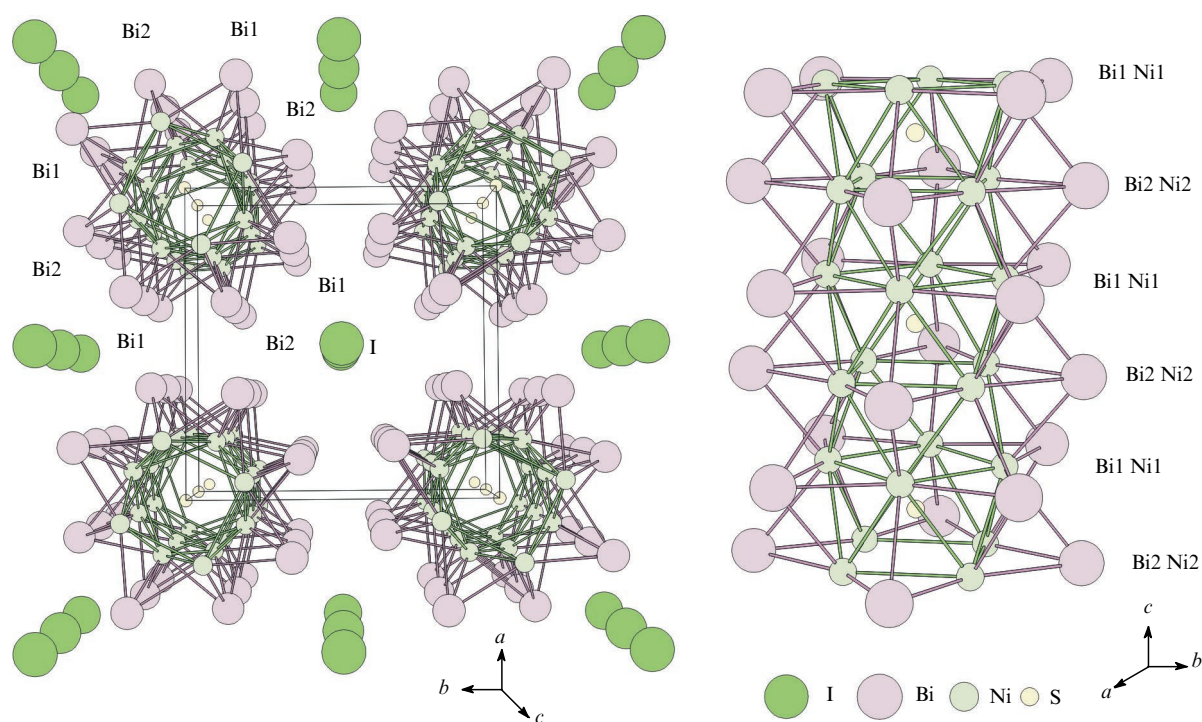**Figure 6.** A fragment of the crystal structure (*a*) and the main structural elements (*b, c*) of $Bi_{10}Nb_3Cl_{18}$.

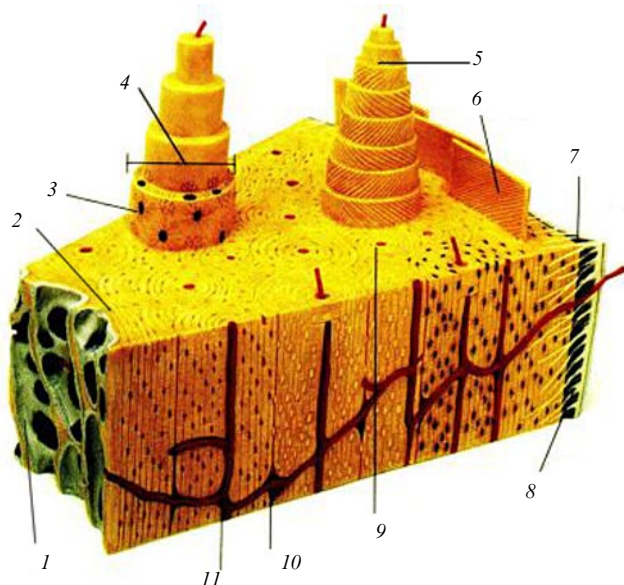**Figure 7.** The crystal structure of Ni_8Bi_8SI.

Figure 8. The levels of structural organisation of the bone tissue. (*1*) Internal bone tissue membrane, (*2*) intermediate plate, (*3*) osteocyte (bone cell), (*4*) osteon (Haversian system), (*5*) Haversian plate, (*6*) outer plate, (*7*) the Sharpie fibre, (*8*) peroosteum, (*9*) Haversian canal, (*10*) lacuna, (*11*) the Volkmann vessel.

Figure 9. A simplified representation of a unit cell of hydroxyapatite.

natural materials as bone and dental tissues. From the standpoint of materials science, the bone tissue is a composite material which comprises both inorganic and organic components,[54–57] *viz.*, hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (63 mass %) and the protein collagen (20 mass %), respectively (Fig. 8). In addition to Ca^{2+} and PO_4^{3-}, bone tissue contains appreciable amounts of Na^+, Mg^{2+}, K^+, Cl^-, F^- and CO_3^{2-} ions. The physicochemical character of the interactions between bone components, which ensures, in particular, its high strength properties, has not been finally established yet. Even the use of modern biotechnological approaches does not permit one to construct a full analogue of the natural bone tissue. Therefore, the use of artificial materials (implants) is still the only way to restore functioning of large regions of damaged bones.

