



HAL
open science

FREEZE DRYING OF SILICA GELS PREPARED FROM SILICIUMETHOXID

E. Degn Egeberg, J. Engell

► **To cite this version:**

E. Degn Egeberg, J. Engell. FREEZE DRYING OF SILICA GELS PREPARED FROM SILICIUMETHOXID. Journal de Physique Colloques, 1989, 50 (C4), pp.C4-23-C4-28. 10.1051/jphyscol:1989404 . jpa-00229479

HAL Id: jpa-00229479

<https://hal.science/jpa-00229479>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

FREEZE DRYING OF SILICA GELS PREPARED FROM SILICIUMETHOXID

E. DEGN EGEBERG and J. ENGELL

Institute of Mineral Industry, Technical University of Denmark, DK-2800 Lyngby, Denmark

Résumé - Les gels étudiés ont été préparés par une hydrolyse en catalyse acide de $\text{Si}(\text{OEt})_4$ dilué dans Bu^tOH . Les acides employés sont H_3PO_4 et acide oxalique. L'acide oxalique fonctionne aussi comme DCCA. Le séchage à froid des gels sans échange du solvant résulte en une désintégration en morceaux de l'ordre du millimètre. La détérioration du gel devient moins importante quand la concentration de EtOH dans la phase liquide est réduite par l'échange du solvant. Une série d'expériences indiquent que le Bu^tOH saturé en air montre une expansion (5 vol%) durant la congélation à l'opposé du Bu^tOH pur qui ne montre qu'un petit changement de volume. Cette expansion du volume est probablement responsable de la fracture des pièces monolithiques.

Abstract - The freeze dried gels were prepared by acid catalysed hydrolysis of $\text{Si}(\text{OEt})_4$ diluted by Bu^tOH . The acids used include H_3PO_4 and oxalic acid. Oxalic acid has DCCA-properties. Freeze drying without prior solvent exchange results in disintegration of the gels into mm size flakes. The fracturing of the gels becomes less severe as the concentration of EtOH in the liquid phase is reduced by solvent exchange. Pure Bu^tOH shows only a very small volume change upon crystallization, but air saturated Bu^tOH expand about 5 vol% upon freezing. This volume expansion is presumably the cause of the crack-pattern observed in the solvent exchanged monolithic pieces.

INTRODUCTION

The drying process is a critical step in the preparation of sol-gel derived monoliths (15, 23). During drying stress caused by capillary forces in the pore structure of the gel results in shrinkage and fracturing unless special precautions are taken.

Monolithic silica xero-gels (ca. 10 cm^3), with bulk densities in the range $1.5\text{-}1.8 \text{ g/cm}^3$, can be produced by controlled conventional drying in about 5 days using acid-catalysed hydrolysis of $\text{Si}(\text{OEt})_4$ and a relative high casting density (9). The use of Drying Controlling Chemical Additives (DCCA) like formamide, oxalic acid or glycol permit a relatively rapid drying (5, 18). Thus, monoliths up to $>100 \text{ cm}^3$ in size of silica xero-gel with bulk densities in the range $1.2\text{-}1.4 \text{ g/cm}^3$ have been made within 2 days using formamide and acid catalysed hydrolysis of $\text{Si}(\text{OMe})_4$ (5). The use of DCCA results in the formation of a narrow pore size distribution by elimination of the smallest pore (1, 5, 18). Hereby the capillary forces are reduced and the drying process facilitated. Mizuno et al. (12) have recently succeeded in producing small monoliths of silica xero-gels with bulk densities as low as 0.73 g/cm^3 by conventional drying of $\text{Si}(\text{OMe})_4$ derived gels. Contrary to conventional wisdom these results were obtained by aqueous solvent exchange before drying. This was done in order to strengthen the gel by eliminating organic groups and thus, favour crosslinking.

Monolithic silica aero-gels with bulk densities in the range $0.02\text{-}0.3 \text{ g/cm}^3$ can at present only be produced by supercritical drying (6, 16, 19) where the liquid-vapour interface is eliminated and capillary stresses thereby avoided.

The present work concerns the preparation of monolithic silica gels by freeze drying, i.e. drying by sublimation of a frozen solvent. Freeze drying is used on a large scale in food and medical technology (21). The technique has also proved very useful for laboratory preparation of high quality ceramic powders (3, 14, 22). In principle the process makes it possible to conserve the structure of the material being dried. However, monoliths can not be made from aqua-gels by this method. The freezing process results in the formation of small flakes, or if directional freezing is used fibres (11). Important factors are here, firstly the large volume expansion upon freezing of water (10 vol%) and secondly the surface tension between the phases

Table 1. Freezing point (20) and calculated upper limit for the rate of sublimation (G_{\max}) for water, Bu^tOH and other alcohols.

