

Molten Silicates  
and their Properties



# Molten Silicates and their Properties

by B. Lőcsei



1970

Chemical Publishing Co., Inc.

200 Park Avenue South

New York, N. Y.

## **Molten Silicates and Their Properties**

© 2011 by Chemical Publishing Co., Inc. All rights reserved.

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning or otherwise, except as permitted under Sections 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 646-8600, or on the web at [copyright.com](http://copyright.com). Requests to the Publisher for permission should be addressed to the Publisher, Chemical Publishing Company, through email at [info@chemical-publishing.com](mailto:info@chemical-publishing.com).

The publisher and the author make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation warranties of fitness for a particular purpose.

ISBN: 978-0-8206-0163-2

Chemical Publishing Company:  
[www.chemical-publishing.com](http://www.chemical-publishing.com)  
[www.chemicalpublishing.net](http://www.chemicalpublishing.net)

First American Edition: Chemical Publishing New York 1970

Printed in the United States of America

# Contents

I. Introduction	7
II. Historical	9
III. Basic principles of molten silicate production	13
(A) Processing of petrous materials	17
(B) Conditions for the formation of vitroceramics	20
IV. The governed crystallization of glasses	23
(A) Homogeneous and heterogeneous nucleus formation	23
(B) Nucleation and nucleating agents	40
V. Preparation of molten silicates	44
(A) Preparation of the raw material	44
(B) Melting	44
(C) Processing and shaping of the melt	48
(D) Crystallization	56
VI. Composition of vitroceramics on feldspar-diopside base	67
(A) Deduction of the composition of crystallized synthetic stone	67
(B) Comparison between the compositions of crystallized synthetic stone and molten rocks	72
(C) Generalization of the production principles of vitroceramics	79
VII. Crystallization mechanism of vitroceramics on feldspar-diopside base	92
VIII. Properties and possible applications of vitroceramics	121
References	131



## Chapter I

# Introduction

The rapid technical development in the 20th century has raised demands for the preparation and application of more and more new structural materials. Of the non-metallic materials, besides the various plastics, the importance of the application of glass and of other silicate products is on the increase. In the latter group belong the substances which may be classified under the collective term “molten silicates” and which up to the first half of the 1950’s were exclusively the by-products of rock processing. Earlier the crystallization of glass was an undesirable source of defects in glass manufacture. For this reason the study of crystallization ability is of special importance. At the same time the efforts to avoid crystallization threw light on crystallization conditions both from the theoretical and practical aspect. The information gained in this field may be utilized for both reducing and promoting crystallization tendencies whereby methods to control crystallization ability are being evolved.

RÉAUMUR was the first to attempt a transformation of glass into a crystalline substance, but all his experiments were frustrated by the deformation of the material during the crystallization process.

In the last 20 years RÉAUMUR’s old idea was brought up again, but now enriched by significant theoretical silicate chemical content to produce ceramic products by way of glass crystallization. Under the collective denomination of “molten silicates” we now understand ceramic materials produced from one or more base materials by melting. The material is molded in its liquid state like any other viscous material and converted in its bulk into a crystalline state by thermal treatment during cooling to avoid any significant change in shape, that is deformation, during thermal treatment [1].

Molten silicates may be classified into two groups:

- (a) Crystallization of the first type begins at a higher temperature during molding. The thermal treatment after molding only completes this process. This type of crystallization may be considered primary crystallization from the aspect of the “thermal past” of the substance. Crystallization begins during cooling when the crystallization temperature range is primarily reached, after having reached the liquidus temperature, that is the material has cooled below the liquidus temperature.

Into this group belong mainly molten silicate products obtained by melting of rocks and slags. This method is applied primarily to the processing of basalt and diabase [2–14].

- (b) In the second group belong the molten silicates called by HINZ [15] vitroceramics. These are characterized by being shaped in the glassy state

and by the fact that their crystallization begins during thermal treatment following forming at a lower temperature and proceeding towards higher temperatures where the crystallization process is terminated. This type of crystallization operation may be considered secondary, since during the crystallization process the substance reaches a second time the temperature range of crystallization. In addition, nucleators are usually added in the course of preparation. Nucleators are small quantities of additives which bring about deformation-free crystallization. This, that is nucleation kinetics, is the theoretical surplus of silicate chemistry by means of which RÉAUMUR's idea could be realized. Nucleators at the same time provide a possibility of varying the composition between wider limits and of arriving at more favorable material structures.

