JOURNAL OF Materials CHEMISTRY Feature Article

Recent progress in cryochemical synthesis of oxide materials

Yuri D. Tretyakov and Oleg A. Shlyakhtin

Department of Chemistry, Moscow State University, 119899 Moscow, Russia

Received 21st April 1998, Accepted 1st July 1998

Recently conventional cryochemical processes have been complemented by cryoextraction, cryoprecipitation, cryoimpregnation and freeze casting techniques. Considerably more attention is being paid to colloidal solution processing and the application of sol–gel procedures like ion exchange treatment and hydrolysis of organometallic compounds. New preparation methods for nanopowders of various oxides and metals have been developed while further treatment of cryochemical powders using powder engineering techniques allows the powder grain size to vary from 0.2 to 5–6 µm. Cryochemical methods are also suitable for preparation of various porous media, like porous silica or cryogels with surface areas close to those of aerogels, and for the synthesis of HTSC powders for different applications. Fundamental and applied aspects of cryochemical processing are discussed.

Traditions

Various chemical routes using low temperatures as a substantial element of the process are considered as cryochemical methods. Unlike cryogenic studies in biology and pharmaceuticals where slow cooling rates are often applied, almost all the cryochemical methods are based on the fast cooling of solutions (freezing rates over 10 K s^{-1}) to prevent separate crystallization for most of the components involved; this is normally achieved by freezing in liquid nitrogen. Cryochemical techniques also involve the elimination of frozen water by physical (freeze-drying) or chemical means. While multicomponent oxide materials cannot be directly obtained from freeze-dried solution (except by suspension drying), further heat treatment is needed to convert salts into oxides. Special precautions are needed during thermal processing in order to maintain system homogeneity close to that of the initial frozen state.

In spite of the large number of cryochemical techniques developed for materials synthesis and processing over the last 30 years, the majority of over 500 works published in this field deal with the processing sequence (Fig. 1, solid arrows) proposed by Landsberg and Campbell in their first study on the freeze-drying synthesis of metal powders[1] and further developed by Johnson and Gallagher and their co-workers for oxides.[2,3] An initial single- or multicomponent true aqueous solution containing cations in the stoichiometric ratio required for the final material is sprayed into liquid nitrogen (or, less frequently, into CO_2-cooled hexane) by means of a pneumatic or ultrasonic nozzle under vigorous stirring. After evaporation of liquid N_2 (or filtering off hexane) frozen microdroplets in metal trays are placed on shelves precooled to $T = 220–230$ K and subjected to freeze-drying at $P = (3–10) \times 10^{-2}$ mbar. The partially dehydrated salt produced by freeze-drying is normally heated at various rates to complete oxide formation.[4]

An important and frequently used variation of this scheme is freeze-drying of gels and suspensions obtained by (co)deposition of components from an initial solution. Low-temperature dehydration is essential in this case to prevent pore coalescence and to keep the specific porous structure of the residue. This method is also used to process separately prepared oxide and hydroxide products and components.

The product of basic cryochemical processing is a fine voluminous powder with submicron-sized crystallites joined into strong aggregates (Fig. 2). Owing to the high initial homogeneity of freeze-dried salt precursors the formation of multicomponent oxide phases, especially the first members of homologous series, normally takes place during the course of thermal decomposition, or, sometimes, a small additional heat treatment is needed. The various applications of these powders are based on the earlier formation of poorly synthesized compounds, the small size of the crystallites resulted in the advanced sinterability of these powders to give specific and stable microstructures with a large volume of different pores suitable for catalyst and support applications.