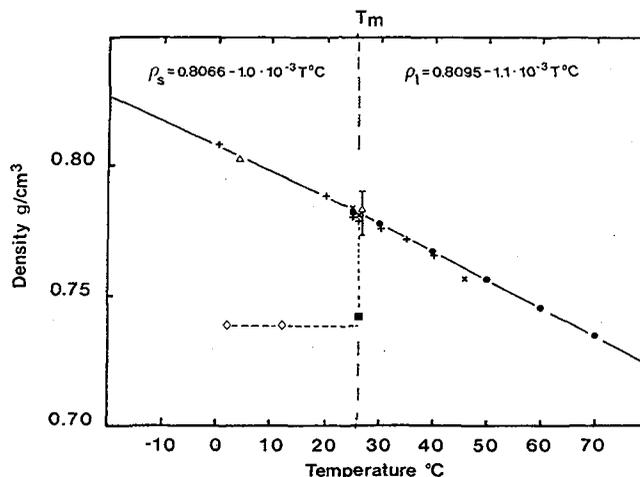
	FREEZING POINT °C	TEMP. °C	G_{\max} kg/m ² h
Water	0	0	505,
		-15	140,
		-30	33,5
		-50	3,5
		-70	0,25
tert-Butanol	25.6	25.6	16.900,
		0	2.800,
		-20	460,
Methanol	-94	-98	0,47
Ethanol	-117	-112	0,009
n-Propanol	-127	-127	0,00003
iso-Propanol	-90	-86	0,45

Table 2. Physical properties of ButOH (tert-butanol; 2-methyl-2-propanol).

Structural Formula	
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$
Melting Point (Phase I)	25.6°C
Crystalline Polymorphs (7, 13)	3
Density, g/cm ³ (10; 2 & new data Fig. 1)	
80 °C < T < 25.6°C	$\rho = 0.8095 - 0.0011 \times T^{\circ}\text{C}$
25.6°C < T < 0 °C	$\rho = 0.8066 - 0.0010 \times T^{\circ}\text{C}$
Viscosity (10) 30°C	$3.3498 \times 10^{-3} \text{ Pa} \cdot \text{sec}$
Vapor Pressure (20) Torr	$\ln P = 22.9308 - 5764.2/T^{\circ}\text{K}$

Fig. 1. Density of Bu^tOH as a function of temperature.

- : Kuss, E. (10).
- + : Beilstein (2).
- x : Shell (17).
- : Air saturated (17).
- ◇ : Air saturated (this work).
- △ : Air free (this work).



involved. The latter affects the degree to which gel-material is expelled from the growing "solvent"-crystals during freezing.

Methanol (MeOH) and ethanol (EtOH) are not suitable for freeze drying because of their low freezing points and sublimation rates (Table 1). However, tert-butanol (Bu^tOH) appears to be very suitable (Table 2). The freezing point of pure Bu^tOH is 25.6°C and the volume change upon crystallization of air free material appears to be very small (Fig. 1). G_{\max} , the upper limit for the rate of sublimation neglecting the effects of pore structure, thermal conductivity and other physical limitations, can be calculated using a simplified formula (8). These calculations (Table 1) indicate that for any given material the drying time can be reduced substantially if Bu^tOH is used instead of water. At temperatures above 0°C three crystalline polymorphs of Bu^tOH are known (7, 13). The freezing point of Bu^tOH decrease in the presence of impurities (H₂O, EtOH, Bu^sOH, BuⁿOH). Furthermore, air saturated Bu^tOH shows a volume expansion upon freezing (5-6 vol%, 17 & Fig. 1). Thus, in order to avoid melting and cracking in the monoliths it is important to use high purity air-free Bu^tOH.

