Inorganic cryogels for energy saving and conversion

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Abstract Cryogels are usually obtained by freezing and thawing or freeze drying of gels and residues. Essential morphological features of the cryogels are bimodal pore size distribution, nanosize of the primary particles (crystallites) and their low agglomeration. Widely used for a decades in the polymer science and technology, cryogels find now a growing number of applications in the electroceramic materials. Freeze casting technique based on the freeze gelation effect is proved to be useful forming method in the production of complex-shaped SiO_2-containing electroceramics. Directed modification of the micromorphology by using solvent exchange schemes allows to obtain SiO_2 cryogel monoliths with density ≤ 0.05 g cm^{-3} and specific surface area 700–800 m^2 g^{-1} suitable for cryogenic thermal insulation of the superconducting devices. Excellent electrocatalytic activity of the macro/mesoporous PtRu/C cryogels in the methanol oxidation reaction makes them perspective anode materials of direct methanol fuel cells. Application of the cryogel-derived starting powders promoted substantial reduction of the sintering temperatures for a number of electroceramic materials. MnO_2- and V_2O_5-based cryogels are efficient cathode materials for secondary lithium batteries with specific capacity up to 300 mAh g^{-1}. Recent studies demonstrated also a feasibility of cryochem- ical approaches to the synthesis of complex oxide-based nanocrystalline electrode materials for electrochemical supercapacitors with high specific capacity at current densities up to 50 mA cm^{-2}.

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1 Introduction

Inorganic cryogels are one of the most successful products of the cryochemical (freeze drying) synthesis of inorganic materials [1] finding increasing number of applications last years. The term "cryogel" was first introduced in the medicine and widely used until now in order to denote sticky gelatinous fraction of the blood plasma formed during its slow cooling and usually associated with several specific kinds of diseases [2, 3]. Since 1980-th this term is widely used in the polymer chemistry for the products of processing of the polymer solutions at moderately low temperatures (freezing, thawing and freeze drying). In the most cases crystallization of the solvent during cooling causes expulsion of the remained solution, its concentration and, usually, its gelation, vitrification or crystallization. Careful removal of the crystallized solvents by freeze drying, or lyophilization, allows to retain the unique micromorphology caused by cryocrystallization and leaves very porous flexible polymer networks proved to be very suitable substrate for a large number of applications in the biopharmaceutical and food industry [4–6].

Soon after the discovery of freeze drying synthesis, based initially on the freeze drying of frozen aqueous solutions, several authors published their studies where

freeze dried precipitates were used successfully in the synthesis of various inorganic materials [7–9]. However, their intermediates were not initially considered as cryogels; this term was introduced into the inorganic materials science by D. Klvana and G. M. Pajonk who have published the first comparative studies of cryogels and aerogels [10, 11]. According to the currently used concept, inorganic cryogels is specific kind of freeze drying synthesis products obtained by low temperature processing of gels and residues containing significant amount of inorganic components. Further discussion will concern only part of these materials and their applications mostly related to the energy saving and conversion processes and will be based mostly on the papers published in 2004–2007. More detailed analysis of the various applications of freeze drying synthesis in 1965–2003 can be found in [1, 12, 13].

2 Formation and general features of the cryogels

Synthesis of cryogels can be considered as a branch both of sol–gel and of freeze drying synthesis methods. In the first case the wet gel or, sometimes, sol obtained in the course of wet chemical processing of the starting solution containing all components in the stoichiometric ratio is cooled down to T<250 K and freeze dried at $P=10^{-1}$–10^{-2} mbar. If wet chemical processing of the starting solution causes formation of residue, this process is rather related to the freeze drying synthesis though there is no distinct boundary between these two methods.

Apart from cryocrystallization of true solutions [1, 12, 13], freezing of cryogels is not usually accompanied by deep chemical transformations. The most of the solvents used in this synthesis, first of all water and *tert*-butanol, have very little tendency to supercooling. In this case cooling of the samples 5–10 °C below the freezing temperature of the solvents or below the eutectic temperature if the solvent contains significant amount of solute causes formation of ice crystals. A size and orientation of the last ones depend greatly on the freezing temperature, temperature gradients inside the sample and, to a lesser degree, on the presence and concentration of solutes. Slow crystallization in the large temperature gradient allows to create oriented ice crystal network that is widely used last years for the development of oriented porosity in ceramics. In the lack of gradients the orientation of ice crystals is stochastic; size of ice crystals is varied from several to several hundred micrometers. Application of other organic solvents having reasonable freezing points and vapor pressures at low temperature is often limited by the low solubility of inorganic components or precipitants, though application of non-traditional solvents in the biopharmaceutical freeze drying is growing last years [14].