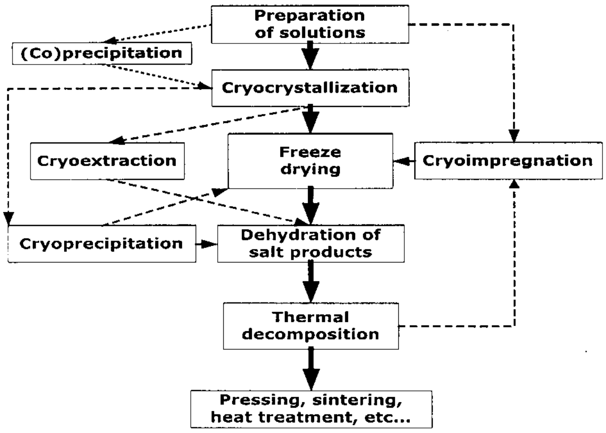

Fig. 1 Scheme of the main processes of cryochemical synthesis.

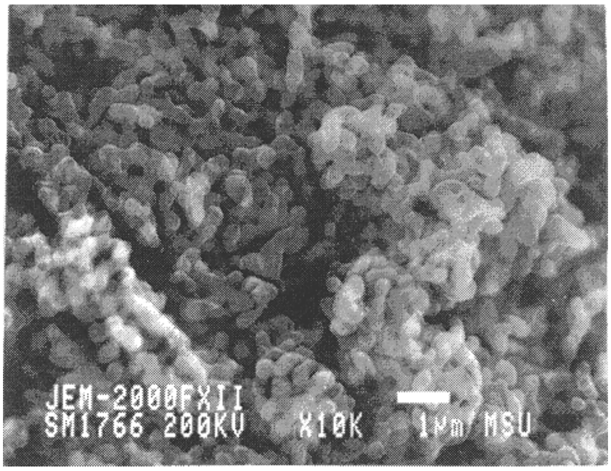

Fig. 2 Microstructure of oxide product of freeze-drying synthesis.

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†Basis of the presentation given at Materials Chemistry Discussion No. 1, 24–26 September 1998, ICMCB, University of Bordeaux, France.

A detailed physico-chemical description of the processes involved in cryochemical synthesis, as well as an extended overview of applications, is given in the recently published monograph[4] and will not be considered in the present paper. We would like to focus our attention on rarely used or recently discovered cryochemical procedures, as well as on recent applications of novel and traditional cryochemical methods in materials synthesis and processing.

Development

Progress in freeze-drying synthesis was substantially influenced by fundamental chemical studies of cryocrystallization and freeze-drying processes. It was demonstrated that transformation of homogeneous liquid solutions of most inorganic salts into freeze-dried solids cannot be considered as a physical process due to the large number of chemical transformations involved. For instance, many salts of rare earths and transition metals demonstrated outstanding resistance to crystallization when the ratio of salt to water corresponded to completed coordination shells of the cation and anion (the so-called boundary of complete hydration).[4] More generally, the behaviour of various inorganic salts during cryocrystallization has been found to depend on the coordination numbers of both the cation and the anion and on the stability of hydrated ions in solution. This dependence is especially important for multicomponent solutions when ions of different chemical nature are present simultaneously and demonstrate different crystallization behaviour.

Unlike biological and pharmaceutical solutions, homogeneity of frozen solutions of inorganic salts during freeze-drying is substantially affected by specific transformation of crystallohydrates at low temperatures and pressures. The evolution of these non-equilibrium and internally strained hydrate forms after completion of freeze-drying also differs from conventional hydration processes.[4,5] These processes occur within microcrystallites of freeze-dried salts, so that final changes in the homogeneity of the system are sometimes not substantial if the formation of the liquid phase is avoided.