In this book the author could of course not attempt to discuss all the problems of vitroceraamics, firstly because of only a limited available space. His analysis will refer mainly to vitroceraamics in the  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO-Na}_2\text{O}$  system and to the mechanism of metal sulphide nucleation. He will also report his own results with heavy metal sulphide nucleating agents and his "micro-eutectic" principle. In the discussion of general theoretical problems he will also deal with certain aspects of  $\text{TiO}_2$  nucleation and this mainly for the sake of comparison, e.g. in the discussion of nucleation, that is of heterogeneous crystallization mechanism, he will demonstrate the control of  $\text{TiO}_2$  nucleation by means of sulphide, selenide and telluride, respectively.

Molten silicates owe their utilization as structural materials partly to their favorable mechanical and chemical properties. In addition because of some other advantages, e.g. dielectric properties, they play an important role in many industries. The basic principles of preparation of vitroceraamics were evolved in the past 20 years and the commercial manufacture of various material types was commenced in the near past.



## Chapter II

# Historical

It appears from the available literature that basalt melting was first performed in 1777 in France by d'ARCEL who, in the course of studying the crystallization conditions of magma, melted basalt in a porcelain crucible [3]. At the end of the 18th century the geologist GOLLOW [2] carried out also some work on the melting of eruptive rocks, and found that depending on the conditions of cooling, molten basalt will solidify to form either a vitreous or a crystalline solid. Somewhat later HALL and WATT melted basalt in a crucible and in a small rotation furnace. FOUQUÉ and MICHEL-LÉVY [1, 3] also carried out some important work in this field. They prepared synthetically a product corresponding petrographically with basalt, and thus, it was demonstrated that the method of cooling has a role in the textural structure of eruptive rocks – besides the chemical composition. They stated that “the origin of eruptive rocks is the consequence of their melting, followed by a slow cooling”. Their method at the same time raises the probability of producing such synthetic materials with compositions differing from that of natural basalt and their composition number adjusted so as to give the optimum application properties to the material. FOUQUÉ and MICHEL-LÉVY did not measure temperature in their experiments and their explanations concerning the phenomena are not right because of the basic concepts of silicate chemistry at that time were not yet clarified. Obviously they did not know the laws governing the solidification of heterogeneous systems [16].

In 1837, a German scientist, BISCHOFF performed experiments on basalt melting. He poured about 350 kg of basalt melt into a clay mold and succeeded in crystallizing the melt. ADCOCK was the first taking out a patent for invention on the melting of basalt and the processing of the melt in the middle of the past century. He wanted to make glass from molten basalt, but did not envisage the difficulty that the basalt melted by blowing may not be molded because of its crystallization on heating. Thus if the ball on the blowing iron is again immersed in the melt, the already blown material will crystallize as shown by Hungarian experiments, too. In the production of large articles cooling rate was not high enough to allow the material to cool in a homogeneous vitreous state and the formation of crystal nuclei made the material brittle. This explains why was ADCOCK's invention a failure and completely forgotten [3].

The Mauritian French doctor RIBBE carried out some melting experiments with French basalts, and established the conditions for their melting and thermal treatment. Later the engineer DRIN investigated the application possibilities of the material in industry. As a result of their work the Compagnie Générale de Bazalte was founded in Paris having two factories,

one in the vicinity of Paris working with gas-heated furnaces and a daily capacity of 10 tons, the other in Auvergne with a capacity of 8 tons per day, and using electric melting furnaces [1, 6, 9].

In 1922 a basalt melting plant was established in Kahlenborn in Germany on the basis of French literature data and experience. In the 1920's the Soviet Union too began research on the melting of basalt, in 1926 GINZBURG in the Laboratory of the Rock Research Institute and FLORENSKII in the State Research Institute for Electrotechnique were working on the problem [2]. The laboratory experiments were soon followed by pilot plant trials on whose experience a factory with a yearly capacity of 5000 tons was built. The first diabase works started operation in Moscow in 1932. Experiments have shown the diabases from the Oniega district to have the most favorable technological properties. In Leningrad the Armenian andesite-basalt deposits were investigated and an appropriate technology for their processing worked out.

After World War II Czechoslovak specialists also began to be interested in molten silicates, since they had some earlier favorable experiences with molten basalt of German origin. They began their experiments in 1948 and within a few years had two plants operating with daily 16 and 10 ton capacities, respectively and today it has become necessary to plan for expansion. Poland set up a similar factory in 1954 [17-19].

