

SYNTHESIS OF ZIRCON

Sridhar Komarneni and Rustum Roy
Materials Research Laboratory
The Pennsylvania State University
University Park, PA 16802

ABSTRACT

This review paper deals with the synthesis of both zircon powders and single crystals. Zircon powders can be prepared by solid state dry firing and hydrothermal reaction; solution-sol-gel derived powders can be combined with both methods. Of the various combinations, the hydrothermal method is the best for obtaining fine (~75 nm) powders at a temperature as low as 200°C under autogeneous pressure. Single crystals of zircon can be made by flux growth as well as hydrothermal methods, the latter using seeds. Although both methods yield large single crystals, the hydrothermal method is superior for obtaining pure crystals with little or no impurities.

INTRODUCTION

Zircon is a naturally occurring mineral and is an important component of igneous and metamorphic rocks. Its occurrence is common in detrital sediments or deposits derived from the above primary provenances. Because of its high stability, zircon has been extensively studied to obtain information on the geochemical and weathering conditions of sediments and soils. Single crystals of zircon, both clear and colored, have long been used as gemstones: the name zircon is very old and is believed to be derived from the Arabic zarqun, in turn derived from zar, gold, and gun color (Deer et al., 1962).¹

Zircon is extensively used in ceramics and related applications and is obtained from major commercial zircon deposits in Australia, U.S. (Florida), South Africa, India, Brazil and the USSR.² The main use of zircon in ceramics is as a refractory material because of its refractoriness, thermal stability and non-reactivity with many glasses and slags. Zircon also has a low thermal expansion and good hardness which are also useful for some ceramic applications. Dense zircon shapes formed by casting or isostatic pressing are used for glass contact areas in glass tanks.^{2,3} Zircon-containing bricks have been used in the most severe wear areas of steel ladles.^{4,5} Alumina-zirconia-silica (AZS) composite refractories made with zircon are used in a variety of applications such as feeder parts of glass, kiln furniture, crucibles and furnace linings. Zircon is the raw material for the manufacture of zirconium oxide and zirconia-alumina abrasives. Another major use of zircon is in the whitewares industry as a glaze pacifier for tile and sanitary ware because of zircon's high index of refraction, light color, low solubility in glass and compatibility with ceramic colors. Zircon is also used in miscellaneous applications such as

special glasses, porcelain enamels because of its high index of refraction, alkali resistance and radiation stability.² Zircon is also used as a minor component of fiber glass to improve the alkali resistance of fiber used for reinforcing concrete. Because of the above technological applications, there is a growing interest in the synthesis of zircon by different methods which can lead to superior products such as glazes. The present paper is a review of zircon synthesis studies and begins with the stability of zircon and the ZrO_2 - SiO_2 phase diagram.

Stability of Zircon and the ZrO_2 - SiO_2 Phase Diagram

Because of the geological and technological importance of the zircon phase, it is desirable to know the information on the thermal stability of zircon. A review of the literature shows that there is even now no consensus on the temperature or the manner of breakdown of zircon. The stability data of various investigators was summarized by Buttermann and Foster⁶ as given in Table I. The data presented in Table I show that there are conflicting opinions about the thermal stability of zircon. The earliest phase diagrams of Washburn and Libman⁷ and Zhirnowa⁸ for this system show that zircon is a congruently melting compound (Table I). However, subsequent work by Geller and Lang⁹ and Cocco and Schromek¹⁰ shows zircon as melting incongruently (Table I). Zircon was shown to decompose in the solid-state at 1540°C by Curtis and Sowman¹¹ and this decomposition temperature is about 135°C lower than the ZrO_2 - SiO_2 eutectic. There is also controversy about the role of liquid immiscibility.^{6,12} These discrepancies could be attributed to the extent of impurities in the zircon samples used.¹³ Two phase diagrams, one by Levin et al.¹⁴ and one by Buttermann and Foster⁶ are shown in Figures 1 and 2.

Zircon Synthesis Studies

As with any other ceramic oxide, zircon powders and single crystals can be prepared by various methods such as solid state, flux growth, hydrothermal, sol-gel, etc. This review of zircon synthesis begins with powders and is followed by single crystals.