Metal alloys based on low-toxic titanium are used in those cases where it is required to restore the bones of parts of the body exposed to heavy cyclic loads (*e.g.*, hip joints). In other cases, preference is given to ceramic or composite materials based on calcium phosphates; their chemical compositions are similar to that of bone.[54–58] Among other modern trends in the field of implant design, special mention should be made of 'regeneration', *viz.*, synthesis and application of materials able to stimulate regenerative processes in damaged tissues owing to their active interaction with the organism.[54] Such implants cannot be prepared without a thorough knowledge of mechanisms of reactions occurring in bone tissues in all steps of their evolution.

It is believed that not only the chemical composition, but also the morphology of synthetic hydroxyapatite (HAP) crystals are important characteristics that determine the response of the organism to the exogenous material of an implant. In this context, an ideal material should possess the chemical composition and granulometric properties similar to those of a bone biomineral, *e.g.*, non-stoichiometric hydroxyapatite, $Ca_{10-x}(HPO_4)_x$·$(PO_4)_{6-x}(OH)_{2-x}$ ($0 < x < 1$). Its crystals have the shapes of plates ($40 \times 20 \times 5$ nm) with an axis *c* lying in the crystal plane (sp.gr. $P6_3/m$ of the hexagonal system; $a = b = 9.432$ Å, $c = 6.881$ Å) (Fig. 9).[55]

Calcium phosphate-based ceramic materials prepared by high-temperature treatment are routinely used in clinical practice.[5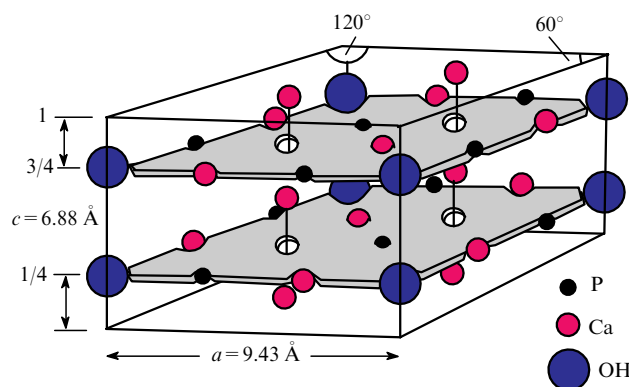9–62] Strong hydroxyapatite ceramic materials are chemically inert, which significantly decelerates the resorption of the material and inhibits the growth of the contact bone tissue. Large specific surfaces of calcium phosphates prepared by solution methods (up to 100 $m^2\,g^{-1}$) make them more reactive in comparison with their high-temperature counterparts (~ 1 $m^2\,g^{-1}$). The results of the use of calcium phosphate-containing cements and biphasic composite materials suggest that in some cases the use of materials that could serve as bioapatite 'sources' *in vivo* is a simpler and more efficient approach (Fig. 10).[54, 59, 61]

Large-scale production of materials strictly corresponding to calcium phosphates of biological origin as regards their chemical and structural characteristics is very problematic. Nevertheless, there is every reason to believe that chemical and morphological match of a biomaterial and a bone mineral is one of the basic principles in the design of novel materials for biomedical purposes. Deviations of the compositions and sizes of artificial crystals from those of their natural counterparts can be employed for the directional synthesis of biomaterials with predetermined bioactivities. The practical implementation of such a programme requires the elucidation of a quantitative relationship, first, between chemical composition and micromorphology of calcium phosphate crystals and parameters of their solution synthesis and, second, between micromorphological parameters and bioactivity of the material.

The existing methods for the synthesis of HAP enable the preparation of highly dispersed powders with particle shapes varying unpredictably in a rather broad range, *viz.*, from equiaxial to needle-shaped, depending on conditions.[55, 56, 63] Nevertheless, no explicit and quantitative information about the effects of parameters of HAP synthesis on the morphology of the target
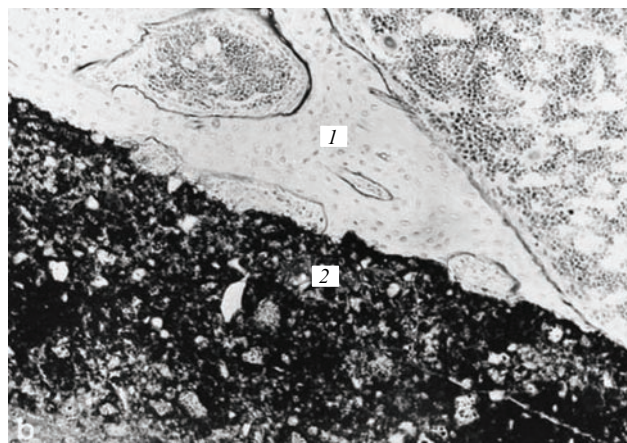