In Hungary investigation of the production conditions of molten silicates began in the Glass Department of the Research Institute for Heavy Chemical Industries in 1951. Beside basalt melting experiments another type was also elaborated first on furnace slag base and later, after having clarified the role and essence of nucleation, a general process based on oxide synthesis and independent of the base material was envisaged. This work may be considered the first step in the production of vitroceraamics or of ceramics produced by the nucleated crystallization of glasses. LŐCSEI and his research group have applied first in 1951, then in 1953 and 1957 for patents covering the production of secondarily crystallizing vitroceraamics [20-23].

BECKER has prepared as far back as the 1930's primarily crystallizing molten silicates with high fluorine content [30, 31]. Later in 1952 WAGNER also produced crystallizing materials with high fluorine content.

STOOKEY applied in 1953 for patents covering pyroceraamic and photo-ceraamic materials which resulted from the development of photosensitive glasses. The material was prepared on lithium silicate, lithium magnesium aluminum silicate base with metal (Ag, Au, Cu) and  $TiO_2$  nucleation [25-29]. In the Corning Works thorough research is in progress under STOOKEY's direction leading to four main types [28]. POLINSZKY and LŐCSEI have reported on the production possibilities of vitroceraamics on furnace slag base [81]. In 1956 LUNGU [32, 33] published his results on a vitroceraamic in the  $SiO_2-Al_2O_3-MgO-Na_2O$  system produced by fluoride nucleation. This was followed by types worked out in Great Britain as a result of the work of CLAYPOOLE, MACMILLAN, PARTRIDGE and HODGSON in the years between 1959 and 1963 [34-39].

In the Soviet Union a new type of vitroceraamic material was marketed in 1960 under the trade-name "Sital" [40]. RINDONE studied the nucleation

mechanism of lithium aluminum silicate crystallization when metallic platinum is added [41].

Since 1960 research is in progress in many institutes of many countries aiming at the preparation of new vitroceraamics and at the clarification of silicate chemical processes [42–68]. In 1960 HINZ and WISHMANN produced a molten silicate of microcrystalline structure from copper slag glass obtained by melting and by the addition of  $\text{Cr}_2\text{O}_3$ .

HINZ and KNUTH studied the effect of small quantities of diverse additives on the properties of pyroceramic type materials in the  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system [69].

In the Institute in Hradetz-Kralove VOLDAN is engaged in the investigation of the silicate chemical principles of vitroceraamic materials and BROUKAL in that of pyroceramic soldering vitroceraamics [70, 71].

In the Soviet Union vitroceraamics on furnace slag base are being produced since 1962, in Poland since 1964, in both countries production is based on principles which are in agreement with LŐCSEI's experimental results [72, 73]. VOGEL and GERTH [74] and later MAURER [75] clarified many details of the nucleation mechanism and the importance of homogeneous and heterogeneous catalysis.

The study of vitroceraamics received particularly great impetus in the past years both from the theoretical and the engineering aspect producing a continuous succession of new results. Interest is focused on the kinetical and thermodynamical study of nucleation [173–179]. The properties of lithium aluminum magnesium silicates nucleated with phosphates were studied by PARTRIDGE and MACMILLAN who found a new method for the processing of vitroceraamics [194, 196]. The development of vitroceraamics which may be used as solders is to a major part also the merit of these authors [197]. HODGSON and MACMILLAN reported on neutron absorbent vitroceraamics [198]. Control of crystallization tendency and within this of crystallization rate by means of the combined application of nucleating agents is again a theoretical result which will obviously bring about an extension of the composition of vitroceraamics [171].

An interesting development of the research on vitroceraamics is the improved strength by surface treatment. When vitroceraamics immersed in some liquid salt are subjected to heat treatment, the surface layer will shrink as a result of ion exchange and a compressive stress will develop resulting in a considerable improvement of crushing strength. KARSTETTER et al. in the Corning Works have been engaged in the study of this problem [186–193].

Another recent result is the influencing of the crystallization mechanism to form on the surface of the vitroceraamic material a crystalline layer of different structure in a single operation during crystallizing thermal treatment. This is another recent solution to improve the flexural strength of vitroceraamics [171].