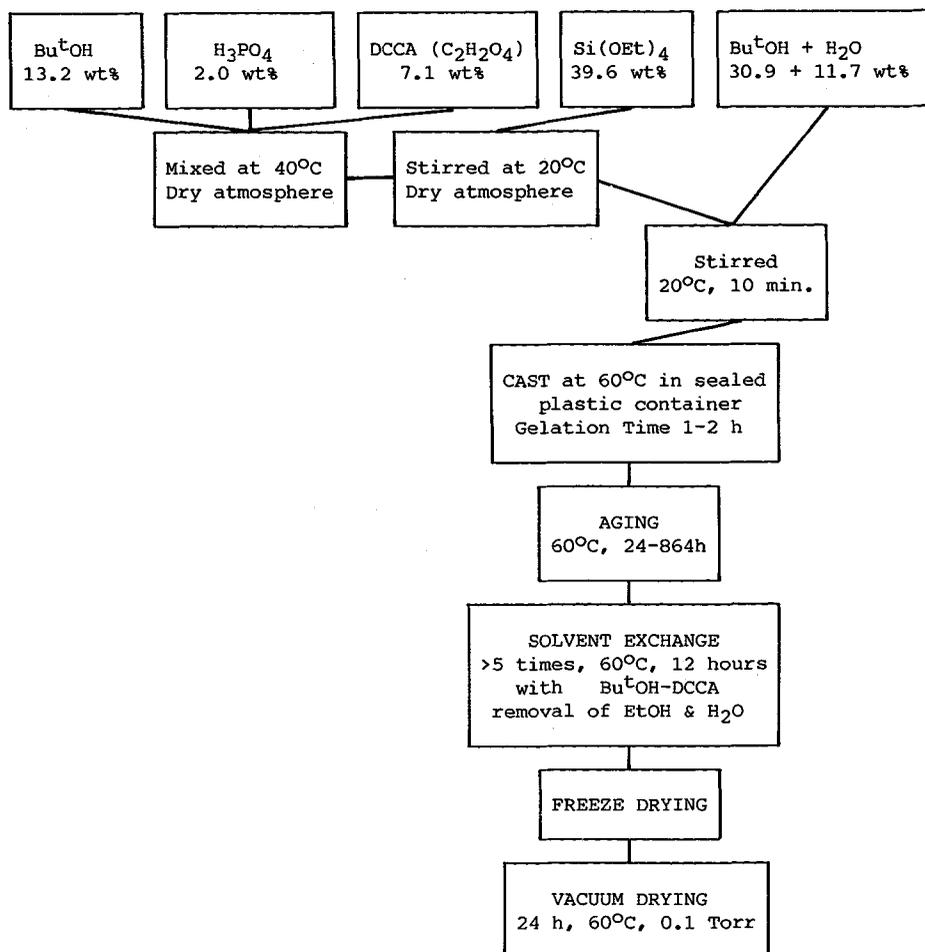


Fig. 2. Flow diagram showing the procedure used for the preparation of freeze dried silica gels.

EXPERIMENTAL

Monolithic silica gels were prepared by acid catalysed hydrolysis of $\text{Si}(\text{OEt})_4$ by the procedure shown in Fig. 2. The acids used include H_3PO_4 and oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$). Two of the acid groups on H_3PO_4 react immediately with $\text{Si}(\text{OEt})_4$ and form copolymers with one remaining acid group (4), this prevent later evaporation of the acid. Oxalic acid was used for its DCCA-properties. The chosen ratio between $\text{Si}(\text{OEt})_4$, H_2O and Bu^tOH was inside the miscible area in the ternary system (Fig. 4) in order to avoid phase separation. The EtOH released by hydrolysis lowers the freezing point of the solvent. Thus, solvent exchange with pure Bu^tOH is necessary in order to ensure crystallization of the major part of the solvent above -18°C . Analyses of the exchanged solvent by gas-chromatography showed that the chosen exchange conditions (60°C , 12h) were sufficient for obtaining equilibrium.

After aging the gels were frozen either unidirectionally (0°C) or homogeneously in a deep-freezer (-18°C) and freeze dried in a HETOSICC freeze dryer (CD 52-1). The gels were further vacuum dried (60°C , 0.1 Torr, 24 h) in order to remove residual solvent.

The dry gels were characterized by He-Pycnometry (apparent density; Micromeritics Multi-volume Pycnometer 1305). Bulk density and open porosity accessible to water were determined by Archimedes method in water. From these data the open porosity accessible to He was calculated.

