

ROLE OF ORGANIC COMPONENTS IN SOL-GEL GLASSES

Schmidt, H., Kaiser, A., Naß, R., and Hörth, F.-J.

Fraunhofer-Institut für Silicatforschung,
Neunerplatz 2, D-8700 Würzburg,
Federal Republic of Germany

Organic groupings play an important role for the preparation of glasses by the sol-gel route. They are responsible for the solubility of precursors, interact during the polycondensation process, the drying and ageing step and during firing. For processing, important parameters e.g. hydrolysis rates and the SiOH formation can be controlled by proper choice of the hydrolysable group. If organics remain in the glass network, remarkable changes of properties (density, hardness, refractive index) occur.

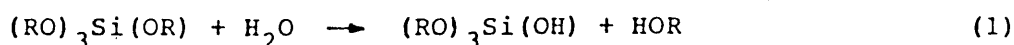
Introduction

The synthesis of non-metallic inorganic materials has become a matter of high interest during the recent three decades. Numerous authors have published results on preparation of glasses, coatings, and ceramic powders. A survey over the state of art can be obtained from the proceedings of the important congresses related to sol-gel work /1-9/. Whereas most papers are concerned with fundamental questions and laboratory scale preparations, only a few sol-gel applications are on the market, e.g. coatings /10-14/. Other industrial applications concern ceramic powders. Fundamentals are mainly investigated in the tetraethylsilicate system (hydrolysis and condensation as well as drying, ageing, and sintering) in alcoholic solutions, less with aqueous systems. Mechanisms in other systems as well as in multicomponent systems are hardly known. In all these reactions, organics are involved in various ways. If the gel derived materials are heated, organics are volatile, can decompose or are oxidized and fairly organic-free materials can be obtained. Residual organics in glassy structures can lead to a remarkable change of properties. Considering the different steps of a sol-gel preparation, the role of organics begins at a very early stage and ends with baking out during heat treatment or with the incorporation into the glass structure.

Precursors, solvents, processing

The sol-gel process in general begins in a homogeneous solu-

tion. This is desirable since it provides an almost homogeneous distribution of the single components, including low concentration components like dopants. In most cases solubility of inorganic oxides is very limited, e.g. SiO_2 , TiO_2 , ZrO_2 , and others. Organometallic precursors like alkoxides with a few exceptions provide excellent solubility in a variety of organic solvents e.g. alcohols, ketones, hydrocarbons. The organic groupings play an important role for solubility. Since homogeneity affects structure and properties of the glass, the proper choice of precursor and solvent is important. The length of the alkyl groups in alkoxides determines its reactivity with respect to hydrolysis. Figure 1 shows the rate constant for the first step (equation 1) as a function of R.



The acid catalysed hydrolysis was determined by FTIR reflection spectroscopy as a first order reaction. The data demonstrate clearly the influence of the chain length. The greatest difference appears between MeO and EtO as ligands.

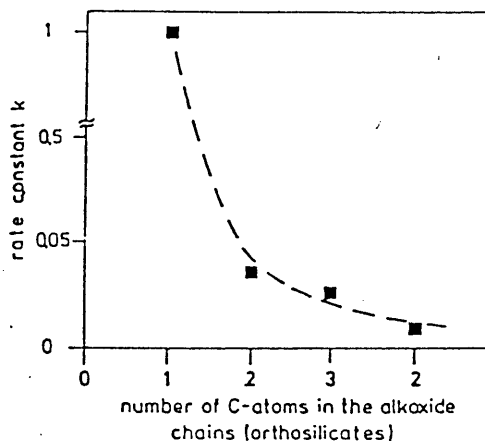


Figure 1. Relative rate constants as a function of the organic chain length in tetraalkylorthosilicates
 1 = $\text{Si}(\text{OCH}_3)_4$; 2 = $\text{Si}(\text{OC}_2\text{H}_5)_4$;
 3 =
 solvent: ethanol; catalyst:
 0.3 mmol HCl;
 H_2O :Silane: 4:1.