The simple and attractive idea of conservation of the microstructure of the residue or gel by means of freeze-drying continuously finds new applications. Advancement of synthesis techniques results in the appearance of new gel and suspension preparation methods having various advantages over traditional deposition from aqueous solutions. The stage of hydrolysis of organometallic precursors makes some of them[6,7] closer to sol–gel processing while freeze-drying is believed to be crucial for attaining the final result. Thus, the remarkable softening of alumina aggregates can give the freeze-dried products of hydrolysis an advantage even over products of true $Al_2(SO_4)_3$ solution freeze-drying which demonstrated poorer densification during sintering.[7] The other new efficient methods used to prepare gel precursors for freeze-drying are hydrothermal synthesis[8] and electrochemical reduction of aqueous solutions.[9]

Non-aqueous solutions have not attracted much attention owing to the limited solubility of inorganic salts and modifications needed to the freeze-drying equipment. An interesting example of their successful application in materials synthesis concerns utilization of liquid ammonia as a solvent for nitrate, acetate and perchlorates followed by freeze-drying of multicomponent solutions either at 179 K and normal pressure or at $P = 150$ mbar without additional refrigeration.[10] Nevertheless, the observed rate of target $YBa_2Cu_3O_x$ phase formation was less than for freeze-dried aqueous solutions, probably owing to local melting during thermal decomposition.

Aqueous solutions of nitrates and chlorides of many multicharged cations like Zr^{4+}, Ti^{4+}, Fe^{3+} are substantially hydrolyzed, which means the appearance of significant amounts of free HNO_3 or HCl in the system:

$$MeCl_n + mH_2O \rightarrow Me(OH)_mCl_{n-m} + mHCl$$

These acids form eutectic mixtures with ice, with rather low melting temperatures (190–210 K); freeze-drying of solutions containing such mixtures is accompanied by low-temperature sintering (collapse) of the salt framework during drying. Increasing the pH of the initial solution over threshold values results in the formation of often undesirable gels and residues. One way out of this situation concerns the application of strong complexing agents which strongly influence the equilibrium conditions of residue formation. Most of these complexes have no low-temperature eutectics and can be easily subjected to freeze-drying.[11,12]

Another way is based on the fact that the formation of the residue is the final stage of hydroxopolymerization process in hydrolyzed solutions far below threshold pH values:

$$x[Me(OH)_m]^{(n-m)+} = [Me(OH)_y]_x^{(n-y)x+} + (m-y)xOH^-$$

The character and rate of hydroxopolymerization is influenced by the pH and, mostly, by the ionic strength of the solution. When the ionic strength is kept low enough, further hydroxopolymerization occurs in colloidal particles until their coagulation at much higher pH values. This transformation may be carried out by anion exchange treatment of acid solution with OH^- to form an anionite resin:

$$An\text{-}OH + NO_3^- \rightarrow An\text{-}NO_3 + OH^-$$

$$OH^- + H^+ \rightarrow H_2O$$

when the increasing pH is accompanied by reducing the total ionic strength of the solution.[4] This process is equivalent to the continuous conversion of the initial MeX_a salt ($X = Cl^-$, NO_3^-) into hydroxide $Me(OH)_a$ *via* the formation of an intermediate colloidal hydroxy salt $Me(OH)_aX_{n-a}$.

Application of such a solution in freeze-drying synthesis has some additional advantages. The first deals with the reduced hygroscopicity of freeze-drying products which is essential for many chlorides and nitrates. Another advantage is the possibility to change the properties of the oxide product systematically. This can be illustrated by the various crystallization temperatures (Fig. 3) and thermal stabilities of Fe_2O_3 particles obtained from $Fe(NO_3)_3$ solution by anionite treatment at different pH values.[13] A similar tendency of increasing crystallization temperature for greater exchange values is also observed for aluminium nitrate where it resulted in crystalliz-