Similarly to the processes in true solutions, intense cryocrystallization of solvent causes expulsion of remained gels and slurries into the space between growing crystals and results in their freeze concentration. Further development of this process in slurries results in complete crystallization of the solvent and formation of the soft micron-sized agglomerates of mechanically bonded primary nanoparticles in the thin layers between ice crystals. In the case of gels freeze concentration often induces sol–gel transition—poorly reversible freeze gelation process well known in the polymer science and technology [15]. In this case even after following thawing and removal of solvent the gels keep their integrity. Due to intensive polymerization of silica chains during freeze gelation this process is used in the freeze casting of complex-shaped silica-containing ceramics [16–20].

The final stage of cryogel synthesis is removal of the frozen solvent usually performed by its sublimation at reduced temperatures and pressures. Application of freeze drying causes minimum disturbance in the porous network formed by the frozen gel or by agglomerated particles around the ice crystal template. The products obtained using these procedures possess the following common features:

– nanosize of primary particles, remained intact during processing due to complicated grain growth at reduced temperatures;
– soft agglomeration of the primary particles and easy redispersibility of as-obtained products due to prevention of the interparticle neck formation (bridging);
– bimodal character of the porosity: large volume of the macro- and supermacropores left by sublimed ice crystals and considerable mesoporosity due to interparticle nanovoids inside the porous framework walls.

3 Application of cryogels

3.1 Synthesis of nanoparticles and nanoparticulate materials

Gels and residues are traditionally used for the synthesis of nanoparticles and related materials. One of the main problems during further development of nanomaterials synthesis methods deals with a lack of information on the particle formation and growth mechanisms. In many cases particle synthesis occurs in the liquid phase while a number of analysis methods demands dry powders or bulk samples. Freeze drying is proved to be rather useful for the isolation of reaction intermediates and final products during wet chemical synthesis of nanocrystalline zirconia [21, 22], titania [23–25], HfO_2-CeO_2 solid solutions [26] and formation and stabilization of hydroxyapatite particles [27, 28]. Similar

approach was used for the isolation of so called "Molecular Minerals"—cluster compounds with 0.5–2 nm ceramic fragments encapsulated with organic ligands that demonstrated a number of unusual luminescent properties [29].

Along with particle size and crystallinity, modification of the sol–gel synthesis conditions allows to change the particle shape, morphology and agglomeration, as it was shown during synthesis of nanocrystalline $LaAlO_3$ powder [30]. Another way to modify the mode of particle rearrangement deals with different tendency of particles to form interparticle bridges in the course of drying by different methods. Unique possibility of the freeze drying to prevent this process was experimentally confirmed during studies of morphological evolution of the nanocrystalline yttria particles: the powders obtained via freeze drying demonstrated not only the minimum grain size after the following processing of the powders at 1100°C, but also the best dilatometric sinterability due to the higher mobility of crystallites and easier spheroidization of agglomerates [31].

Application of freeze drying demonstrated also its efficiency in the investigation of magnetic nanomaterials. Increasing application of the ferrofluids (stabilized suspensions of ferro- or superparamagnetic particles) in the biology and medicine promoted considerable interest to the properties of superparamagnetic particles often obtained using sol–gel procedures. However, a number of instrumental investigation methods demand immobilization of these particles, for instance, in order to avoid Brownian relaxation in the liquid. This task is routinely solved by means of freeze drying of the frozen ferrofluids [32–35]. Another important magnetization issue investigated using freeze drying immobilization is the influence of aggregation and interparticle interactions on the properties of magnetic nanomaterials [36, 37].

In spite of the domination of oxide materials among the products of cryogel synthesis, several groups demonstrated successful freeze drying isolation and immobilization of the metal nanoparticles. Wet chemical reduction of noble metal salts in solution causes formation of the nanocrystalline metal particles. Immobilization of intermediate and final reaction products by freeze drying allows to study the mechanism and to control the process of nanoparticle formation in order to obtain desired size and morphology, for example, of the branched gold nanocrystals [38]. Similar approach allowed to obtain efficient unsupported nanocrystalline Pt/Rh, Pt/Ru/Rh and Pt/Au catalysts for the direct methanol fuel cells [39, 40].