The hydrolysis rate determines the concentration of condensable $\equiv\text{SiOH}$ groups and, together with other parameters like catalyst, the condensation rate and particle growth process. Control of $\equiv\text{SiOH}$ groups is necessary, if cocondensation of easily hydrolysable alkoxides is carried out. If water is added to a mixture of $\text{Si}(\text{OR})_4$ and $\text{Ti}(\text{OR})_4$, TiO_2 precipitates. Prehydrolysis of $\text{Si}(\text{OR})_4$ to $\equiv\text{SiOH}$ groupings containing prepolymers and $\text{Ti}(\text{OR})_4$ addition leads to homogeneous liquid systems /15/ which remain clear after water

detailed knowledge of its influence is necessary for two or more component synthesis.

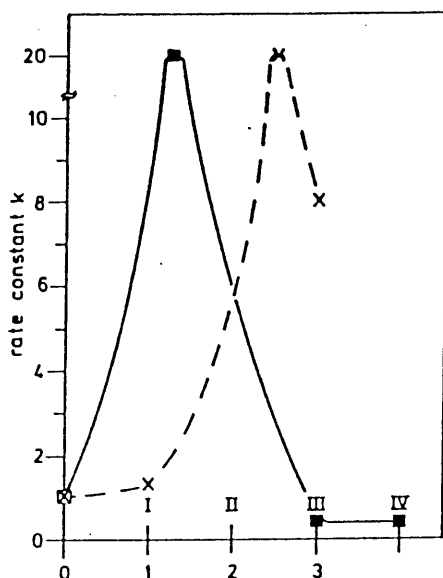


Figure 3. Hydrolysis of $R'_n \text{Si}(\text{OC}_2\text{H}_5)_{4-n}$
 , I, II...: $n = 1$;
 $R' = \text{CH}_3 \dots \text{C}_2\text{H}_5 \dots$
 X, 1, 2 ...: $R' = \text{CH}_3$;
 $n = 1, 2 \dots$
 solvent: ethanol; cata-
 lyst: 0.3 mmole HCl;
 $\text{H}_2\text{O}:\text{silane} = 4:1$

Complex ligands like β -diketones or organic acids like acetates can severely interact with alkoxides /18/. The effect on sol-gel processing is scarcely investigated. For alumina, zirconia or titania containing systems, different mechanisms take place. E.g. acetylacetonate in the case of alumina decreases condensation rate and increases the solubility of the hydrolysed species /16/. For zirconia, a drastical solubility increase can be observed /19/ and for titania, complexed with acetates, more linear polymers are obtained /20/. Complexation can be an important mean for tailoring intermediates for sol-gel processing especially with respect to improve coatings /21/. An important finding for large piece processing was the observation that densification and shrinkage can be controlled by addition of organic materials like formamides or glycols /22/.

Organics incorporated into glass structure

In general, sol-gel processing requires a densification step at higher temperature (close to T_g) to obtain dense glasses. Organic groupings can act as network modifier, reducing network connectivity /22/ and can affect a drastical change of properties compared to inorganic glasses. If organic groupings are cross-linked, they can act as network formers. A survey over preparation techniques is given in /23/ and literature cited therein. In the

following some specific aspects of material properties due to organic incorporation will be discussed.

Therefore, different compositions have been investigated (I: $(C_6H_5)_n Si(O_{1/2})_{4-n}$ (a), MeO_2 (b); Me = Si, Ti; II = $OCH_2CH(CH_2)_3$, $SiO_{3/2}$ (a); Me (III, IV) O_x (b); x = 2, 3/2, Me = Al, Ti, Zr). First of all it has to be remarked, that only in systems with very low molar contents of organics, porous gels can be obtained /22/, e.g. in I for n = 1 and a:b > 0.3:1 remarkable porosities can be determined. This is different for CH_3 as ligands where high porosities can be obtained /23/. In the system II no porosity was observed in the investigated range a:b > 1.5:1. It is remarkable since the system II contains only threedimensional crosslinking units. Since the OH content is low /24-25/ the inorganic network is nearly fixed. Taking into account that despite high concentration of inorganic units (e.g. ZrO_2 = 40 mol%, table 1, a theoretical density of $\rho = 2.55$ (increments: baddeleyit: 6.0; silica: 2.2; PEO: 1.2 g/cm³) should be expected, whereas only 1.63 has been measured. It is surprising that almost no influence on n_D and only a low influence on ρ can be detected. An explanation can be given by the drastic influence of the organic grouping creating a high free volume compared to the organic-free inorganic compound. Whereas in the systems I and II glass temperatures have been found between room temperature and several hundred degrees /22/, in type III systems, where the epoxy-Si grouping is substituted by the methacroyl-Si /26/ and polymerized, no Tg can be detected up to the decomposition temperature of the organics (composition table 2). This leads to the conclusion that the free rotation of the type