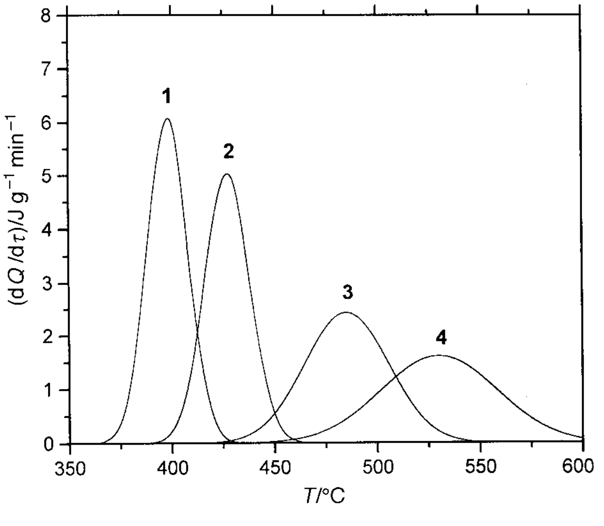

Fig. 3 DSC curves of heat evolution during crystallization of Fe_2O_3 from amorphous products obtained by freeze-drying of anionite processed $Fe(NO_3)_3$ solutions with pH = (1) 2.0; (2) 2.5; (3) 3.0; (4) 4.0.[13]

ation of γ-Al_2O_3 at temperatures as high as 800 °C.[14] Recent analysis of anionite treatment efficiency for various multicharged cations demonstrated the possibility to use a 'charge to ionic radius' criterion for preliminary estimates: all cations successfully used to date in this way (Zr^{4+}, Ti^{4+}, Fe^{3+}, Cr^{3+}, Al^{3+}, Be^{2+}) have this ratio in the range $4.6 < R < 5.6$ e A^{-1}.[16,17] Further extension of this range can be achieved by the application of other processing techniques, including cationite exchange treatment which was recently developed for doped SnO_2 synthesis.

The cryoextraction technique has been developed as an alternative to freeze-drying in order to reduce the duration of ice removal from frozen droplets—the main drawback of freeze-drying processes. Cryogranules, obtained by cryocrystallization of the initial solution, are placed into the low-temperature thermostat with an organic solvent precooled to temperatures below the melting point of the cryogranules (230–240 K). Dissolution of ice proceeds under intensive stirring while the salt framework remains almost unchanged; the resulting salt product is separated from the solvent by filtering. The normal duration of the process is 2–4 hours, which is 10–20 times faster than freeze-drying.

Systematic studies of these processes (see ref. 4 and refs. therein) demonstrated that the efficiency of application of various organic solvents in cryoextraction is determined by both thermodynamic and kinetic factors. The capacity of the solvent, *i.e.* the maximum amount of water that can be absorbed by the solvent at a given temperature, is determined by the position of the boundary between the 'solution' and 'ice + solution' fields in the low-temperature part of the water(ice)–solvent phase diagram (point C, Fig. 4 and Table 1); the maximum capacity corresponds to the lowest solvent content at point C. Freezing temperatures for most of the widely used solvents are low enough to be used in these processes, so this factor is usually not the limiting one. More essential are the different diffusion coefficients (Table 1) because liquid phase diffusion of water from the extraction area is often the limiting stage of the complex cryoextraction process. This last feature makes clear the need for intensive stirring of the solvent throughout the process. Comparison of different solvents by the sum of these factors allows them to be placed in the following order of efficiency: methanol $\gg$ acetone > ethanol > ethoxyethanol > isopropanol > propanol.

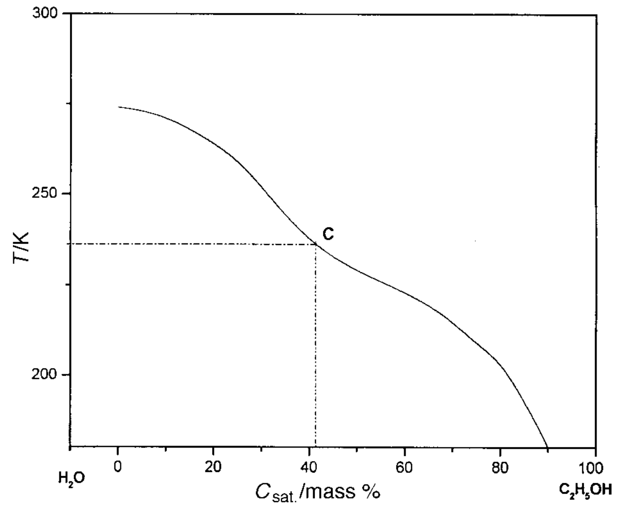

Fig. 4 A fragment of the T–x phase diagram of the ethanol–water system.