The new possibility of coloring vitroceraamics has also extended the application possibilities of these materials [181, 184]. Materials with high thermal expansion coefficients in the  $\text{SiO}_2-\text{P}_2\text{O}_5-\text{Al}_2\text{O}_3-\text{CaO}-\text{MgO}$  system or vitroceraamics with ZnO or BaO content can be coated with metals [180,

## References

1. FOUQUÉ and MICHEL-LÉVY, in LŐCSEI, B.: *The silicate chemical basis of the preparation of crystallized synthetic stone* (Thesis, in Hungarian) Budapest, 1956
2. GOLLOW, in GINZBURG, A. C.: *Nemetallicheskie iskopaemye* **16** 7 (1943)
3. FOUQUÉ et MICHEL-LÉVY, in PORTEVIN, A.: *Le basalte fondu*. Mém. Compt. rend. Soc. Ing. Civ. de France. 1928, 266—300
4. McMILLAN, P. W.: *Glass-Ceramics*. Academic Press, London, New York, 1964
5. RÉAUMUR, M.: *Mémoires de l'Académie des Sciences*. 1739, pp. 370—388
6. KNAPP, O.: *Crystallization of Silicate Glasses*. Akadémiai Kiadó Budapest, 1964 (in Hungarian)
7. RISSE, K.: *Archiv f. d. Eisenhüttenwesen* **3** 437 (1930)
8. KEIL, F.: *Hochofenschlacke*. Düsseldorf, 1949
9. ORMONT, B. F.: *Acta Physicochimica U.R.S.S.* **20** 503 (1945)
10. ORMONT, B. F.: *Acta Physicochimica U.R.S.S.* **20** 737 (1945)
11. ORMONT, N. N.: *Vestnik Moskovskogo Universiteta* **5** 117 (1950)
12. FENNER, C. N.: *Amer. J. Sci.* **18** 219 (1929)
13. JUGOVICS, L.: *Magyar Technika* **1** 35 (1949)
14. BARTH, T. F. W.: *Amer. J. Sci.* **31** 321 (1936)
15. HINZ, W.: *Silikate. Einführung in Theorie und Praxis*. Veb. Verlag für Bauwesen, Berlin 1963
16. EITEL, W.: *The Physical Chemistry of the Silicates*. The University of Illinois, Chicago Press, Chicago 1954
17. PELIKAN, A.: *Molten rocks*. Nakl. Prace, Praha, 1955 (in Czech)
18. VOLDÁN, J.: *Sklar a keramik.* **14** 220 (1964)
19. NEBRENSKIJ, J. and VOLDÁN, J.: New methods for the crystallization of glass. *Informationi prochled SVUS* (1961) (in Czech)
20. LŐCSEI, B., POLINSZKY, K., SCHLIESS, J. and SOLTÉSZ, E.: Hungarian Patent No. 243, 012/1952
21. LŐCSEI, B., SOLTÉSZ, E., FODOR, E. and VÁRTAY, E.: Hungarian Patent No. 143.041
22. LŐCSEI, B. P.: Hungarian Patent No. 146.137
23. LŐCSEI, B. P.: DRP 1.085.804
24. WAGNER, H.: DRP 863.176
25. STOOKEY, S. D.: DRP 962.110
26. STOOKEY, S. D.: DAS 1.045.056
27. STOOKEY, S. D.: *Ceramic Fabrication Process* **21** 189 (1958)
28. STOOKEY, S. D.: *Engng. Chem.* **51** 805 (1959)
29. STOOKEY, S. D.: USA Patent 2.515.939
30. BECKER, H.: DRP 410.351
31. BECKER, H.: DRP 430.387
32. LUNGU, S. N. and POPESCU-HAS, D.: *Studii si cercetari de chemie* **7** 225 (1955)
33. LUNGU, S. N. and POPESCU-HAS, D.: *Építőanyag* **10** 86 (1958)
34. MAURER, R. D.: *J. Appl. Phys.* **29** 1 (1958)
35. CLAYPOOLE, S. S.: Brit. Patent, No. 822.272 (1959)
36. McMILLAN, P. W. and HODGSON, B. P.: Brit. Patent, No. 31718 (1959)
37. McMILLAN, P. W. and HODGSON, B. P.: Brit. Patent, No. 944.571 (1963)
38. McMILLAN, P. W. and PARTRIDGE, G.: Brit. Patent, No. 8738 (1959)
39. McMILLAN, P. W. and PARTRIDGE, G.: Brit. Patent, No. 924.996 (1963)
40. KITAIGORODSKY, I. I. and BONDARYEV, K. T.: *Steklo i Keramika* **20** 1 (1963)
41. RINDONE, G. F.: *Amer. Cer. Soc.* **41** 41 (1958)