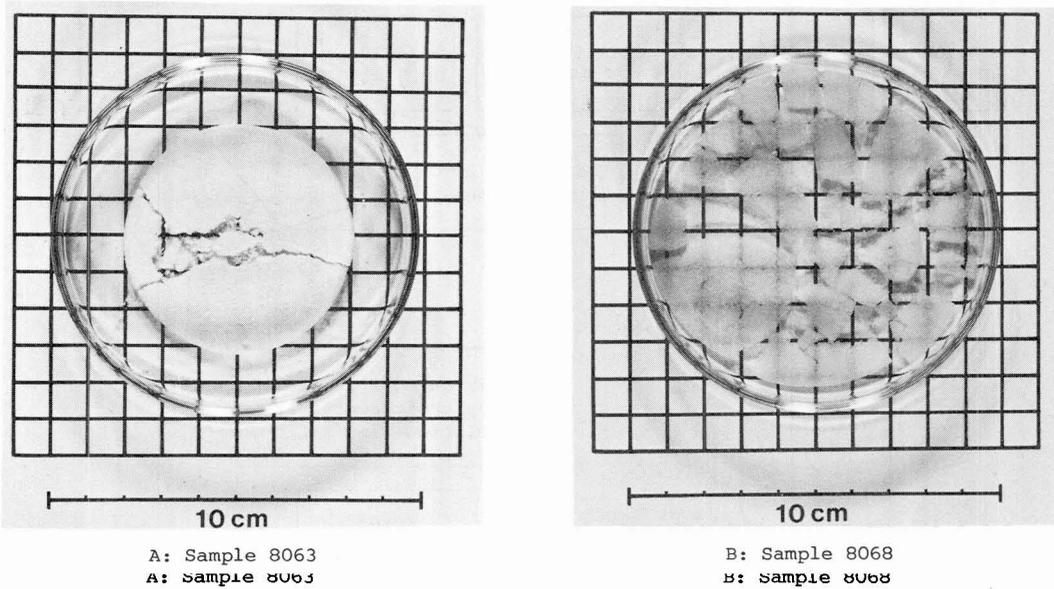


Fig. 3. Photographs of freeze dried silica monoliths reported in Table 3.

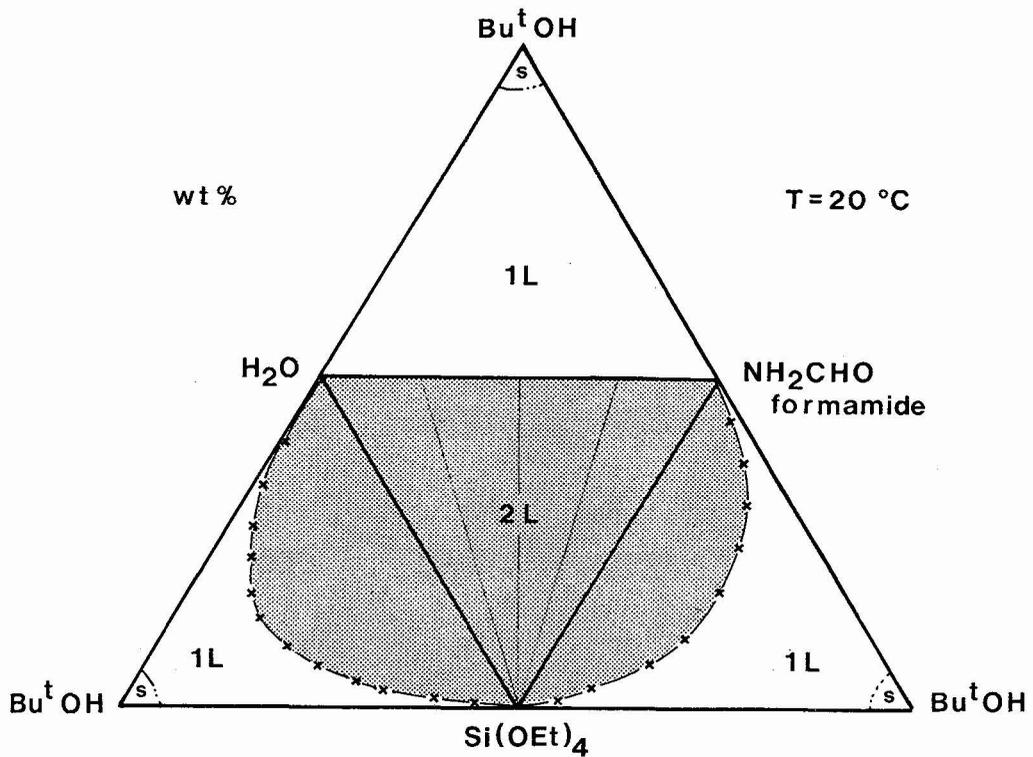


Fig. 4. Liquid immiscibility in the system $\text{Si}(\text{OEt})_4$ - Bu^tOH - H_2O - NH_2CHO (pers.com. K.T. Winther).