Table 1. Densities and refractive indices of some organically modified ceramics (ORMOCERs).

	molar ratio	density (g/cm ²)	n_D
Epoxy-Si/TiO ₂	90/10	1.34	-
	80/20	1.37	1.517
	65/35	1.45	-
Epoxy-Si/ZrO ₂	90/10	1.33	-
	80/20	1.40	1.508
	60/40	1.63	-
Epoxy-Si/Al ₂ O ₃	90/10	1.34	-
	80/20	1.34	1.498
	60/40	1.34	-

Table 2. Composition of methacryl containing ORMOCERS.

ORMOCER system	composition molar ratio
M Me Al	45 30 25
M Ph Al	45 30 25
M T	75 25
M Al	75 25

M = γ -methacryloxypropyltrimethoxysilane
 Me = methyltrimethoxysilane
 Ph = phenyltriethoxysilane
 T = tetraethoxysilane

III materials is strongly hindered by additional polymerization suggesting a structure between inorganic and organic glasses. The free rotation of non-crosslinked organic groupings has been recently observed by neutron scattering techniques on condensed aminosilane systems /27/.

Mechanical properties of these hybrid glasses often are related to inorganic glasses. They are brittle and, compared to organic polymers, very abrasive resistant /28/. Due to the free volume causing an open structure, gas permeation is high (for H_2O ranging between two and 0.3 g/m \cdot d at 10 μ m thickness). The low values (\approx one tenth of highly water impermeable plastics) can be obtained by hydrophobizing the inorganic network as described in /29/. Structural investigations by TEM/EDAX do not show any inhomogeneities on type III compositions whereas in type I sub-micron structure (Figure 4) could be detected but not quantified.

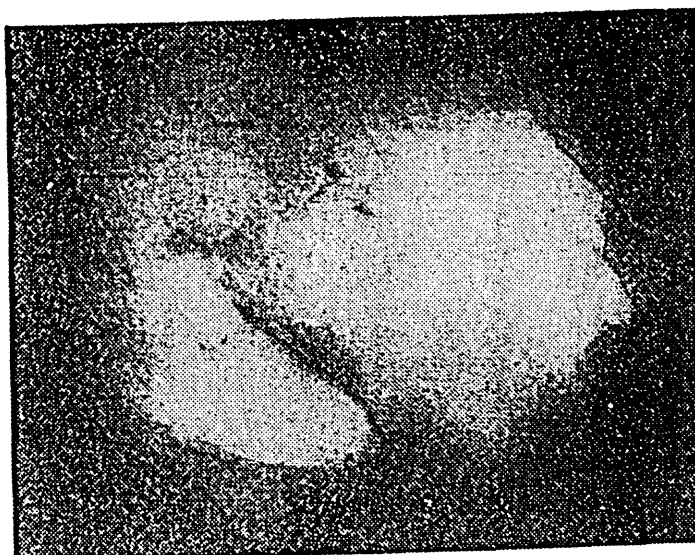


Figure 4. TEM micrograph of a modified type I gel (10 Na₂O/20 Al₂O₃/70 (C₆H₅)₂SiO)₂SiO₃)
 ─── 50 nm

In this case, probably due to the different affinities of the groupings (hydrophobic C_6H_5 versus hydrophilic $=SiOH$ and $=AlOH$ groupings) phase separation is likely on a submicron scale.

Conclusion

The role of organics during sol-gel processing is a very important one, as a few examples have shown. Due to the concentration onto the properties of the final product, only a few data exist on this matter and the large potential has to be exploited. Organic groupings remaining in the final product change its properties drastically. These new materials (ORMOCERS) exhibit a wide variety of properties and interesting structural aspects.

Acknowledgements

The authors wish to thank Dr. Haas and Mr. Rudolph for their helpful discussions and experimental work, and the Bundesminister für Forschung und Technologie and the Bayerische Staatsminister für Wirtschaft und Verkehr for their financial support.