Figure 10. Formation of new bone tissue at the boundary of a cement implant with the composition 75% $Ca_3(PO_4)_2$ + 20% $Ca_4P_2O_9$ + 5% $CaHPO_4$.[62] (*1*) New tissue, (*2*) implant.
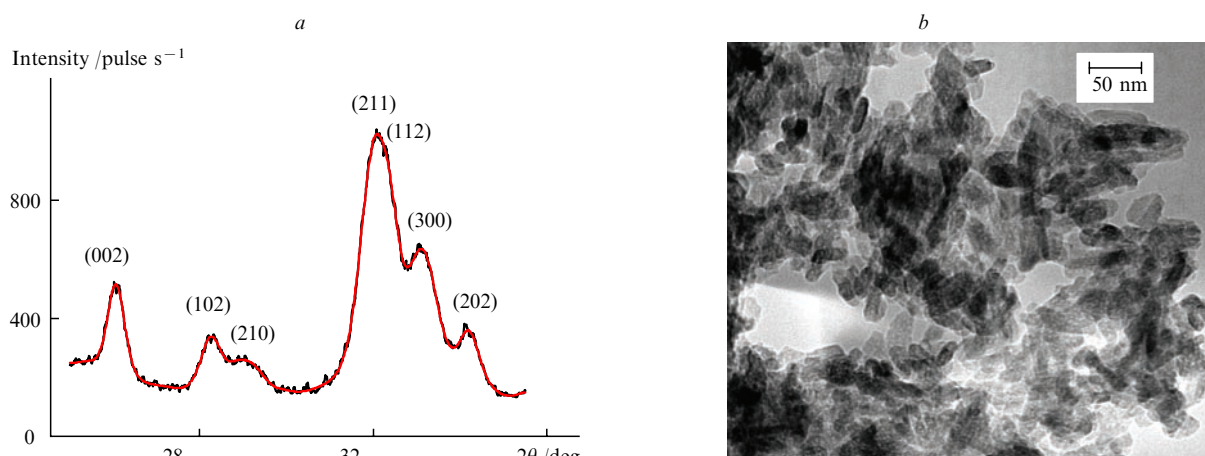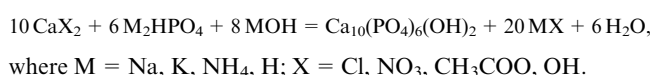
Figure 11. The results of studies of HAP powders using a multiprofile X-ray analysis (*a*) and transmission electron microscopy (*b*);[64] (*a*): crystal size 55×18 nm, the numbers in parentheses indicate Miller indexes.

product is available. It is noted that samples of calcium phosphate powders prepared according to one synthetic procedure elicit different responses of an organism up to a complete rejection of the material. This brings forth a vast variety of chemical and materials science-related problems connected with the synthesis of calcium phosphates with predetermined compositions and micro-morphological characteristics as well as with prediction of their bioactivities *in vitro* and development of methods for the bio-activity correction by chemical modification of the synthetic product.

In practice, synthesis of HAP is mainly carried out in aqueous solutions and the existing methods can be classified into three main groups: (1) precipitation in solutions with constant or variable composition; (2) hydrothermal synthesis and (3) hydrolysis of calcium phosphates.[55, 56, 58, 63, 64] Precipitation of HAP from aqueous alkaline solutions yields fine-crystalline calcium hydroxyapatite.

$$10 \, CaX_2 + 6 \, M_2HPO_4 + 8 \, MOH = Ca_{10}(PO_4)_6(OH)_2 + 20 \, MX + 6 \, H_2O,$$

where $M = Na, K, NH_4, H; X = Cl, NO_3, CH_3COO, OH$.

The formation of HAP is usually preceded by precipitation of amorphous calcium phosphate.[57, 65] The degree of crystallinity of the precipitated HAP increases with temperature and duration of ageing, while its non-stoichiometry, *i.e.*, the deviation of the Ca/P ratio from 1.67, increases with a decrease in pH, temperature and duration of synthesis.[55] The hydroxyapatite powders prepared by solution methods have a large specific surface (~ 100 m^2 g^{-1}) and a small size of crystallites ($\sim 100 - 200$ nm). The size and the habitus of crystals depend on a number of factors, such as duration of crystallisation, temperature, composition of solution, degree of supersaturation, ionic strength, pH, the order of addition and mixing rates of reactants.[55, 56, 58, 64] The diversity of morphology of HAP crystals can be attributed to the fact that the synthesis is performed under strictly non-equilibrium conditions; the shape of the crystals strongly depends on the presence of admixtures.[65–68] In the presence of carbonate ions in the solution, carbonate apatite crystals of type A $[Ca_{10}(PO_4)_6(OH)_{2-x}\cdot(CO_3)_{x/2}]$ or type B $[Ca_{10-x}Na_x(PO_4)_{6-x}(CO_3)_x(OH)_2]$ differing in shape (plates or needles) depending on the carbonate content are formed.

As was mentioned above, the micromorphology of HAP powders is an important property which largely determines the areas of application of calcium phosphate-based biomaterials. It is of note that the choice of experimental conditions for the synthesis of HAP crystals of predetermined morphology implies knowledge of the contribution of each parameter (factor) of synthesis to, and of the result of their mutual action (interaction of factors) on, the two characteristic sizes of anisotropic HAP crystals, *viz.*, along

and perpendicular to the axis [001]. This information, which has not been explicitly and quantitatively documented in the literature concerning the methods of apatite synthesis, is considered in a review.[64] A systematic study of effects of various parameters of HAP synthesis by precipitation from salt solutions (initial con-centration of reagents, pH and temperature) on the sizes and shapes of the crystals formed has been carried out. The morpho-logical characteristics of HAP crystals were established through mutual application of a comprehensive X-ray diffraction analysis and transmission electron microscopy (Fig. 11).

Mathematical models based on the results of statistical analysis of morphological characteristics of crystals allowed quantitation of various factors on HAP synthesis by precipitation. These factors (separately and in combination) determine ionic equilibria in solutions, since changes in temperature, pH and initial concentrations of solutes induce changes in the concen-trations of ionic forms as can be judged from the calculations on activities of ions and ion pairs. One can state that there is a tendency towards an increase in the size of HAP crystals as the activities of the ion associates of $CaPO_4^-$ and $CaOH^+$ in solutions increase. The formation of HAP occurs in two steps. Amorphous calcium phosphate is formed from ion associates with the compo-sition $Ca_9(PO_4)_6$ (the 'Pozner clusters') by a sol–gel transition mechanism in the first, relatively fast step. This has a mesoporous structure and hydroxyapatite nanocrystals formed in the second step by an AFC dissolution–HAP precipitation mechanism inherit porosity.[64, 65]

The use of hydrolytic reactions of calcium orthophosphates of the type

$$3 \, Ca_3(PO_4)_2 + H_2O = Ca_9HPO_4(PO_4)_5OH$$
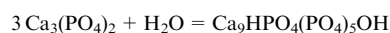
is yet another convenient approach to the synthesis of HAP crystals with different micromorphological features (needles, plates)[55, 63, 69, 70] (Fig. 12).