Zircon Powder Synthesis

a. Solid State Method. According to Frondel and Collette,¹⁵ zircon was first synthesized by Deville and Caron (1958)¹⁶ by the action of SiF_4 on ZrO_2 and ZrF_4 on SiO_2 at red heat. Zircon has been synthesized from the oxides of zirconium and silicon by various investigators at different temperatures. Zircon synthesis was reported at 1460°C by Clark and Reynolds,¹⁷ at 1500°C by Barlett¹⁸ and Stot and Hilliard¹⁹ and at 1700°C by Geller and Yavorsky.²⁰ These authors, however, did not investigate the maximum and minimum temperatures at which zircon can be synthesized. However, Curtis and Sowman¹¹ found a lower temperature limit of about 1315°C for zircon synthesis in zircon crucibles using milled zirconia and silica, the latter in the form of either quartz, cristobalite, amorphous silica, or tridymite. Frondel and Collette¹⁵ used

coprecipitated ZrO_2 and SiO_2 gels and found that they did not react when heated for 24 hours in air at 800° or 900°C but reacted to form zircon in the temperature range of 1000° to 1500°C .

Mumpton and Roy²¹ prepared zircon by dry heating 1:1 zirconia:silica gel starting material to about 1300°C for 24 hours to study its dissociation at high temperatures.

b. Hydrothermal Method. Maurice²² is one of the first to use hydrothermal method to synthesize zircon from $\text{ZrO}(\text{OH})_2$ and silicic acid. Frondel and Collette¹⁵ synthesized microcrystalline zircon over the range 150° to 700°C by heating gelatinous ZrO_2 and SiO_2 with water in steel bombs under hydrothermal conditions. They found that the reaction is speeded by adding traces of ZrF_4 to the mixture. The hydrothermally synthesized zircon gave all unit cell dimensions identical with those of dry-sintered ZrSiO_4 at 1000°C (Table II).

Mumpton and Roy²¹ used concentrated NH_4OH to simultaneously precipitate ZrCl_4 and SiCl_4 as hydroxide gel and treated the 1:1 composition gels under hydrothermal conditions which consistently yielded well-crystallized zircon as low as 250°C under $40,000 \text{ lb/in}^2$ water pressure in 30-day runs. However, at 200°C and lower, in runs of less than 1 week these gels yielded poorly crystallized zircon-like material.

Zircon has been synthesized²³ from SiO_2 and ZrO_2 , a large number of zirconium mineral salts such as $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, and $\text{ZrF}_4 \cdot \text{H}_2\text{O}$ and an organic compound of zirconium, $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4$ serving as the ZrO_2 source under hydrothermal conditions. Well-crystallized zircon was obtained at 200°C or above with 350 or 700 bars of confining pressure.

Vilmin, Komarneni, and Roy²⁴ prepared a zircon sol hydrothermally by treating at 175° - 200°C for 48 hours in a mixture of the appropriate volumes of a $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ solution and tetraethylorthosilicate (TEOS) in ethanol. The ZrSiO_4 crystallites prepared at 175°C are non-uniform in size (Fig. 3A) while those prepared at 200°C are lense shaped, 60 nm thick and 300 nm diameter (Figs. 3B, 3C). The above hydrothermal experiments conducted with autogeneous pressure led to ultrafine powders of zircon. These powders are potentially useful in glazes. It is obvious from the above results that zircon fine powder can be prepared at a much lower temperature under hydrothermal conditions than possible under solid state dry firing conditions.

c. Solution-Sol-Gel Method. A sol-gel method was reported by Yokihiro and Yamato²⁵ for the preparation of zircon at low temperatures of about 1180° to 1200°C . This method involves the mixing of an aqueous solution of $\text{Si}(\text{OC}_2\text{H}_5)_4$ and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ with 0.06 mole of HCl per mole of $\text{Si}(\text{OC}_2\text{H}_5)_4$ as catalyst, drying the solution over a period of several days to form the gel from the solution and calcining the gel at different temperatures to crystallize zircon.