Nanosize and, hence, rather large surface energy of metal particles is usually associated with rather moderate morphological stability due to their strong tendency to agglomeration and particle coarsening. One of the traditional ways to prevent bridging and grain growth at elevated temperatures is matrix isolation method when nanoparticles are isolated from each other by immersion to the inert matrix. Different thermal stability of alumina and platinum oxide allows to obtain Pt/Al_2O_3 nanocomposites retaining nanosize of Pt particles up to 1200°C directly by thermal processing of coprecipitated $(Pt, Al)(OH)_x$ cryogels [41]. Similarly, hydrogen reduction of the coprecipitated Fe–Mo–Al hydroxide cryogel allowed designing the efficient multiphase catalyst for the synthesis of single wall carbon nanotubes by catalytic decomposition of methane [42].

Another original cryogel-based approach to the synthesis of nanocomposites was used in [43] where mesoporous molecular sieve was impregnated with preliminary synthesized nanocrystalline particles of beta zeolite. One of the most energetic applications of the cryogel-based nanocomposites is related to the industrial production of explosives. Safe and dust-free cryochemical processing promotes uniform distribution of the energetic materials in the mesoporous fuel matrix, or, conversely, coating of the energetic nanoparticles by the fuel material [44].

Low tendency of the cryogel nanocrystallites to bridging and their high mobility can be used for directed self-organization of the nanoparticles and synthesis of the various low dimensional structures. Authors [45] reported the formation of rod-like structures (20–50 nm × 100–200 nm) during thermal processing of the cryogel-derived 3 nm ceria nanoparticles. TiO_2 nanoparticles have demonstrated their ability to form nanosheets and hollow nanotubes even during low temperature processing of the corresponding slurries [46], the process of self-organization was found drastically dependent on the pH values. Isolation of ZnO precursor particles by freeze drying followed by matrix isolation in NaCl promoted formation of ZnO nanowires at reduced temperatures during further thermal processing [47, 48].

3.2 Cryogels in batteries and supercapacitors

Along with well-known advantages, active exploitation of the Li-ion secondary batteries demonstrated the need in developing new, more stable, inexpensive and more efficient electrode materials. Low cost and easy change of valence state of Mn made manganese oxides one of the most attractive materials for various battery systems. Along with traditional MnO_2-based batteries, various oxides and hydroxides of Mn demonstrated their ability to intercalate reversibly significant amount of Li ions. However, the intercalation properties of these nanocrystalline and usually amorphous materials depend on a large number of factors and, hence, poorly reproducible. Freeze drying stabilization of the MnO_x gels obtained by redox reaction of fumaric acid with permanganates is proved rather reliable preparation method for the Li battery cathodes demonstrating enhanced specific capacity values (up to 290 mAh g^{-1} at

C/100) and reasonable rate capability (175 mAh g^{-1} at 2C) [49, 50]. High specific surface area of these nanocrystalline materials (350 m^2 g^{-1}) ensures extended interface between the electrode and the electrolyte and, hence, reduces the mean pathway length of Li diffusion in the solid state known as the slowest and, hence, rate determining step of the battery charge–discharge process.

Another group of nanocrystalline amorphous oxides demonstrated their usefulness as cathode material for Li batteries is hydrous oxides of vanadium. Both cryogel-derived V_2O_5 with specific surface area 250 m^2 g^{-1} [51] and metastable VO_2[B] [52] obtained by its thermal treatment at reduced pressure demonstrated outstanding initial specific capacities over 500 mAh g^{-1} at small discharge rates and rather moderate fade rate during further cycling. Important feature of the cryogel processing technique applied in these cases deals with exchange of polar solvents in wet $V_2O_5 \times H_2O$ gels for nonpolar cyclohexane suitable for freeze drying but rarely used in the inorganic syntheses.

In spite of significant progress in developing amorphous cathode materials, the most of the studies were concentrated at the optimization of the composition and synthesis properties of the crystalline cathode materials. The major hope in this direction dealt last years with Li(Ni,Mn)O_2-based structures and materials where the tendency of Ni to form antisite defects with Li was suppressed by the introduction of another transition elements or by Li excess. (Ni,Mn)(OH)$_x$ - cryogels were used in these syntheses as a useful precursor promoting faster formation and crystallographic ordering of the final multicomponent oxide. It is known, however, that the introduction of Li at the early stages of synthesis often causes formation of the kinetically preferable Li-Mn oxides thus complicating crystallographic ordering of the final Li-containing multicomponent oxide. Recent studies of the synthesis and electrochemical performance of $LiNi_{0.425}Mn_{0.425}Co_{0.15}O_2$ and $Li_{1+x}NiMnO_{2+y}$ followed this rule: coprecipitation of Ni and Mn by LiOH resulted in significantly smaller electrochemical capacity of the final material (140 mAh g^{-1} [53]) compared to materials obtained using preliminary coprecipitated Ni-Mn hydroxide (180–190 mAh g^{-1}, [54, 55]).