The sizes of HAP crystals obtained upon heating of solutions exceed significantly those synthesised by precipitation ($\sim 0.5 - 5$ μm and $\sim 20 - 100$ nm, respectively). It was noted above that materials with particles of submicrometric sizes are preferable for practical use. If HAP are prepared by hydrolysis of poorly soluble calcium orthophosphates [$CaHPO_4$, $CaHPO_4 \cdot 2 \, H_2O$, α- and β-$Ca_3(PO_4)_2$, $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5 \, H_2O$, $Ca_4(PO_4)_2O$], the composition of the solution can be considered as being quasi-equilibrium, this depending on the solubility product of the solid phase. Like the majority of hetero-genous processes, hydrolysis of calcium orthophosphates is char-acterised by a low rate, since the layer of the product formed blocks the surface of the starting material. The reaction can be accelerated by increasing the temperature and/or activating the
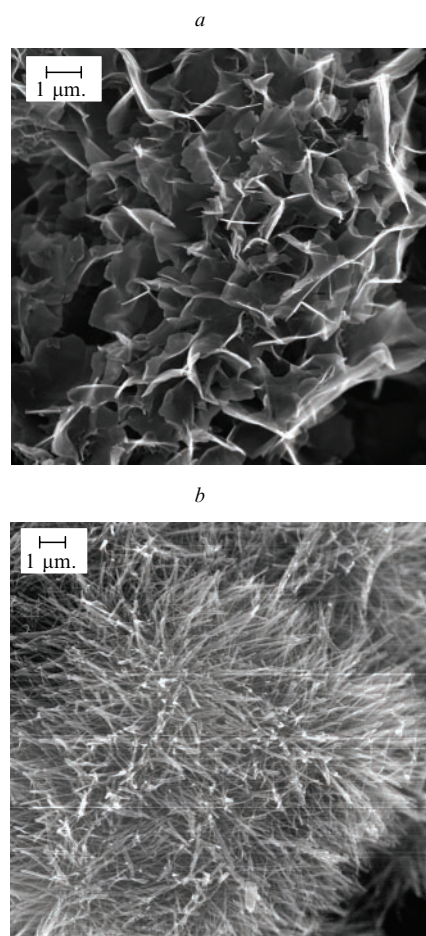
a

b

Figure 12. Micrographs of samples prepared by hydrolysis of α-Ca$_3$(PO$_4$)$_2$ at 40 (*a*) and at 100 °C (*b*).

reagent surface by sonication. It was shown that the conversion rate of a CaHPO$_4$ – Ca(OH)$_2$ mixture into HAP upon sonication of the suspension is 20% – 30% per 1 h, which is comparable with the rate of HAP synthesis from the same mixture at 60 °C. This is accompanied by the formation of aggregates consisting of spherical hydroxyapatite particles with a diameter of ∼ 100 – 300 nm.[64]

The biological activities of calcium phosphates can be increased by increasing the specific surfaces of the powders and decreasing the sizes of the crystallites as well as by changing the physicochemical characteristics of the surface. An alternative approach consists of chemical modification of calcium phosphates aimed at preparing materials able to undergo active resorption upon interaction with body fluids. In this context, special attention is given to the development of methods for the synthesis of carbonate-containing hydroxyapatite Ca$_{10-0.5x}$(PO$_4$)$_{6-x}$(CO$_3$)$_x$(OH)$_2$ as well as silicon-containing hydroxyapatite, Ca$_{10}$(PO$_4$)$_{6-x}$(SiO$_4$)$_x$(OH)$_{2-x}$.[64, 68] The latter can be synthesised by precipitation of HAP from solution using a reaction of amorphous calcium phosphate with tetraethoxysilane in an alkaline medium. It was found that silicon-containing HAP is more soluble in weakly acidic solutions than non-substituted hydroxyapatite.[64]

The very fact of design of materials stimulating osteogenesis suggests that the nearly half a century-old history of intense application of biomaterials has led to the comprehension that regeneration and replacement of bone tissue is an extremely complex and ambiguous problem. The use of one or another material depends on both the biomedical characteristics of a bone defect and, perhaps, the clinical case. Therefore, the solution of this problem is possible only if a broad range of biomaterials is available, while the choice of a maximum suitable material, which meets all the specific requirements, is the key to success.

VIII. Inorganic synthesis of functional materials using sonication, hydrothermal treatment and microwave irradiation

Inorganic synthesis of functional materials always requires the activation of the starting reactants whatever the mechanisms of chemical transformations involved. The simplest method is heating; its efficiency is estimated from the activation energy in the Arrhenius equation. However, this parameter, which is determined experimentally as a temperature coefficient of the reaction rate, has a physical meaning only if it is associated with a particular elementary process which limits the reaction rate in a given temperature range.

In real systems used in the synthesis of functional materials, chemical interactions involve at least two fundamental processes, *viz.*, the chemical reaction itself and transfer of a substance to the reaction zone. Since the latter occurs owing to diffusion and the diffusional mobility of components of the solid is determined by the imperfection of its structure, it can be expected that the defects influence substantially the conditions of the solid-phase synthesis. This in turn suggests that the rate and direction of chemical transformations can be controlled through physical actions, which occur either simultaneously with the thermal activation or separately. It is often recommended that high-temperature factors are excluded, since both the reactants and the reaction products may be subject to undesirable changes which include:

— dissociation of the solid-phase product of inorganic synthesis, *e.g.*, thermal dissociation of ferrites having a spinel structure according to the reaction:

$$6\,MFe_2O_4 \longrightarrow 4\,Fe_3O_4 + 6\,MO + O_2\,.$$
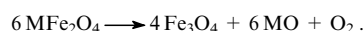
The magnetic and dielectric properties of the material are usually deteriorated by the reaction products;

— changes in the composition of reaction products due to the loss of volatile components, especially in gaseous media containing water vapour and CO$_2$. These changes are substantial, *e.g.*, in the synthesis of solid electrolytes based on alkali metal polyaluminates and lithium-containing ferrites.