Another unusual but much more promising technique of cryochemical processing is cryoprecipitation. Based on low-temperature (230–250 K) treatment of frozen granules in a precooled solution of the precipitant, this method has advantages over both room-temperature precipitation and cryoextraction processes. Unlike the first technique, slow layer-by-layer dissolution of droplets allows greater supersaturation values to be achieved and prevents the redistribution of components during precipitation. An additional advantage of low-temperature processing is the smaller difference of solubility products and precipitation rates for chemically different components. In contrast to cryoextraction, the solubility of precursor salts in water–solvent mixtures is necessary and desirable here to accelerate precipitation. Moreover, the ability of solvents to dissolve inorganic substances is essential in order to ensure higher concentrations of inorganic precipitants.

The selection of precipitants is similar to the conventional coprecipitation method—hydroxides, carbonates, oxalates of alkali metals and ammonia, oxalic acid—except for some limitations for aqueous solutions, concerning their freezing temperatures. Nevertheless, aqueous ammonia remains one of the most popular cryoprecipitating agents for many systems.[4] The application of alcohol solutions of precipitants (ammonium oxalate or oxalic acid) provides more complete precipitation and a broader range of processing temperatures. The mechanism of the process varies from control by the chemical reaction at the boundary of the solid and liquid phases to diffusion control depending on the salt system, precipitant and solvent.

One of the interesting phenomena discovered during studies of cryoextraction processes is so-called 'liquid phase dehydration'. Treatment of $CoSO_4 \cdot 6H_2O$ in absolute ethanol resulted in complete dissolution of the salt followed by precipitation of $CoSO_4 \cdot H_2O$ some 15–120 minutes later. This phenomenon, based on the anomalous stability of some complex ions of the $[Me(ROH)_a(H_2O)_{6-n}]^{2+}$ series, seems to be rather general; formation of metastable solutions was observed also for sulfates of some other transition metals (Cu, Ni, Mn) and for other lower alcohols.[4]

Most current applications of the cryoprecipitation technique are not specific for this method, although definite advantages can be demonstrated when components of the material are poorly compatible in solution or are unsuitable for direct freeze-drying. At the same time the absence of aggregation and the low decomposition temperature of the cryoprecipitation product allowed the formation of silver metal nanoparticles[16] used to produce Ag–CdO composite electrical contacts with excellent wear resistance. Even in the case of chemically compatible components, the application of cryoprecipitation led to substantial acceleration of the solid state synthesis of $Bi_2Sr_2CaCu_2O_x$.[17]

Table 1 Some properties of organic solvents relevant to their ability to be used in cryoextraction processes

Solvent	Freezing temperature/K	Equilibrium composition (C) of liquid phase (wt.% of solvent) $T = 243$ K	$T = 233$ K	Diffusion coefficient of water molecules in extractant $D_{H_2O}/10^6$ cm^2 s^{-1} ($T = 248$ K)
Methanol	175.2	33.0	40.0	4.0 ± 1.2
Acetone	178.4	71.0	87.0	2.1 ± 0.9
Ethanol	161.0	64.8	75.5	0.33 ± 0.11
Isopropanol	187.2	73.0	77.0	0.26 ± 0.11
Propanol	146.0	87.0	91.0	0.21 ± 0.11

Relatively small and continuous changes of microstructure during freeze-drying and further thermal treatment of hydroxides brought about a new method of powderless processing, freeze casting,[18] developed mostly for shaping porous SiO_2. During this process the slurry containing hydrated silica is moulded into shape and then freeze-dried, so that powder forming stage is avoided and the net-like shape of the mould is kept throughout the process.