Apart from Li-ion batteries where coarse grained electrode materials can be also used due to usually applicable low and moderate discharge rates, application of the nanocrystalline cryogels is much more essential for the electrochemical supercapacitors. The most part of the energy in these thin layer batteries is stored in the double electric layer adjacent to the electrode surface that makes small particle size of the electrode materials one of the most critical demands. Thus, nanocomposite electrode from well-known and inexpensive nanocrystalline SnO_2 coated with expensive but demonstrating excellent electro-

chemical performance RuO_2 was used in the development of hybrid power source with cryogel anode and lithium metal cathode [56]. Another example concerns cryogel synthesis of the nanocrystalline Ni-Mn double oxides and hydroxides (Fig. 1) demonstrating specific electrochemical capacitance over 150 F g^{-1} at rather high discharge rates (> 20 mA cm^{-2}) [57].
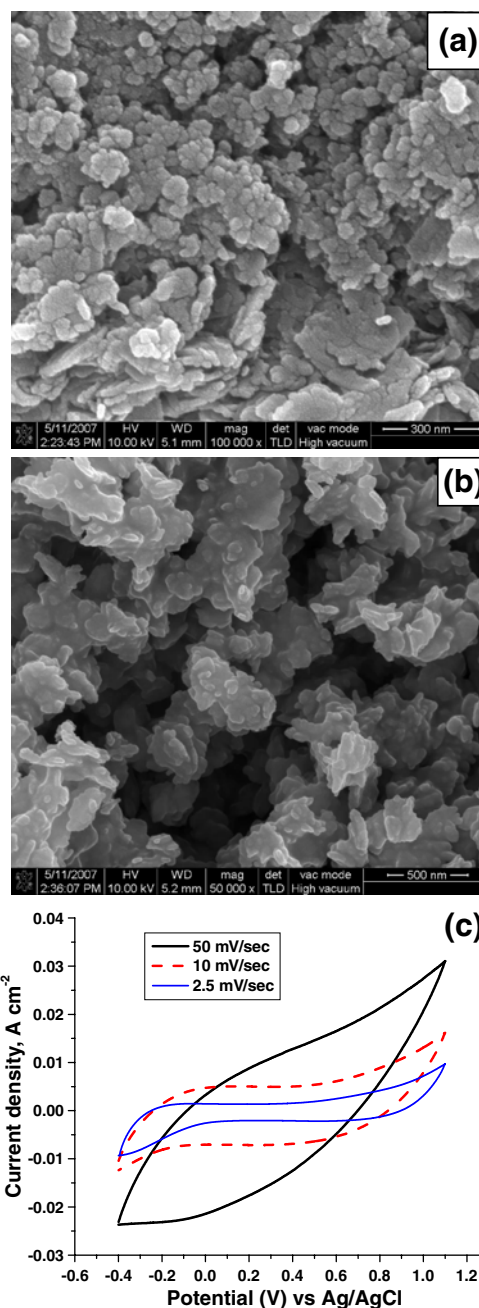

Fig. 1 SEM micrographs of (Ni,Mn)(OH)$_x$ cryogel (a) and cryogel-derived electrode material for electrochemical supercapacitor (b); Cyclic voltammograms of (Ni,Mn)(OH)$_x$ cryogel electrode at various sweep rates in 1M Na_2SO_4 (c)

3.3 Carbon aerogels and their applications

First generation of the non-Faradaic supercapacitors was made of the activated carbons combining high specific surface area and high electrical conductivity. Substantial part of the modern mesoporous carbons are obtained from the dried gel-like polycondensation products of resorcinol and formaldehyde—so called RF gels. Due to the drastic dependence of the carbon properties on the features of polycondensation reaction RF-derived carbons belong rather to derivatives of the polymeric cryogels and, hence, fall outside the scope of the present paper. However, carbon cryogels is one of the most intensively studied cryogel-based products last years and, hence, deserves at least brief survey.