The efficacy of sonication in reactions occurring in various reaction systems in the synthesis of materials[71, 72] depends on the phase state of a system. In liquid-phase systems (solutions, melts), cavitation, *i.e.*, the formation, oscillation and collapse of microvesicles, is the main result of sonication which leads to the formation of short-living hot zones with characteristic temperatures up to ∼ 5000 K and pressures up to 1000 atm. In some cases, 'collapse' of cavitation vesicles is accompanied by formation of intense microcurrents of fluids and potent shock waves, which enhance the mass transfer. As a consequence, in physicochemical systems (both homogenous and heterogenous) decomposition of volatile compounds, like metal carbonyls, acceleration of redox reactions, formation of stable emulsions and suspensions and disaggregation of particles in colloid solutions take place. Sonication of liquid-phase systems has proved to be efficient in classical reactions of organic and inorganic synthesis[73, 74] as well as in the synthesis of amorphous and crystalline metal, oxide and carbide nanopowders.[75, 76]

In solid-phase systems, sonication is efficient only if a certain power threshold of acoustic vibrations is exceeded concomitantly with a significant (by one or two orders of magnitude) increase in the number of dislocations and in the values of effective diffusion coefficients and the formation of new interphase contacts.[77, 78] As a consequence, sonication of reaction mixtures may change the reaction mechanism, decrease considerably the apparent activation energy and the temperature of vigorous interactions of the reactants.[79 – 81] Acoustic activation of solid-phase processes enables synthesis of various oxide materials[80, 81] and active forms of

precursors [82] and, in some special cases, directed modulation of the structure-dependent properties of solid-phase products.[83]

It has been found [83] that the concentration of structural defects in sonicated compounds depends non-linearly on the amplitude of input acoustic vibrations and the temperature. The defectiveness of samples increases significantly (by more than one order of magnitude), in a definite temperature interval and at a definite ultrasound volume, *i.e.*, the acoustic and thermal effects are synergistic.

At fixed temperatures, a significant (2–3-fold) increase in effective diffusion coefficients of carbon in steels is observed only at definite acoustic input vibration amplitudes.[84] Similarly, at fixed ultrasound volume the defectiveness of simple metal oxides increases anomalously, however, only in a narrow temperature range.[85] It is of note that the temperature range corresponding to the maximum activation is determined by the chemical nature of the oxides that undergo sonication. Thus it has been shown that in high-temperature sonication of iron(III) oxide ultrasonic generation and annihilation of defects and their thermal annealing compete.[85] The rates of each of these processes depend differently on temperature; therefore, the defectiveness of α-Fe_2O_3 and the corresponding reactivity change non-linearly reaching a maximum at ~ 800 °C.

Combination of different factors allows one to change both the kinetics and the mechanisms of solid-phase reactions. Studies of interactions in the system $Fe_2O_3 + Li_2CO_3$ have shown [79] that superposition of an acoustic field at definite temperatures induces changes in the reaction mechanism, *viz.*, the chemical interaction at the interphase becomes a limiting step, whereas under normal conditions this reaction is limited by the formation of nuclei and their progressive diffusion-dependent growth. In turn, the reaction rate increases significantly with a change in the reaction mechanism and an increase in the mass transfer rate. It is noteworthy that in this case the temperature, which corresponds to the maximum effect of the ultrasound, is lower than the temperature of the onset of the reaction in the system under ordinary conditions, *i.e.*, sonication allows one to reduce significantly (by 100–150 °C) the temperature of synthesis. Studies of solid-phase reactions of ferrite formation

$$LiFeO_2 + 2\,Fe_2O_3 \xrightarrow{530-650\,°C} LiFe_5O_8\,,$$

$$ZnO + Fe_2O_3 \xrightarrow{600-800\,°C} ZnFe_2O_4\,,$$

$$NiO + Fe_2O_3 \xrightarrow{600-800\,°C} NiFe_2O_4$$
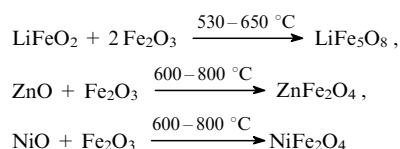
have shown [86, 87] that temperatures of the onset of the reaction decrease by 50–200 °C in the case of sonication, while the time of synthesis of monophasic ferrites diminishes 1.5–2-fold. A change in the reaction mechanism is due to a direct formation of the reaction zone in the acoustic field; its most characteristic feature is the presence of a well-defined initial step of a sonochemical reaction mediated by a special mechanism of formation of intercrystallite contacts in the ultrasonic field.