42. ALBRECHT, F.: *Beispiele angewandter Forschung. Neuartige Hartstoffe aus Glas. München*, 1955 pp. 19–22
43. BÁRTA, R.: *Silikáty* **2** 296 (1958)
44. HINZ, W.: *Silikattechnik* **10** 596 (1959)
45. KOPECZKY, L. and VOLDÁN, J.: *Crystallization of molten rocks*. Prague, 1959
46. LILLIE, H. R.: *Glass Technology* **1** 115 (1960)
47. LIN, F. C.: *Glass Ind.* **40** 717 (1959)
48. LUNGU, S. N. and POPESCU-HAS, D.: *Industria Usoara* **2** 64 (1958)
49. LUNGU, S. N. and POPESCU-HAS, D.: *Silicates Industries* **22** 391 (1958)
50. MORIYA, T., SAKAIONI, T., SAINO, H. and ENDO, M.: *J. Cer. Ass. Japan* **68** 44 (1960)
51. MUNIER, J. H.: *Proc. Engng.* **29** 87 (1958)
52. RINDONE, F. E.: *J. Amer. Ceram. Soc.* **45** 7 (1962)
53. ROSENBERG, W.: *Mach. Design.* **31** 29 (1959)
54. SIMPSON, H. E.: *Glass Industry* **40** 13, 17 (1959)
55. SELYUBSKY, V. I. and VAISFELD, N. N.: *Steklo i keramika* **17** 23 (1960)
56. TAMURA, Y.: *J. Cer. Assoc. Japan* **66** 325 (1958)
57. TASITO, H. and WADA, S.: *J. Cer. Assoc. Japan* **66** 390 (1958)
58. TRANZEN, C.: DRP 569.310
59. TURNBULL, D. and VONNEGUT, B.: *Ind. Engng. Chem.* **44** 1292 (1952)
60. BECKER, B.: DRP 630.898
61. WAGNER, H.: DRP 910.038
62. WAGNER, H.: DRP 927.978
63. WAGNER, H.: DRP 952.514
64. MAURER, R. D.: *J. Appl. Phys.* **29** 1 (1958)
65. VOLDÁN, J.: Czechoslovak. Patent 92.750
66. WEYL, W.: *Sprechsaal* **93** 128 (1960)
67. WIHSMANN, F.: *Thesis*. Bergakademie Freiberg, 1959
68. ZHUKOVSKY, E. V. and PORTUGALOV, D. I.: *Steklo i keramika* **15** 41 (1958)
69. HINZ, W. and KNUTH, P. O.: *Silikattechnik* **11** 605 (1960)
70. VOLDÁN, J.: *Silikattechnik* **7** 48 (1956)
71. BROUKAL, J.: *Silikattechnik* **13** 48 (1962)
72. KITAIGORODSKY, I. I.: *Zhurn. Vses. Khim. Obshsh. im. D. I. Mendeleeva* **8** 192 (1963)
73. ZIEMBA, B. and CHLOPICKA, E.: *Steklo i Keramika* **12** 69 (1965)
74. VOGEL, W. and GERTH, K.: *Zeitschr. Chemie* **2** 261 (1962)
75. MAURER, R. D.: *J. Appl. Phys.* **33** 2132 (1962)
76. TAMMANN, G.: *Kristallisieren und Schmelzen*. J. A. Barth, Leipzig, 1903
77. TAMMANN, G.: *Aggregatzustände*. L. Voss Verlagsh. Leipzig, 1923
78. TAMMANN, G.: *Der Glaszustand*. L. Voss Verlagsh. Leipzig, 1933
79. LŐCSEI, B.: *Experiments to produce glass and synthetic stone profiles*. NEVIKI, Report No. 79. (in Hungarian) 1952
80. GROFCSIK, J.: *Preparation of crystallized synthetic stone (Five Years of NEVIKI)*. Veszprém, 1954 (in Hungarian)
81. POLINSZKY, K. and LŐCSEI, B.: *Magyar Technika* **6** 216 (1954)
82. PREBUS, A. F. and MICHENER, J. W.: *Physic. Rev.* **87** 201 (1952)
83. SELYUBSKY, V. I.: *Steklo i Keramika* **11** 19 (1954)
84. OBERLIES, F.: *Naturwiss.* **43** 224 (1956)
85. VOGEL, W. and GERTH, K.: *Glastechn. Ber.* **31** 15 (1958)
86. VOGEL, W. and GERTH, K.: *Silikattechnik* **9** 353 (1958)
87. VOGEL, W. and GERTH, K.: *Silikattechnik* **9** 495 (1958)
88. SKATULLA, W., VOGEL, W. and WESSEL, H.: *Silikattechnik* **9** 19 (1958)
89. VOGEL, W.: *Silikattechnik* **9** 323 (1958)
90. VOGEL, W.: *Silikattechnik* **10** 241 (1959)
91. HOFFMANN, L. C. and STATTON, W. O.: *Nature* **176** 561 (1955)
92. PORAX-KOSHITS, E. A.: *Glastechn. Berichte* **3** 450 (1959)
93. VOGEL, W. and GERTH, K.: *Zeitschr. Chemie* **2** 261 (1962)
94. VOGEL, W.: *Symposium sur la fusion du verre*. Bruxelles 1958. *Compte rendu, Union scientifique Continentale du verre*. 741
95. STOOKEY, S. D.: *Glastechn. Ber.* **32** 1 (1955)