Table 3. Compositions, conditions and results of the freeze drying experiments on silica gels.
 * Number of times gels has been exchanged (60°C, 12 hours); added volume of Bu^tOH or Bu^tOH-C₂H₂O₄ > volume of gel.

SAMPLE	1204	1904	0205	1705	8063	8065	8066	8068
COMPOSITION, mole%								
Si(OEt) ₄	8.9	15.4	15.4	12.8	12.8	12.8	12.8	12.8
(CH ₃) ₃ COH	32.2	43.4	43.4	36.3	36.3	36.3	36.3	36.3
H ₂ O	50.7	39.7	39.7	44.1	44.1	44.1	44.1	44.1
H ₃ PO ₄	1.2	1.5	1.5	1.4	1.4	1.4	1.4	1.4
C ₂ H ₂ O ₄	7.0	-	-	5.4	5.4	5.4	5.4	5.4
H ₂ O/Si(OEt) ₄	5.7	2.6	2.6	3.4	3.4	3.4	3.4	3.4
SiO ₂ ,	wt%	9.0	12.6	12.6	11.4	11.4	11.4	11.4
AGING at 60°C, hours								
Linear Shrinkage, %	24	48	48	48	96	192	384	864
	20	10	10	9	10	10	10	10
SOLVENT EXCHANGE*								
Residual EtOH, wt%	none	x5	x5	x5	x6	x6	x6	x6
	29.6	2.9	1.6	1.0	0.5	0.6	0.5	0.5
FREEZING								
Undirectional °C	-18	-	-18	-18	-18	-18	-18	-18
Directional °C	-	0	0	-	-	-	-	-
FREEZE DRYING								
Condensor Temp. -50°C								
Pressure, Torr	0.05	10	11	0.05	0.05	0.05	0.05	0.05
Time, hours	93	157	120	45	24	24	24	24
Remarks	boiling		melting					
FINAL RESULTS								
After Vacuum Drying								
24h, 60°C, 0.1 Torr								
Bulk Density, g/cm ³	-	-	-	0.316	0.528	0.483	0.479	0.333
App. Density, g/cm ³	1.770	-	1.840	1.750	1.815	1.765	1.742	1.838
Open Porosity								
accessible to H ₂ O %	-	-	-	74.8	66.6	67.3	66.7	73.3
accessible to He %	-	-	-	81.7	70.9	72.6	72.5	78.1
Organic Residual, wt%	73.4	40.0	30.0	55.4	28.9	26.7	13.8	33.9

RESULTS AND DISCUSSION

The results are listed in Table 3 and examples of the freeze dried materials obtained are shown in Fig. 3. All the gels were clear and homogeneous after gelation and aging. Attempts to freeze a gel (1204; -18°C) without exchanging the solvent showed that EtOH-enriched liquid was entrapped inside the frozen gel. During freeze drying at low pressure this liquid boil and the gel disintegrate into small flakes. A reduction of the EtOH concentration to ca. 0.5 wt% by solvent exchange appear to be sufficient to solve this problem (8063-8068).

The Bu^tOH tend to form needle like crystals. Attempts to remove the EtOH by directional freezing (zone refinement) proved unsuccessful (1904 & 0205). Repeated freezing and thawing of gels containing air saturated Bu^tOH results in development of an increasingly finer crack-pattern. It is believed that this problem can be solved by using air-free Bu^tOH.

Gels prepared with oxalic acid, repeated solvent exchange and long aging time gave large (6x3x0.5 cm) translucent pieces of low density gels even though air saturated Bu^tOH was used. It is encouraging to observe that the bulk densities of the dried gels are in the range 0.3-0.5 g/cm³. Thus, with further improvements it should be possible to produce monolithic aerogels by freeze drying.

CONCLUSIONS

Monolithic silica gels have been prepared from $\text{Si}(\text{OEt})_4$ diluted by Bu^tOH , H_3PO_4 , oxalic acid and H_2O . After several solvent exchange and long aging time freeze drying of such gels gave large translucent pieces (6x3x0.5 cm) with bulk densities in the range 0.3-0.5 g/cm³.