Of special interest are studies of effects of sonication on hydrothermal synthesis of simple and complex oxides and chalcogenides.[88] First of all, it has been established [89] that sonication causes cavitation both in hydrothermal solutions and ordinary liquid media the intensity of which at 250 °C is 70%–80% of that observed at 25 °C. Cobalt, titanium and zirconium oxides as well as ferrites $Ni_{1-x}Zn_xFe_2O_4$ were used as subjects in these studies. Hydrothermal treatment and sonication of a suspension of an amorphous gel of $Co(OH)_2$ in water at 250 °C yielded the phase Co_3O_4; no such phase was formed without sonication. Most probably, sonolysis of water in hydrothermal solutions gives rise to hydrogen peroxide which induces the oxidation of Co(II) into Co(III). The particle sizes of the oxide products of hydrothermal synthesis in an ultrasonic field are significantly smaller than those of an analogous product synthesised without sonication (Fig. 13).
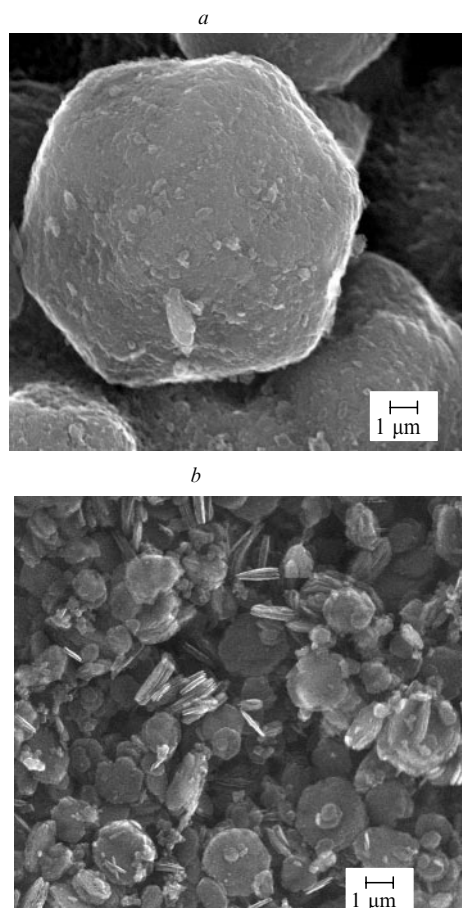
Figure 13. Micrographs of products of hydrothermal syntheses in the absence (*a*) and in the presence of an ultrasonic field (*b*).

Hydrothermal treatment of amorphous gels $ZrO_2 \cdot n\,H_2O$ and $TiO_2 \cdot n\,H_2O$ and simultaneous sonication result in a significant increase in the rates of their crystallisation, whereas sonication of products of hydrothermal synthesis favours the formation of thermodynamically more stable phases (Fig. 14).[90]

Although the idea of large-scale application of microwave heating for domestic and technological purposes was realised rather long ago [91] and numerous studies were undertaken in the past decade on the microwave-induced synthesis and sintering of functional materials,[92, 93] the physicochemical nature of the processes occurring in microwave synthesis still remains obscure. Oxides, hydroxides, salts or their mixtures were used as precursors for various functional materials including ferrites, manganites, cobaltites, nickelates and cuprates subject to microwave radiation.[94–96]

According to theoretical concepts on the interaction of microwave radiation with matter,[97] effective absorption of energy requires the presence in the matter of either dipoles capable of changing their orientation and rotating under the action of microwave radiation, or free charge carriers able to move in an applied microwave field. Many inorganic salts possess low electronic, hole or ionic conductivities. At the same time, water molecules, which are present in the crystal lattices of crystal hydrates, and some anions have high dipole moments. Thus, in the majority of salt systems the most probable mechanism of absorption of microwave radiation is related to dipoles.

It has been found experimentally [94] that compounds devoid of chemically bound water (carbonates, nitrates and oxalates of alkali and alkaline-earth elements) virtually do not adsorb microwave radiation. In contrast, crystal hydrates of inorganic salts interact with a microwave field, the mode of this interaction being
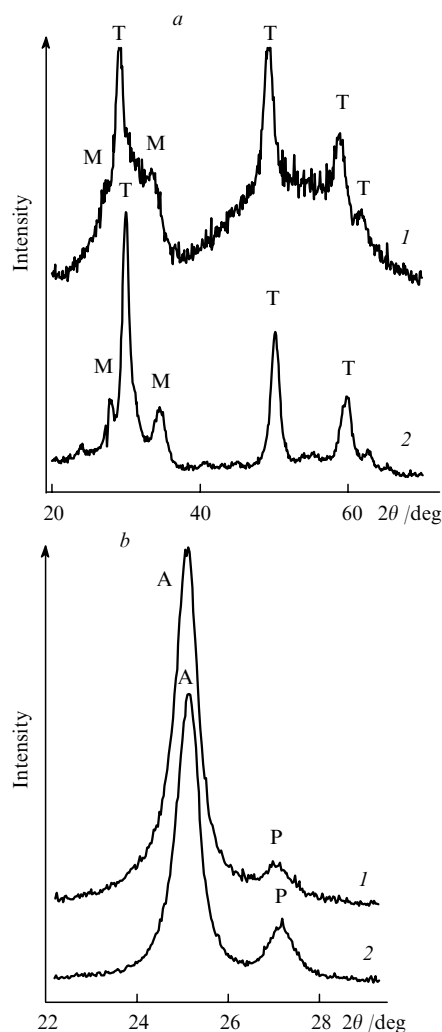
Figure 14. X-ray diffraction spectra of products of hydrothermal treatment of $ZrO_2 \cdot n\,H_2O$ (*a*) and $TiO_2 \cdot n\,H_2O$ (*b*) performed at 250 °C for 3 hours without (*1*) and with (*2*) sonication.
Designations: T, tetragonal phase of ZrO_2; M, monoclinic phase of ZrO_2; A, anatase; P, rutile.

Figure 15. Interaction of crystal hydrates with microwave radiation. *P*, energy of a microwave field.

dependent on the chemical nature of the cations (Fig. 15). Later, it was shown that the decomposition of crystal hydrates in the microwave field to oxides takes place only if the oxide formation occurs prior to the removal of all the water present in the system. Of all the salt crystal hydrates tested in this study,[94] only 3d-metal nitrate crystal hydrates meet this requirement and can be used as active (with respect to microwave radiation) components in the synthesis of complex oxide phases. A generalised scheme of interaction of metal salt crystal hydrates with microwave radiation is shown in Fig. 16. Studies of salt precursors have demonstrated the expediency of *in situ* application of microwave treatment of salt mixtures in solid-phase reactions, since highly dispersed oxide particles formed upon decomposition of salt mixtures and distributed uniformly throughout the reaction bulk react actively with one another.