References

1. Gottardi, V., ed. // J. Non-Cryst. Solids. 1982. Vol. 48. Amsterdam, North-Holland Physics Publishers.
2. Scholze, H., ed. // J. Non-Cryst. Solids. 1984. Vol. 63. Amsterdam, North-Holland Physics Publishers.
3. Zarzycki, Z., ed. // J. Non-Cryst. Solids. 1986. Vol. 82. Amsterdam, North-Holland Physics Publishers.
4. Sakka, S., ed. // J. Non-Cryst. Solids. 1988. Vol. 100. Amsterdam, North Holland Physics Publishers.
5. Hench, H. L., Ulrich, D. R., eds. // Proceedings of the International Congress on Science of Ceramic Chemical Processing. 1986. New York, John Wiley & Sons.
6. Mackenzie, J. D., Ulrich, D. R., eds. // Proceedings of the International Congress on Ultrastructure Processing of Ceramics, Glasses and Composites. February 1987, San Diego/Florida, USA (in print).
7. Brinker, C. J., Clark, D. E., Ulrich, D. R., eds. // Mat. Res. Soc. Symp. Proc. 1984. Vol. 32. New York, Materials Research Society.
8. Brinker, C. J., Clark, D. E., Ulrich, D. R., eds. // Mat. Res. Soc. Symp. Proc. 1986. Vol. 73. New York, Materials Research Society.
9. Proceedings of the International Congress Better Ceramics Through Chemistry III. April 1988, Reno/Nevada, USA (in print).
10. Dislich, H. // Glass: Science and Technology. Vol. 2. Processing I. 1984. New York, Academic Press. P. 251 - 283.
11. Dislich, H. // Proceedings of the European Meeting Inorganic Coatings on Glass. 1988. L'Aquila, University. P. 113 - 128.

12. Hench, L. L., Orcel, G. // Proceedings of the International Congress on Ultrastructure Processing of Ceramics, Glasses and Composites. February 1987, San Diego/Florida, USA (in print).
13. Ohta, H. // Proceedings of the First International Symposium on New Glass. 1988. Tokyo, Association of New Glass Industries. P. 27 - 34.
14. Klein, L. C. // Sol-gel technology for thin films, fibers, preforms, electronics, and speciality shapes. New Jersey, Noyes Publications. 1988.
15. Yoldas, B. E. // J. Mater. Sci. 1977. Vol. 12. P. 1203 - 1208.
16. Schmidt, H., Naß, R., Sporn, D., Ray, S. // Materials Science Forum. 1988. Vol. 34 - 36, Part 2. Sydney, Trans Tech Publications Ltd. P. 833 - 839.
17. Schmidt, H., Scholze, H., Kaiser, A. // J. Non-Cryst. Solids. 1984. Vol. 63. P. 1 - 11.
18. Bradley, D. C., Mehrotra, R. C., Gaur, D. P. // Metal alkoxides. New York, Academic Press. 1978.
19. Rinn, G., Schmidt, H. // Proceedings of the First International Conference on Ceramic Powder Processing Science. November 1987, Orlando/Florida, USA. Advances in Ceramics (in print).
20. LaCourse, W. C., Kim, S. // Science of ceramic chemistry processing. 1986. New York, John Wiley & Sons. P. 304 - 310.
21. Schmidt, H., Rinn, G., Naß, R., Sporn, D. // Proceedings of the International Congress Better Ceramics Through Chemistry III. April 1988, Reno/Nevada, USA (in print).
22. Scholze, H., Strehlow, P. // Wiss. Ztschr. Friedrich-Schiller-Univ. Jena, Naturwiss. R. 1987. Vol. 36. P. 753 - 762.
23. Schmidt, H. // ACS Symposium Series. 1988. Vol. 360. P. 333 - 344.
24. Philipp, G., Schmidt, H. // J. Non-Cryst. Solids. 1986. Vol. 82. P. 31 - 36.
25. Schmidt, H., Seiferling, B. // Mat. Res. Soc. Symp. Proc. 1986. Vol. 73. P. 739 - 750.
26. Philipp, G., Schmidt, H. // J. Non.-Cryst. Solids 1984. Vol. 63. P. 283 - 292.
27. Charbouillot, Y. // Ph.D. thesis, L'Institut National Polytechnique de Grenoble, July 1984.
28. Schmidt, H., Seiferling, B., Philipp, G., Deichmann, K. // Proceedings of the International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites. February 1987, San Diego/Florida, USA (in print).
29. Hutter, F., Haas, K. H., Schmidt, H. // Proceedings of the Second International Meeting on Chemical Sensors. 1986. Bordeaux, C.R.T.M. P. 443 - 446.