In spite of the wide application of mesoporous carbons in supercapacitors the mechanism of the energy storage and the relationship between electrochemical capacitance and morphological and physico-chemical features of the electrode material are still under intense investigation. Recent studies demonstrated that cryochemical processing of RF gels allows obtaining carbon cryogels with specific capacitance up to 250 F g^{-1} and specific surface area over 1200 m^2 g^{-1} [58–60]. According to these studies, contribution of micropores to the total capacitance value is usually higher than that of mesopores in spite of recent discussion on the incomplete wetting of the last ones. Along with non-Faradaic supercapacitors, carbon cryogel - based composites with silicon can be successfully used also as anode materials for lithium-ion batteries [61].

Another important application of the carbon cryogels is related to their chemical stability and high specific surface area that make them a useful substrate material for various electrocatalysts including PtRu-coated anode materials for direct methanol fuel cells (DMFC) [62]. Cryogel-supported Pt nanoparticle electrocatalyst of hydrogen oxidation demonstrated considerably better activity compared to the same catalyst at the commercially available Vulcan XC-72 microporous carbon [63].

Properties of these materials and other supported catalysts depend greatly on the morphological features of applied substrates. Similarly to inorganic cryogels, directed crystallization of ice during freezing of RF gel in the temperature gradient allows to develop carbon cryogel substrates with oriented bimodal porosity. Capillary-like macropores ensure faster transport of gas or liquid while mesoporous capillary walls are very suitable for the catalyst allocation [64]. Another way to optimize the macromorphology of carbon substrate in order to ensure better balance between faster transport through catalytic bead and contact time enough to perform catalytic action is synthesis of the mesoporous microspheres using microemulsion synthesis [65]. Gas transport and adsorption

parameters of the carbon cryogels can be successfully modified by means of solvent selection and careful optimization of the freezing and freeze drying conditions [66–68] or by ultrasonic irradiation during RF gel formation [69]. Enhanced mesoporosity of carbon cryogels ($S_{BET} \geq 2000$ m^2 g^{-1}) makes them also a useful sorbent for a low-pressure methane storage [70]. Mass production of carbon cryogels could be favored by using cheaper starting materials like wattle tannin and furfural or phenol and formaldehyde [71].

Reverse approach to the problem of cost to quality ratio was demonstrated recently during synthesis of cryogel consisting of rather expensive but demonstrating excellent electrical conductivity and mechanical stiffness carbon nanotubes from their diluted aqueous suspensions [72]. The density of this fragile but self-sustaining cryogel was 10–30 mg ml^{-1} without PVA reinforcement and 40–60 mg ml^{-1} with 1 wt. % PVA.