Specific 'non-thermal' effects of microwave radiation caused by generation of ionic currents on intercrystallite and interaggregate boundaries make a significant contribution to diffusional processes occurring in the solid-phase reactions; the intensity of ionic currents increases in highly dispersed systems. Consequently, microwave irradiation of a reaction mixture can be accompanied by an increase in the rate and a decrease in the
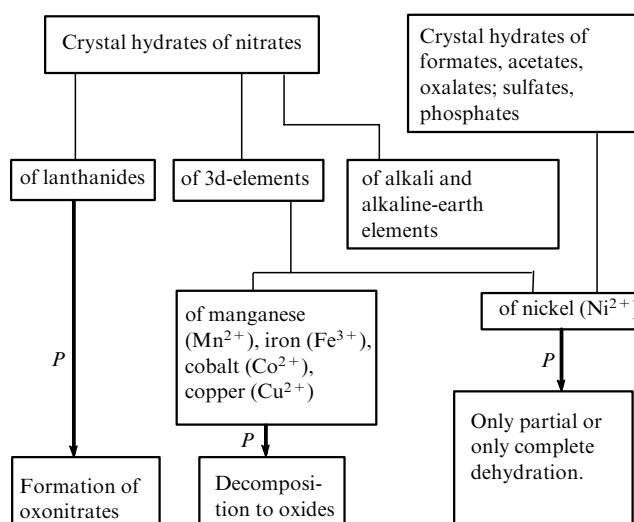
temperature of solid-phase interactions. It is this effect that is observed in synthesis of functional materials.[98–105]

However, it would be erroneous to think that microwave-induced synthesis always makes use of salt precursors able to convert microwave energy into thermal energy starting from room temperature. It is known that the energy (*P*) absorbed by an object placed into a uniform microwave field is expressed by the equation:

$$P = 2\pi f \varepsilon_0 \, K \tan\delta \, |E|^2,$$

where *f* is the microwave frequency, ε_0 is the vacuum permittivity, *K* is the dielectric constant of the sample, $\tan\delta$ is the dielectric loss tangent and *E* is the microwave field intensity in the sample under assay. The *K* and δ values depend on temperature and on the nature of the phases used as precursors. For example, the mixture $SrCO_3 - Co(NO_3)_2 \cdot 6\,H_2O - Fe_2O_3$ used in the synthesis of $SrFeCo_{0.5}O_y$, a promising electron-ionic conductor, can absorb low-wavelength energy only in those cases where microwave irradiation is preceded by ordinary heating as a result of which the oxidative thermolysis of cobalt nitrate yields Co_3O_4. The latter effectively absorbs microwave energy and favours rapid heating of the entire reaction mixture to temperatures above 1000 °C, although other components of the reaction mixture ($SrCO_3$, Fe_2O_3) are inert in the microwave field and are thermally activated only upon interaction with Co_2O_3.[106]

Non-stoichiometric oxides of the type TiO_{2-x} or Ta_2O_{5-x},[107] hydroxides or basic salts[95] as well as amorphous carbon used as soot[108] or a highly dispersed metal[109] can be used as active components for microwave irradiation. In the manufacture of compact piezoelectric ceramic materials of the type $(Ba,Sr)TiO_3$ (see Ref. 110) or ion-conducting ceramic materials of the type Na-β-alumina,[111] the powdered precursor with the identical composition is synthesised by ordinary heating, whereas sintering is performed in a microwave field.

And, finally, the use of the so-called monomodal microwave heating[112, 113] based on the propagation of an electromagnetic beam from a magnetron along a waveguide where a standing wave is established opens up radically new opportunities for inorganic synthesis, for it allows one to focus the microwave energy in a small volume of the reaction mixture and to initiate very rapidly chemical and structural transformations that are impossible in the case of ordinary thermal or multimodal microwave heating.
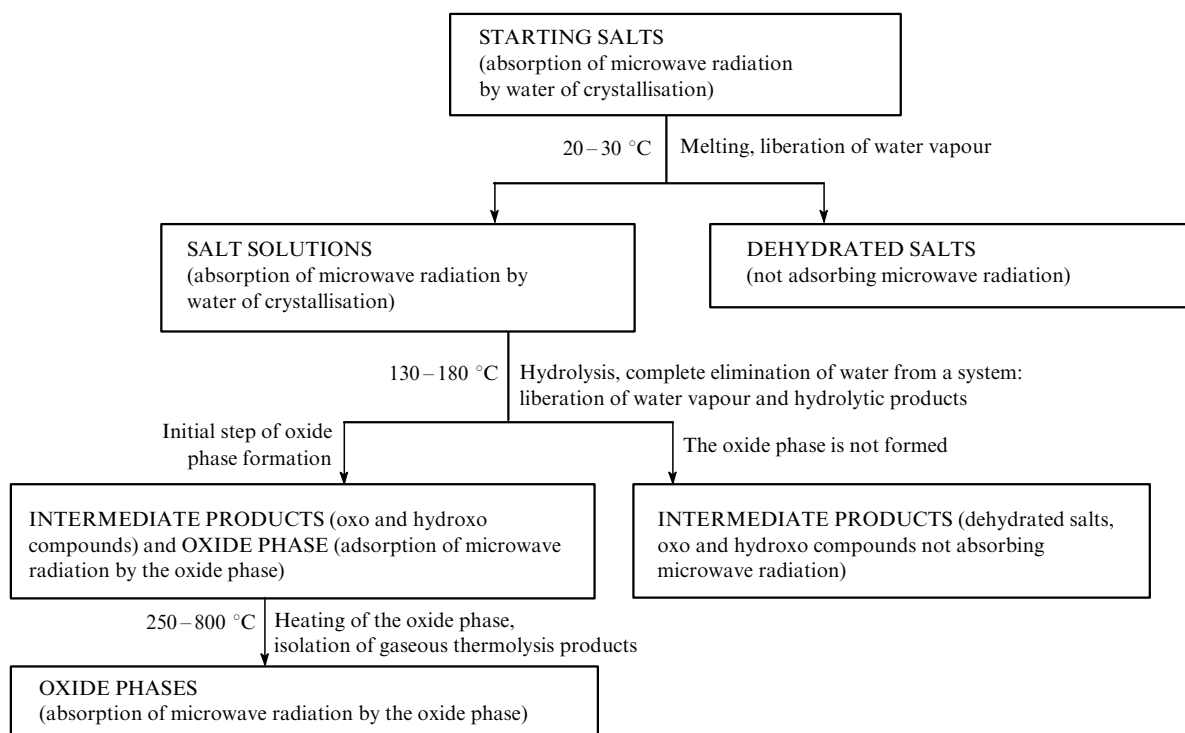
```
                           ┌────────────────────────────────────┐
                           │ STARTING SALTS                     │
                           │ (absorption of microwave radiation │
                           │ by water of crystallisation)       │
                           └────────────────────────────────────┘
```