96. VOGEL, W. and GERTH, K.: Symposium on nucleation and crystallization in glasses and melts. *Amer. Ceram. Soc.* p. 11 (1962)
97. ROY, R.: Symposium on nucleation and crystallization in glasses and melts. *Amer. Ceram. Soc.* p. 39 (1962)
98. OHLBERG, S. M., GOLOB, H. R. and STRIKLER, D. W.: Symposium on nucleation and crystallization in glasses and melts. *Amer. Ceram. Soc.* p. 55 (1962)
99. RINDONE, G. E.: Symposium on nucleation and crystallization in glasses and melts. *Amer. Ceram. Soc.* p. 63 (1962)
100. LÖCSEI, B. P.: Symposium on nucleation and crystallization in glasses and melts. *Amer. Ceram. Soc.* p. 71 (1962)
101. HILLIG, W. B.: Symposium on nucleation and crystallization in glasses and melts. *Amer. Ceram. Soc.* p. 77 (1962)
102. WESTMANN, A. E. R. and KRISHNA-MURTHY, M.: Symposium on nucleation and crystallization in glasses and melts. *Amer. Ceram. Soc.* p. 91 (1962)
103. VOGEL, W.: *Zeitschr. Chemie* **3** 313 (1963)
104. VOGEL, W.: *Zeitschr. Chemie* **3** 154 (1963)
105. VOGEL, W.: *Zeitschr. Chemie* **3** 271 (1963)
106. LÖCSEI, B. P.: *Interceram.* No. **2** 133 (1966)
107. FRENKEL, J.: *Kinetic Theories of Liquids*. Clarendon Press. Oxford 1946
108. LÖCSEI, B. P.: *Építőanyag* **14** 241 (1962)
109. LÖCSEI, B. P.: *Silikattechnik*, in press
110. VOLMER, M.: *Kinetik der Phasenbildung*. Dresden-Leipzig 1939
111. ZACHARIASEN, W. H.: *J. Amer. Chem. Soc.* **54** 3841 (1939)
112. WARREN, B. E.: *Zeitschr. Krist.* **86** 349 (1933)
113. MACKENZIE, J. D.: *Modern Aspects of the Vitreous State*. Reinhold, New York 1959
114. VOGEL, W.: *Struktur und Kristallisation der Gläser*. V. f. Grundstoffindustrie, Leipzig 1965
115. McMILLAN, P. W.: *Glass Ceramics*. Academic Press, London-New York 1964
116. JEBSSEN-MARWEDEL, H.: *Glastechn. Ber.* **29** 223 (1956)
117. JEBSSEN-MARWEDEL, H.: *Kolloid-Zeitschr.* **137** 118 (1954)
118. JEBSSEN-MARWEDEL, H.: *Naturwiss.* **45** 260 (1958)
119. JEBSSEN-MARWEDEL, H.: *Kolloid-Zeitschr.* **150** 137 (1957)
120. JEBSSEN-MARWEDEL, H.: *Glastechn. Ber.* **31** 431 (1958)
121. JEBSSEN-MARWEDEL, H.: *Glastechnische Fabrikationsfehler*. Springer Verl. Berlin, 1959
122. VERESS, Z.: Verbal communication; 1960
123. DIETZEL, A.: *Zeitschr. Elektrochem.* **43** 9 (1942)
124. KLOBER, W.: *Silikattechnik* **13** 5 (1962)
125. GARNER, W. E.: *Chemistry of the Solid State*. Clarendon P., London, p. 159, 1955
126. GUTZOW, J.: *Zeitschr. anorg. allg. Chem.* **302** 259 (1959)
127. HINZ, W.: *Silikattechnik* **10** 119 (1959)
128. FOUQUÉ, F. and MICHEL-LÉVY, A.: *Synthèse des Roches*, Paris, 1889
129. AVGUSTINNIK, A. I.: *Silikattechnik* **12** 275 (1961)
130. SALMANG, H.: *Physikalische und chemische Grundlagen der Keramik*. Springer Verl. 1958
131. OKOROKOV, S. D., VOLFSO, S. L. and KORNEEVA, T. F.: *Rab. Leningr. Tehn. Inst. im. Lensoveta* **56** (1960)
132. TOROPOV, N. A., VOLFSO, S. L. and SICHEV, N. M.: *Rab. Konf. Cement, Promstroizdat* 1956
133. ZHURAVLEV, V. F., VOLFSO, S. L. and SICHEV, N. M.: *Cement SSSR* **3** (1950)
134. KUKOLEV, G. V. and YALIMOVA, M. A.: *Petrografi i prikladnoi mineralogii SSSR* **2** (1953)
135. BUDNIKOV, P. P. and BEREZHNOI, A. S.: *Solid state reactions*. Promstroizdat, Moscow, 1949 (in Russian)
136. BEREZHNOI, A. S.: *Zhurnal prikladnoi khimii* **13** 800 (1940)
137. HEDVALL, J. A.: *Zeitschr. phys. Chem.* **33** 125 (1926)
138. BOBROVNIK, D. P. and BUDNIKOV, P. P.: *Zhurnal prikladnoi Khimii* **21** 7 (1948)
139. POLUBOYARINOV, D. N. and VIDIK, G. A.: *Doklady AN SSSR* **88** 325 (1953)
140. KUKOLEV, G. V. and DOLGIKH, G. S.: *Ogneypory* **12** 536 (1950)
141. NAZARENKO, M. F. and PAZUMOVA, V. L.: *Ogneypory* **65** 12 (1957)