GLASS 89

*XV INTERNATIONAL CONGRESS
ON GLASS LENINGRAD 1989*

PROCEEDINGS

Volume 2a

*Properties of glass.
New methods of glass
formation.*

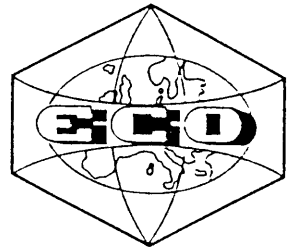
Technical sessions

Edited by O.V. Mazurin



LENINGRAD
„NAUKA“
LENINGRAD BRANCH
1989

PROCEEDINGS



Glasses for Optoelectronics

Giancarlo C. Righini
Chair/Editor

24-27 April 1989
Paris, France

ECO2

The Congress of

EPS—European Physical Society

Europtica—The European Federation for Applied Optics

SPIE—The International Society for Optical Engineering

Cooperating Organizations

ANRT—Association Nationale de la Recherche Technique

Associazione Elettrotecnica ed Elettronica Italiana

CNES—Centre National d'Etudes Spatiales

ICG—International Commission on Glass

GIFO—Groupement Industriel Français pour l'Optique

GNEQP—National Group on Quantum Electronics and Plasma Physics

Office of Solar Heat Technologies, U.S. Department of Energy

SEE—Société Française des Electriciens, des Electroniciens
et des Radioélectriciens

SPSE—The Society for Imaging Science and Technology

Published by

SPIE—The International Society for Optical Engineering
P.O. Box 10, Bellingham, Washington 98227-0010 USA
Telephone 206/676-3290 (Pacific Time) • Telex 46-7053

Volume 1128

SPIE (The Society of Photo-Optical Instrumentation Engineers) is a nonprofit society dedicated to advancing engineering and scientific applications of optical, electro-optical, and optoelectronic instrumentation, systems, and technology.



The papers appearing in this book comprise the proceedings of the meeting mentioned on the cover and title page. They reflect the authors' opinions and are published as presented and without change, in the interests of timely dissemination. Their inclusion in this publication does not necessarily constitute endorsement by the editors or by SPIE.

Please use the following format to cite material from this book:

Author(s), "Title of Paper," *Glasses for Optoelectronics*, Giancarlo C. Righini, Editor, Proc. SPIE 1128, page numbers (1989).

Library of Congress Catalog Card No. 89-62610
ISBN 0-8194-0164-1

Copyright © 1989, The Society of Photo-Optical Instrumentation Engineers.

Copying of material in this book for sale or for internal or personal use beyond the fair use provisions granted by the U.S. Copyright Law is subject to payment of copying fees. The Transactional Reporting Service base fee for this volume is \$2.00 per article and should be paid directly to Copyright Clearance Center, 27 Congress Street, Salem, MA 01970. For those organizations that have been granted a photocopy license by CCC, a separate system of payment has been arranged. The fee code for users of the Transactional Reporting Service is 0-8194-0164-1/89/\$2.00.

Individual readers of this book and nonprofit libraries acting for them are permitted to make fair use of the material in it, such as to copy an article for teaching or research, without payment of a fee. Republication or systematic or multiple reproduction of any material in this book (including abstracts) is prohibited except with the permission of SPIE and one of the authors.

Permission is granted to quote excerpts from articles in this book in other scientific or technical works with acknowledgment of the source, including the author's name, the title of the book, SPIE volume number, page number(s), and year. Reproduction of figures and tables is likewise permitted in other articles and books provided that the same acknowledgment of the source is printed with them, permission of one of the original authors is obtained, and notification is given to SPIE.

In the case of authors who are employees of the United States government, its contractors or grantees, SPIE recognizes the right of the United States government to retain a nonexclusive, royalty-free license to use the author's copyrighted article for United States government purposes.

Address inquiries and notices to Director of Publications, SPIE, P.O. Box 10, Bellingham, WA 98227-0010 USA.