3.4 Cryogel-based porous structures and ceramics

Extensive macroporosity of the hydroxide cryogels makes them a useful precursor for the production of various kinds of porous ceramic materials. After first experiments described by Y. Trambouze [7, 8] the cryogel-derived powders of the individual refractory oxides were carefully studied by D. Klvana, J. Kirchnerova and J. Chaouki [10, 73]. Recent investigations continue to open the new features and applications of the cryogel-derived porous materials. First of all it concerns application of the cryogel-based approaches to the synthesis of complex oxide ceramics. Analysis of the influence of different synthesis methods on the thermal shock properties of porous cordierite ($2MgO$ $2Al_2O_3$ $5SiO_2$) ceramics confirmed high efficiency of the low temperature processing methods. Ceramic materials with 39% porosity obtained using freeze drying demonstrated the minimum thermal conductivity and the maximum thermal shock strength [74]. During studies of Al_2O_3–TiO_2 ceramics for catalyst supports it was demonstrated that multiphase cryogel-derived ceramics displays higher specific surface area values compared to single oxide prototypes. Freeze drying of precipitates promoted also considerable reduction of the pore size and narrowing its distribution compared to thermal drying [75]. Freezing of the soluble Na_2O K_2O SiO_2 aqueous solutions causes freeze gelation and formation of the cellular structures similar to that ones observed during cryoprocessing of the gel species [76]. Freeze gelation remains to be an essential part of the freeze casting processes used in the production of new advanced ceramic materials. One of them is so called biocers—macroporous hybrid materials containing both ceramic fragments and embedded biocomponents [77–79]; retaining bioactivity of the last ones in the
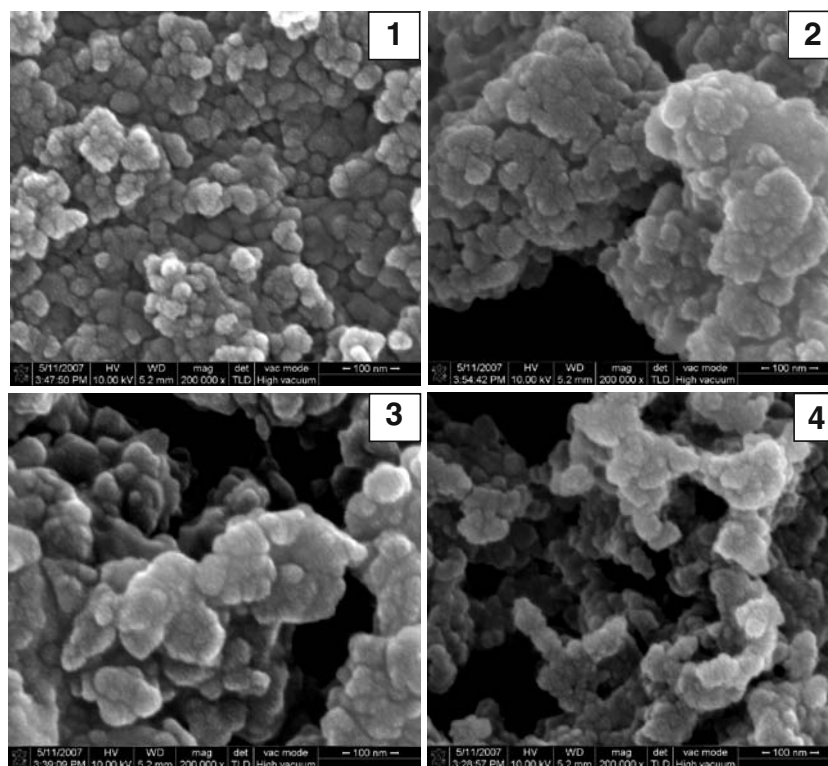
Fig. 2 SEM micrographs of SiO$_2$ monoliths obtained from the same gel precursor by solvent exchange with various solvents followed by freezing and freeze drying: 1—cyclohexane; 2—dimethyl carbonate; 3 (*tert*-butyl alcohol + H$_2$O); 4–(*tert*-butyl alcohol + non-polar solvent). Morphological properties of samples 1–4 are described in Table 1

course of cryoprocessing was confirmed by the yeast cells survival. If the sintering process follows the casting in a short time, a freeze casting can be performed without colloidal component, but in this case a freeze drying becomes a critically important element of the freeze casting procedure [80, 81]. This method is proved especially useful in the production of functionally graded materials from the suspension of powders with various density and physico-chemical properties [82].

Essential feature of the many modern cryogel studies is their turning from the gathering, application of the naturally existing cryogel micromorphologies, to the farming, direct-ed artificial development of the structural elements of desired shape and size. This kind of processing demands exact and profound knowledge of the mechanisms of processes involved. Useful step in this direction was done in [83] when morphological evolution of the porous structure of SiO$_2$ cryogels was studied in the course of its

thermal processing. Rather simple but very efficient method of tuning the pore size was demonstrated in [84] where the permeability of porous alumina support was controlled by the deposition of silica gel inside the pores followed by freezing and freeze drying. Artificially developed macro-structures—two-dimensional 0.2–0.8 μm thick leaf-like structures named by authors "KK leaves"—were designed during thermal processing of the cryogel-based alumina coating on the various substrates [85]. One of the most traditional instruments of microstructure control is applica-tion of templates. Authors of [86] applied carefully controlled foaming in order to modify the macroporous structure of silica scaffolds. Similarly to other cryogel-processed species, these samples contained large amount of mesopores in the bubble walls; their amount and size distribution were little concerned by the foaming procedures.

Possibilities of the traditional methods of the cryogel microstructure control are also far from exhausting yet.

Table 1 Properties of SiO$_2$ cryogel after various kinds of morphological modification.