Another non-traditional application of freeze-drying is cryoimpregnation, when soaking an oxide powder with a solution of another component is followed by freeze-drying and thermal treatment of the product. This method is especially useful for components that are poorly compatible in aqueous solution or when a minor component has to be distributed through the surface of the matrix phase. The most obvious application of this technique is supported catalyst preparation or introduction of sintering aids.

Along with solution-based cryochemical techniques new kinds of other materials processing methods were developed, where application of low temperatures is a necessary and substantial feature of the process. One such procedure is the pulsed-plasma channel method used to prepare nanoparticles of $YBa_2Cu_3O_x$.[19] Two electrodes, one made from $YBa_2Cu_3O_x$ ceramic, are immersed in liquid oxygen. Electrical pulses between electrodes generate a large number of spherical 20 nm sized $YBa_2Cu_3O_x$ particles quenched by the surrounding cooling agent. Application of liquid oxygen as cooling medium resulted in the appearance of superconductivity with $T_c > 77$ K in the as-quenched state. This method provides the unique possibility to prepare nanosized $YBa_2Cu_3O_x$ particles with undamaged crystalline structure.[19]

A new original method of cryoelectrophoretic deposition was recently developed for the preparation of high temperature superconductor (HTSC) coatings. Liquid nitrogen is used in this case, not only as a cooling agent to keep particles in the superconducting state but also as an electrophoresis medium. In contrast to conventional electrophoresis in organic solvents, much higher voltages (up to 11 kV) are applied to ensure reasonable process rates. Special precautions, like external cooling of the processing dewar and a small overpressure therein, allowed boiling of liquid N_2 and subsequent disturbances to be minimized. The strongly anisotropic character of HTSC particles makes possible their orientation by applying an additional weak magnetic field near the Ag electrode during deposition. This orientation is maintained during subsequent heat treatment of the obtained 30–80 μm thick $YBa_2Cu_3O_x$ films at 910 °C and resulted in considerable enhancement of their critical current density values.[20]

Applications

Owing to the growing interest in preparation of nanosized particles of various phases and compounds, some efforts have been made to apply cryochemical methods for these purposes. The large difference in specific molar volumes of a precursor salt and the oxide product of its thermal decomposition causes transformation of salt crystallites due to large internal strains. Unlike hydroxide precursors, where such a transformation is similar to continuous shrinkage of precursor particles, thermal decomposition of many salts is accompanied by decay of the salt crystallites into a porous oxide framework of almost the same size and shape as the initial crystallite (Fig. 5). The rate and direction of further evolution of this strained intermediate depend on various factors, especially on the following thermal treatment, causing rearrangement and sintering of the framework elements of 10–40 nanometers in size into larger aggregated particles of 50–300 nm in size[21] (Fig. 2). It is these sintered particles which are referred to as oxide products of freeze-drying synthesis in most preceding works.

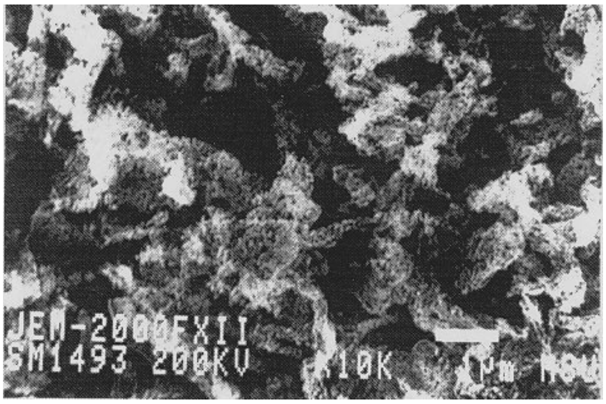

Fig. 5 Formation of the porous network during thermal decomposition of salt products of freeze-drying.