20 – 30 °C | Melting, liberation of water vapour

```
┌────────────────────────────────────┐      ┌────────────────────────────────────┐
│ SALT SOLUTIONS                     │      │ DEHYDRATED SALTS                   │
│ (absorption of microwave radiation by│    │ (not adsorbing microwave radiation)│
│ water of crystallisation)          │      │                                    │
└────────────────────────────────────┘      └────────────────────────────────────┘
```

130 – 180 °C | Hydrolysis, complete elimination of water from a system:
liberation of water vapour and hydrolytic products

Initial step of oxide phase formation

The oxide phase is not formed

```
┌────────────────────────────────────┐      ┌────────────────────────────────────┐
│ INTERMEDIATE PRODUCTS (oxo and     │      │ INTERMEDIATE PRODUCTS (dehydrated  │
│ hydroxo compounds) and OXIDE PHASE │      │ salts, oxo and hydroxo compounds   │
│ (adsorption of microwave radiation │      │ not absorbing microwave radiation) │
│ by the oxide phase)                │      │                                    │
└────────────────────────────────────┘      └────────────────────────────────────┘
```

250 – 800 °C | Heating of the oxide phase, isolation of gaseous thermolysis products

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┌────────────────────────────────────┐
│ OXIDE PHASES                       │
│ (absorption of microwave radiation │
│ by the oxide phase)                │
└────────────────────────────────────┘
```

Figure 16. A scheme of the interaction of metal salt crystal hydrates with microwave radiation.

IX. Conclusion

In the past two decades, inorganic chemistry has experienced impressive changes owing to its integration with physical chemistry, physics of solids, organic chemistry and biochemistry and the use of advanced instrumental methods. The range of subjects of inorganic chemistry has been extended considerably. Now, these encompass not only chemical compounds, but also materials, sometimes even those which contain, along with an inorganic component, organic, polymeric or biopolymeric fragments. At present, studies of the majority of subjects are carried out at several levels. In addition to crystal or molecular structures, they involve electronic and magnetic structures of various compounds, specific defects of their crystal structures, distribution of microadmixtures, structures of interfaces in multicrystalline compounds, nanostructures, micro- and mesopore structures and surface structures as well as the effects of the aforementioned organisational levels of a substance on its properties. Special mention should be made of the unusual extension of the range of the impact of different kinds of energy on substances aimed at determining their limit characteristics and the development of methods for the construction of novel materials.

The spectrum of problems considered in this review does not encompass all the trends in inorganic chemistry related to the design of novel functional materials. For example, the problem of organisation of the reaction zone in the synthesis of materials considered in the review [7] was mentioned only briefly. Neither was the problem of the development of microcomposite materials based on superconducting cuprates [114] discussed in proper detail. In addition to the functional inorganic materials considered in the present review, the subjects under study at the Division of Inorganic Chemistry of the Department of Chemistry and the Department of Materials Science of MSU include:

— inorganic structures as materials for gas sensors;[†]
— barrier materials based on $BaMO_3$ (M = Zr, Hf, Th, Ce, Ti);[116, 117]
— luminescent nanocomposites based on $A^{IV}B^{VI}$;[118, 119]
— low-dimensional structures and superlattices;[120, 121]
— new generations of semiconductors and semiconductor heterostructures;[122 – 124]
— oxygen-conducting membranes and solid electrolytes;[125, 126]
— materials for lithium current sources;[127 – 129]
— magnetic nanocomposites based on glassy matrices;[130]
— photonic crystals;[131]
— ceramic pigments based on hydroxyapatites containing copper ions in an unusual linear coordination.[132]

It should be mentioned in conclusion that other promising trends of research related primarily to the development of molecular electronics,[133] spintronics [134] and biocrystal systems [135] require active participation of inorganic chemists. Taking into account the extreme dynamism shown by the scientific community towards the design of novel functional materials, it has become necessary to follow closely the new trends in this field which are especially successfully documented in journals such as 'MRS Bulletin', 'Advanced Materials', 'Materials Today' and 'Materials Chemistry'. Unfortunately, no domestic analogues are available so far.

† A review devoted to this subject [115] will be published in the next issue of 'Russian Chemical Reviews'.

Drs A V Lukashin, A G Veresov, A R Kaul and E A Goodilin are especially highly appreciated.

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