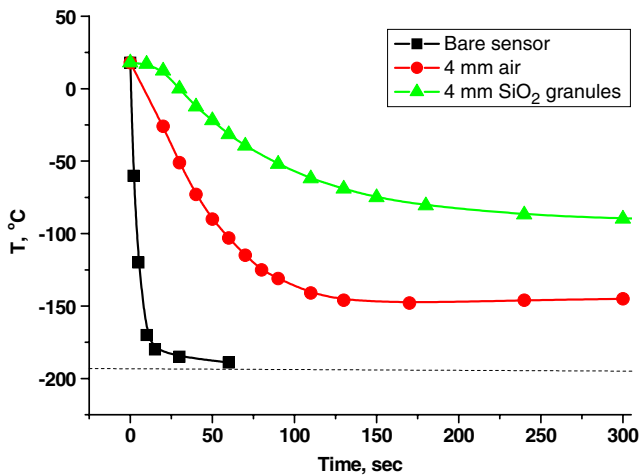| Sample No.	Density, g cm^{-3}	S$_{BET}$, cm^2 g^{-1}	Average pore diameter, nm	Specific volume of mesopores, cm^3 g^{-1}	Specific volume of pores (total), cm^3 g^{-1}
1	0.4	792	2.6	0.52	2.05
2	0.46	694	2.1	0.36	1.7
3	0.16	735	11.3	2.1	5.8
4	0.05	825	14.1	2.9	19.5

Fig. 3 Comparative efficiency of the thermal insulation by air and by silica cryogel (sample 4 in Fig. 4 and Table 1): cooling curves of the temperature sensor immersed to liquid nitrogen with and without 4 mm thick thermal insulation

Water and *tert*-butyl alcohol are usual dispersion media for the most of cryogels in spite of their small tendency to supercooling and strong tendency to form rather large ice crystals even at high cooling rates. Cryocrystallization processes in other solvents able to freeze drying are studied
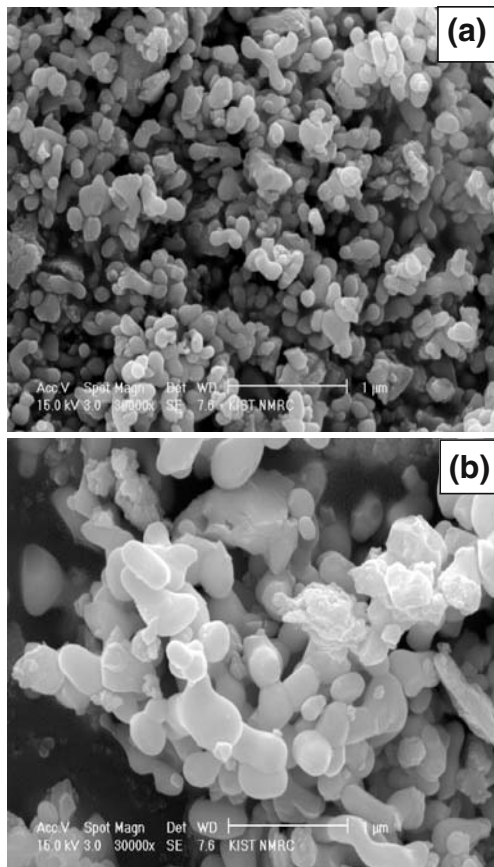

Fig. 4 SEM micrographs of BiNbO$_4$ powders obtained by thermal processing of cryogel precursor at 400°C (**a**) and 700°C (**b**)

rather poor until now, especially behavior of the mixed solvents. However, even simple solvent exchange in combination with usual sol–gel procedures allows to modify substantially the macroporous structure of the cryogels (Fig. 2, Table 1). Similarly to other cryogel processing methods, solvent substitution has minimum influence on mesoporosity and related BET specific surface area. Meanwhile, the volume of macro- and supermacro-pores can be increased substantially. Cooling curves in Fig. 3 demonstrate a thermal insulation capability of the 4 mm layer of monolithic SiO$_2$ cryogel (d=0.05 g cm^{-3}) enough to sustain the 100°C temperature difference in contact with liquid nitrogen.