142. LŐCSEI, B.: *Ber. d. Deutsch. Keram. Ges.* **42** 277 (1965)
143. KUKOLEV, G. V. and SCHEGLOV, S. I.: *Zhurn. Prikl. Khimii* **29** 1502 (1956)
144. BESBORODOV, N. A.: *Glass Ceram. Bull. India* **54** (1960)
145. HEDWALL, J. A.: *Glass Ceram. Bull. India* **29** (1960)
146. RICHARDS, R. G. and WHITE, J.: *Trans. Brit. Ceram. Soc.* **40** 53 (1954)
147. LAYDON, G. A. and MCQUERRIE, W.: *J. Am. Ceram. Soc.* **42** 89 (1959)
148. LŐCSEI, B.: The effect of nucleators on the crystallization of glasses. *Éakki Report*, Budapest 1966 (in Hungarian)
149. WEYL, W. A. and MARBORE, E. C.: *Glass Ind.* **41** 429, 487, 549, 620 (1960)
150. NEVEUX, V.: *Génie civil* **87** 57 (1925)
151. DRIN, L.: *Chimie et Industrie* **4** 662 (1922)
152. DALY, R. A.: *Igneous Rocks and the Depth of the Earth*. New York 1933
153. BEYERSDORFER, P.: *Silikattechnik* **5** 381 (1954)
154. VOLDÁN, J.: *Sklar a Keramik* **5** 14 (1955)
155. VOLDÁN, J.: *Sklar a Keramik* **5** 27 (1955)
156. LŐCSEI, B.: Glass melting in shaft furnaces. *SziKKI Report*, Budapest 1965 (in Hungarian)
157. LŐCSEI, B.: Experiments to produce crystalline synthetic stone. *NEVIKI Report*, No. 109, Veszprém 1955 (in Hungarian)
158. BEREZSNOI, A. I.: Svetochyivstvitelnie stekla i steklokristallicheskie materialy tipa "Pirokeram". *VINITI* Moscow (1960) (in Russian)
159. KORACH, M.: *Építványag* **10** 1 (1958)
160. HARTMAN, F.: *Stahl u. Eisen* **53** 509 (1933)
161. LAMORF, J.: *Stahl u. Eisen* **56** 1006 (1936)
162. ENDELL, K.: *Stahl u. Eisen* **40** 213, 1 (1960)
163. LŐCSEI, B.: *Acta Chim. Acad. Sci. Hung.* **22** 1 (1960)
164. EYSTROPYEV, K. S. and TOROPOV, N. A.: *Chemistry of silicon and physical chemistry of silicates*. (In Hungarian) Nehézipari Kiadó, Budapest 1951
165. EITEL, W.: *Die heterogenen Schmelzgleichgewichte silikatischer Mehrstoffsysteme* Springer, Leipzig 1941
166. MOREY, G. W.: *The Properties of Glass*. Reinhold, New York 1952
167. OSBORNE, E. F.: *J. Amer. Ceram. Soc.* **33** 219 (1950)
168. VOLAROVICH, M. F. and LEONTYEV, A. A.: *Compt. rend.* **55** 241 (1947)