At the same time, careful selection of the thermal decomposition conditions allows the evolution process to stop at the stage of framework formation. High chemical homogeneity of cryochemical precursors and their porous, gas permeable microstructure substantially (50–200 °C) decrease the thermal decomposition temperature, leading, in turn, to better stability of the framework structures. Combination of these features with the ability to form multicomponent oxide compounds in the course of thermal decomposition makes thermal decomposition of cryochemical precursors a useful way to obtain aggregated, but definitely detectable, nanoparticles of $BaTiO_3$[22] and $LiFe_5O_8$.[23]

More intensive thermal treatment of decomposition products leads to the formation of larger but still submicron (100–150 nm) particles of $BaFe_{12}O_{19}$.[24] The low tendency to grain growth during heat treatment is inherent to freeze-dried products owing to their specific microstructure—a poorly connected network of more closely packed aggregates. Modification of this microstructure by thermal or mechanical means allows the grain size in powders and ceramics to vary from 0.2–0.3 to 5–6 μm.[25,26]

When the temperature of decomposition is low enough (~270 C), the formation of individual nanosized Fe_2O_3 particles can be observed.[27] Hydrogen reduction of these 3–5 nm aggregated spherical particles at 200 C leads to formation of ultrafine (6–18 nm) particles of metallic iron.[28] As mentioned above, nanoparticles of Ag with outstanding sinterability can be obtained directly by thermal decomposition of cryoprecipitation product.[16]

Similar particles of SiO_2 have been obtained in the course of a specially developed procedure of cryogel synthesis, considered as an alternative to aerogels used as supports for catalyst coatings. The specific area of the product obtained by hydrolysis of Na_2SiO_3 followed by freeze-drying reached 750 $m^2\ g^{-1}$ even without special precautions during water elimination.[29] Similar treatment of nickel doped alumina hydrogel results in lower (but still comparable with aerogels) surface area values (*ca.* 350 $m^2\ g^{-1}$) while the economic efficiency of this method is proved to be higher than supercritical drying of aerogels.[30]

One of the cryochemical techniques which is closest to industrial application is utilized in a study[31] where a way to prepare porous silicon on a standard Si wafer is proposed. Electrochemical etching of the substrate by HF followed by rinsing with water and freeze-drying allows the preparation of thick silicon film with porosity over 90% and good adhesion to the initial wafer. One of the substantial advantages of the proposed method is its full compatibility with existing Si technologies.

Similarly to pharmacy and biology, freeze-drying in materials synthesis can be applied to fix not only the microstructure of the powders but also unstable or unusual chemical states and compounds useful in materials synthesis. A good example is $Fe(OH)_3$, which could not be otherwise obtained in the solid state to study its crystallographic structure.[32] The newly discovered binary hydroxonitrate $LnCu_6NO_{11}$ is formed during the freeze-drying synthesis of $LnBa_2Cu_3O_x$-based materials from nitrate precursors.[33] Reducing the temperature of phase formation allowed the observation of new metastable, vacancy-ordered and catalytically active $La_{1-x}Sr_xCoO_3$ phases.[34] Interesting correlations between the microstructure and phase transitions were observed for TiO_2 where thermal evolution of the phase composition and microstructure strongly depended on the drying method of the Ti isopropoxide hydrolysis products. For the freeze-dried product, the undesirable transformation of catalytically active anatase to rutile proceeds at a temperature 170 °C higher than for the oven-dried hydrolysis product. The reason for such a behaviour seems to be connected with the later achievement of the critical nucleus size of rutile in voluminous, poorly packed products of freeze-drying.[35]

Cryochemical synthesis was used in the preparation of new materials with colossal magnetoresistance[36] and, especially, high-temperature superconductors (HTSCs). A large number (over 100 references[4]) of cryochemical synthesis applications over the last 10 years concern HTSC materials; some of them, where cryochemical methods were first applied to the synthesis of a specific phase or composition, are mentioned in Table 2. Along with the fast synthesis of good quality samples of new phases for studies of HTSC properties, freeze-drying synthesis is used for the preparation of HTSC powders,[17,25] composites,[40,46] ceramics,[39,41,47,48] thick films and tapes,[42–45] including materials with the highest values of HTSC parameters.[45]