In order to facilitate the freezing process, and to avoid boiling during the freeze drying, it is necessary to reduce the EtOH concentration below 0.5 wt%. Using a volume of Bu^tOH equal to the volume of the gel, 5 solvent exchanges are sufficient in order to reduce the EtOH content to an acceptable level. It is necessary to use high purity, air-free Bu^tOH for the solvent exchange, since impurities lower the freezing point and air saturated Bu^tOH expands upon freezing.

With further improvements it should be possible to produce monolithic aero-gels by freeze drying.

ACKNOWLEDGMENT

This work was financed by the Danish Energy Research Program through contract no. EFP-87-1213-701-01-01 and the Danish Technical Research Council through contract no. 5.17.1.6.19.

REFERENCES

- (1) Artaki, I., Bradley, M., Zerda, T.W., Jonas, J., Orcel, G. & Hench, L.L.: In Hench, L.L. & Ulrich, D.R. (Ed.): Ceramic Chemical Processing (John Wiley & Sons 1986) 73-80.
- (2) Beilsteins Handbuch der Organische Chemie. H1, 24, 380; 1E, 24, 192; 2E, 24, 413; 3E, 24, 1569; 4E, 24, 1609.
- (3) Cormack, B., Freeman, J.J. & Sing, K.S.W.: J. Chem. Tech. Biotechnol. 30 (1980) 367-373.
- (4) Engell, J., Mortensen, S. & Møller, L.: Solid State Ionics 9&10 (1983) 877-884.
- (5) Hench, L.L.: In Hench, L.L. & Ulrich, D.R. (Eds.): Ceramic Chemical Processing. (John Wiley & Sons 1986) 52-64.
- (6) Henning, S.: In Fricke, J. (Ed.): Aerogels, Proc. of 1st International Symposium, Springer-Verlag (1986) 38-41.
- (7) Janelli, L., Lopez, A. & Azzi, A.: J. Chem. Eng. Data, 24, 3 (1979) 172-175.
- (8) Karel, M.: In Glodblith, S.A., Rey, L. & Rothmayr, W.W. (Eds.): Freeze drying and advanced food technology. (Academic Press 1975) 177-202.
- (9) Klein, L.C. & Garvey, G.J.: In Hench, L.L. & Ulrich, D.R. (Ed.): Ultrastructure Processing of Ceramics, Glasses and Composites (John Wiley & Sons 1984) 88-99.
- (10) Kuss, E.: Zeitschrift Ang. Phys. 7 (1955) 373.
- (11) Mahler, W. & Chowdhry, U.: In Hench, L.L. and Ulrich, D.R. (Eds.): Ultrastructural Processing of Ceramics, Glasses and Composites. (John Wiley & Sons 1984) 207-218.
- (12) Mizuno, T., Nagata, H. & Manabe, S.: J. Non-Cryst. Solids 100 (1988) 236-240.
- (13) Oetting, F.L.: J. Phys. Chem 67 (1963) 2757-2761.
- (14) Ramme, R. & Hauser, H.: cfi/Ber. DKG, 7/8 (1986) 373-377.
- (15) Scherer, G.W.: J. Non-Cryst. Solids 100 (1988) 77-92.
- (16) Schmitt, W.J., Grieger-Block, R.A. & Chapman, T.W.: In Paulaitis (Ed.): Super Critical Fluid Cond. (Chem. Eng. 1983) 445-460.
- (17) Shell Chemical Corporation, New York: Technical Bulletin SC 49-2 (1949) 1-31.
- (18) Siqiang, L. & Kairong, T.: J. Non-Cryst. Solids 100 (1988) 254-262.
- (19) Tewari, P.H., Hunt, A.J. & Lofftus, K.D.: In Fricke, J. (Ed.): Aerogels (Springer-Verlag 1986) 31-37.
- (20) Weast, R.C. & Astle M.J.: CRC Handbook of Chem. and Phys. (CRC Press, 63rd ed. 1982).
- (21) Willemer, H.: In Glodblith, S.A., Rey, L. & Rothmayr, W.W. (Eds.): Freeze drying and advanced food technology. (Academic Press 1975) 461-477.
- (22) Xue, L.A., Riley, F.L. & Brook, R.J.: Br. Ceram. Trans. J. 85 (1986) 47-48.
- (23) Zarzycki, J.: In Hench, L.L. & Ulrich, D.R. (Ed.): Ultrastructure Processing of Ceramics, Glasses and Composites (John Wiley & Sons 1984) 27-42.