169. LŐCSEI, B.: *Építványag* **11** 247 (1959)
170. LŐCSEI, B.: *Silikattechnik* **17** 249 (1966)
171. LŐCSEI, B.: Unpublished data
172. LITTLE, J. R. and DEC�ERK, D. H.: *Mitt. Deutsch. Emailfachleute E. V.* **14** 93 (1966)
173. MASKOVICH, M. O. and VARSAL, B. G.: *Neorganicheskie materialy* **3** 1668 (1967)
174. KUMAR, S. and NAG, B. B.: *J. Am. Ceram. Soc.* **49** 10 (1966)
175. LAJARTE, S.: *Silic. Ind.* **38** 177 (1958)
176. KITAIGORODSKY, I. I., RABINOVITS, E. M. and SELYUBSZKY, V. I.: *Steklo i keramika* **1** 20 (1963)
177. McDOWELL, J. F.: *Ind. a Eng. Chem.* **58** 39 (1966)
178. THACH-LAN, T.: *Verre. Refr.* **56** 416 (1965)
179. BAYER, G. and HOFFMANN, F.: *Glass Techn.* **7** 94 (1966)
180. LITTLE, J. R., DEC�ERK, D. H.: *Mittl. V. D. Email* **14** 93 (1966)
181. LŐCSEI, B. P. and KARABÉLYOS, P.: *Építványag* **20** 74 (1968)
182. FEDOROVSKY, A. and TIKACHINSKY, J. D.: *Steklo. Inst. Stekla* **15** 51 (1964)
183. ANON: *Steklo i keramika* **17** 85 (1966)
184. EMRICH, B. R.: *Mater. Des. Eng.* **62** 95 (1965)
185. SCHLEIFER, P.: *Steklo i keramika* **17** 85 (1966)
186. KIVLIGHN, H. D.: USA Patent 3.146.114 (1964)
187. McDOWELL, F.: USA Patent 3.201.266 (1965)
188. MWKHERJEC, S. P. and ROGERS, P. S.: *Phys. Chem. of Glass* **8** 81 (1967)
189. SCHARBACH, H.: *Werkst. u. Korr.* **16** 2 (1965)
190. DUKO, D. A., McDOWELL, J. F. and KARSTETTER, B. R.: *J. Am. Ceram. Soc.* **50** 67 (1967)
191. BEALL, G. H., KARSTETTER, B. R. and RITTLER, H. L.: *J. Am. Ceram. Soc.* **50** 181 (1967)
192. KARSTETTER, B. R. and VOSS, R. O.: *J. Am. Ceram. Soc.* **50** 133 (1967)

193. Brit. Patent 822.272 (1966) Corning Glass Works
194. McMILLAN, P. W. and PARTRIDGE, G.: Brit. Patent. 943.599; 944.571 (1960)
195. Brit. Patent. 869.315 (1958), Corning Glass Works
196. Brit. Patent. 924.996 (1959)
197. McMILLAN, P. W., HODGSON, B. P. and PARTRIDGE, G.: *Glass Technol.* **7** 121, 128 (1966)
198. HODGSON, B. P. and McMILLAN, P. W.: *Glass Technol.* **4** 173 (1963); **5** 142 (1964)
199. TASHIRO, M.: *Glass Ind.* **46** 366 (1966)