Low-temperature techniques, especially freeze-drying, have been proved to be simple, easily accessible and useful laboratory tools for solving many problems of materials synthesis. These methods are especially effective for the preparation of a large number of materials (Fig. 6) where chemical homogeneity is essential for the functional properties of materials. New approaches to better homogeneity and reproducibility of their properties can be based upon the concept of deterministic chaos.[49] According to this theory, the properties of products are considered as fundamentally irreproducible due to the strongly non-equilibrium character of the synthesis processes and special chaos suppression algorithms should be applied during the development of processing techniques. Another promising direction for cryochemical methods development is based on the fundamental background created in the field of freeze-drying of polymers and organic compounds and aimed at the creation of hybrid organic–inorganic composites.

Table 2 First references for freeze-drying synthesis of various superconducting materials

Composition	Year of publication	Research group
$YBa_2Cu_3O_x$	1987	Johnson *et al.*[37] Shabatin *et al.*[38]
$RBa_2Cu_3O_x$ ($R = Eu$, Ho, Sm)	1987	Avdeev *et al.*[39]
$YBa_2Cu_3O_{7-x}$–Ag	1989	Elashkin *et al.*[40]
$YBa_2Cu_4O_8$	1991	Horn *et al.*[41]
$Bi_2Sr_2CaCu_2O_x$	1989	Shabatin *et al.*[17]
$(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$	1990	Dou *et al.*[42]
Pb-free $Bi_2Sr_2Ca_2Cu_3O_x$	1992	M'Hamdi and Lacour[43]
Bulk $(Bi, Pb)_2Sr_2Ca_2Cu_3O_x$ with $J_c > 10^5$ A cm^{-2} at $T = 77$ K	1995	Lelovic *et al.*[45]
$Bi_2Sr_2CaCu_2O_x$–$SrZrO_3$	1997	Pupysheva *et al.*[46]
$Tl_2Ba_2Ca_3Cu_4O_y$	1989	Zalishchansky *et al.*[47]
$HgBa_2Ca_2Cu_3O_{8+x}$	1995	Lee *et al.*[48]

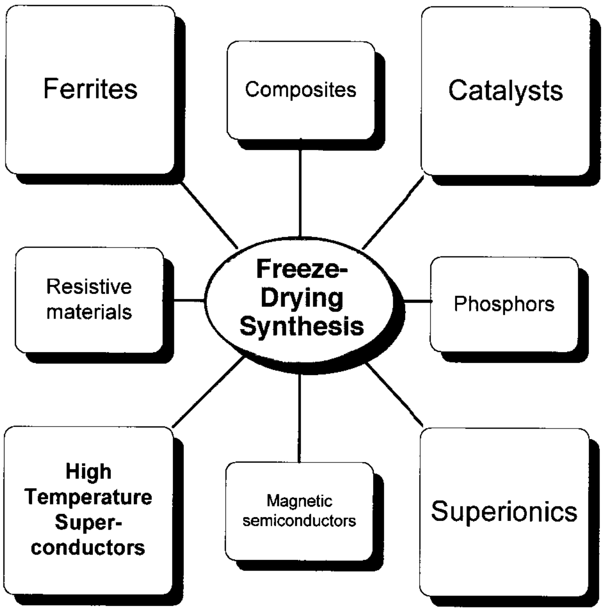

Fig. 6 Major classes of oxide materials obtained by freeze-drying synthesis.

The authors are grateful to Dr. Yu. G. Metlin and Prof. N. N. Oleynikov for their valuable comments and to V. V. Ischenko and A. L. Vinokurov for their kind help during manuscript preparation. The work is supported by the National Program of Russia 'Actual directions in the physics of condensed matter', Russian Foundation for Basic Research (Grant 96-03-33322a) and State Program 'Universities of Russia'.

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