One of the most demanded types of the catalytic substrate materials is porous ceramic with oriented bimodal structure. Analysis of the unidirectional low temperature crystallization processes allowed authors [19, 87, 88], using micron-sized ice crystallites as templates, to develop production techniques for the SiO$_2$ cryogel-based ceramics with honeycomb, lamellar, polygonal and flat fiber structures. Along with low cooling rate, essential feature of the applied synthesis procedure was solvent exchange in freeze-gelled sample for t-butanol having lower thermal expansion during freezing and, hence, demonstrating less tendency to cracking. Similar approaches were used for the preparation of polygonal TiO$_2$ cryogel nanofibers with enhanced photocatalytic activity [89], SiO$_2$–Al$_2$O$_3$ nanocomposites with oriented porosity and specific surface area ~ 700 m^2 g^{-1} [90], ZrO$_2$ ceramics with oriented porosity [91], TiO$_2$-coated porous glass structure with oriented porosity [92] and flexible hydroxyapatite/collagen composites with porous structure suitable for bone tissue penetration [93]. Along with oriented porous structures, nanocomposites of biocompat-
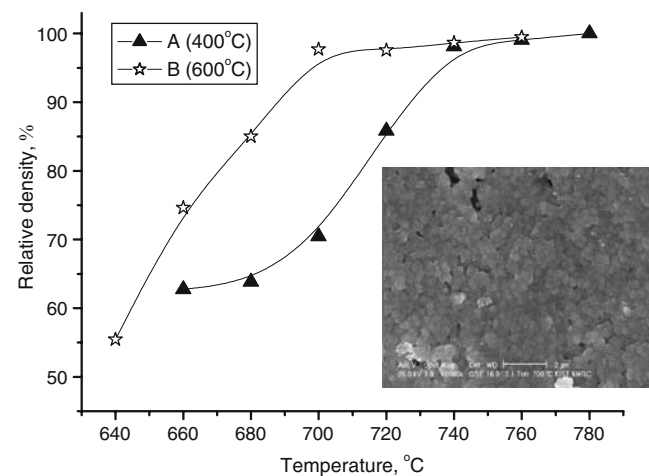

Fig. 5 Density of BiNbO$_4$ ceramics produced by isothermal sintering of cryogel-derived powders A and B obtained at various processing temperatures. Inset: SEM micrograph of the BiNbO$_4$ ceramics (700°C, 10 min)

ible ceramic materials with natural biopolymers is another fast growing area of the cryogel applications, but this kind of materials falls outside the scope of present paper.

3.5 Dense ceramic materials from cryogel precursors

In spite of numerous applications in porous ceramics, cryogel-based powders can be also a suitable precursors for the production of the dense oxide materials due to attractive combination of the nanosize of crystallites and their low aggregation both promoting their mobility at the first stages of sintering [1, 31]. Due to complex character of processes occurred during low temperature sintering caused by the competition of particle mobility and grain inter-growth processes, nanosize of precursor powder does not automatically cause substantial reduction of the sintering temperature; it usually demands careful optimization of the powder synthesis and processing conditions. However, high chemical homogeneity of the cryogel-based powders promotes synthesis of the complex oxide compounds at reduced temperatures and ensures high chemical homogeneity of the cryogel-derived ceramics. Both features make the application of cryogel precursors reasonable during studies of the fundamental physico-chemical properties of various oxide materials [94–98].

Sharp particle size distribution of the nanocrystalline particles makes cryogels attractive precursor for the synthesis of transparent lanthanum silicate ceramics because small inhomogeneities can have dramatic influence on the optical properties of material even during application of the spark plasma sintering [99]. Unique possibilities of the cryogels in the synthesis of nano-composites can be used also for the development of new dense $(Ce, Sm)O_x$-based cermet cathode and anode materials for solid oxide fuel cells with reduced overpotential of the electrodes, increased terminal voltage and power density of the cells with $(Ce,Sm)O_x$ electrolyte [100].

For a long time the application of chemically derived precursors in the synthesis of microwave dielectric ceramics was considered undesirable due to large dielectric losses at the numerous grain boundaries in as-obtained dense but fine-grained ceramic materials. The only possible application area for these precursors was dielectric ceramics with high sintering temperatures (1500–1600°C) where densification is accompanied by the intensive grain growth. Recent studies demonstrated that synergistic effect of the simultaneous application of cryogel-derived precursor powders with optimized micromorphology and melt-forming sintering aids allows reducing the sintering temperature of niobate-based ceramics below 700°C (Figs. 4 and 5). Interesting feature observed during these studies dealt with maximum sintering activity that was never observed for the powders with minimum grain size. Simultaneous

promotion of the intensive grain growth during sintering allowed to produce microwave dielectric materials with $Q \times F = 20000 - 35000$ GHz [101–103].

4 Conclusions

Small size of crystallites, their soft agglomeration and extensive porosity make inorganic cryogels useful precursors for a number of applications in materials science and technology. Cryogel synthesis is one of the simplest but very efficient methods of nanoparticle isolation from the liquid phase. Varying the ice crystallization conditions can substantially modify size and anisotropy of the cryogel macropores. New versions of the freeze casting process open new horizons for this widely used forming method. Low level of aggregation and high chemical homogeneity of the multicomponent cryogel nanoparticles are rather useful for the production of dense ceramic materials at reduced temperatures, especially in combination with melt forming sintering aids.

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