Recently, Vilmin, Komarneni, and Roy²⁴ prepared zircon by using different sol-gel precursors and to see their effect on zircon crystallization. A monophasic gel was prepared by mixing appropriate volumes of tetraethoxysilane and a zirconium oxychloride solution in ethanol and heating the mixture at 40°C. The addition of hydrothermally prepared zircon seeds to the same solution prior to gelation yielded a structurally diphasic gel. A compositionally diphasic gel was made using a monoclinic zirconia sol and a commercial silica sol and gently heating at 70°C to gel. The zircon gels which are both compositionally and structurally diphasic were made by simply mixing the crystalline zircon seed sol with the mixture of silica and zirconia sols and gelling at 70°C. All these zircon precursor gels were calcined to determine the crystallization temperature of zircon (Table III) which showed that both the compositionally and structurally diphasic gels yielded zircon at the lowest temperature.

d. Combined Sol-Gel and Hydrothermal Methods. In this method, Komarneni et al.,²⁶ first made single and diphasic gels of zircon composition and then treated them hydrothermally. The single phase zircon gels were made by mixing stoichiometric amounts of $ZrOCl_2 \cdot 8H_2O$ and tetraethoxysilane and aging at 60°C while the diphasic gels were made by mixing stoichiometric amounts of zirconia and silica sols and aging at 60°C. These gels were then treated hydrothermally in gold capsules in cold-seal vessels at 450° to 600°C under a confining pressure of 100 MPa. The crystallization behavior of single and diphasic gels was found to be different under these hydrothermal conditions. The single phase gels yielded zircon under all the treatment conditions (Table IV) while the diphasic gels resulted in only zircon at the highest temperature of treatment, i.e., 600°C but yielded zircon and baddeleyite at 400° and 500°C. The silica and zirconia components in the diphasic gel appear to react independently at low temperatures and thus forming the zirconia phase, baddeleyite. On the other hand, the single phase gels resulted in zircon at all temperatures due to atomic scale mixing of the two components. Zircons formed from the two types of gels showed different morphologies, i.e., the single phase gels formed aggregates of ~ 75 nm zircon particles as vermicular morphological entities (Fig. 4A) and the diphasic gels formed thin plates of ~ 75 nm in size (Fig. 4B). Thus, it appears, one can control the morphology of zircon by combining both sol-gel and hydrothermal methods.

Synthesis of Zircon Single Crystals

Single crystals of zircon are possible candidate materials for polarizer use²⁷ in high-power laser systems and hence there is a need for their synthesis. Single crystals of zircon cannot be grown at ordinary pressures using the Czochralski method because it melts incongruently. There are two main methods for the growth of single crystals, i.e., flux and hydrothermal methods.

a. Flux Method. This method uses the cooling of molten salt fluxes for the growth of single crystals of zircon. Ballman and Laudise²⁸ grew single crystals of zircon as large as 0.7 cm

from molten alkali metal vanadates and molybdates. They reported the growth of the best zircon crystals in platinum crucibles by slow cooling $\text{Na}_2\text{O}\cdot 3\text{MoO}_3$ or $\text{Li}_2\text{O}\cdot 3\text{MoO}_3$ solutions saturated with $\text{SiO}_2 + \text{ZrO}_2$ from 1400° to 900°C at a rate of 2° per hour. Chase and Osmer²⁹ also used a similar procedure to grow well-formed, large single crystals. Zircon single crystals were also grown in platinum capsules by Dharmarajan et al.,³⁰ from a lithium tungstate melt. Although these flux methods are useful in obtaining large single crystals, one of the disadvantages of this method is the incorporation of impurities during growth.³⁰

b. Hydrothermal Method. Using natural zircon seed crystals and sintered ZrO_2 and SiO_2 as nutrient Dharmarajan et al.³⁰ grew single crystals of zircon in a 3-molar aqueous solution of KF under hydrothermal conditions. They found the optimum hydrothermal conditions to be 500°-600°C and 30000 psi.

Uhrin et al.,³¹ grew single crystals of zircon (from 0.5 to 1.0 cms) hydrothermally at 700°C and 25000 psi using seeds of zircon (100) and 2m KF or 1 m LiF as mineralizers and a thermal gradient of 20°C. Caruba et al.,²³ recently reported a new method of hydrothermal growth of zircon on natural and synthetic seeds using $\text{Zr}(\text{SO}_4)_2\cdot 4\text{H}_2\text{O}$ and SiO_2 gel at 750°C under a confining pressure of 0.5 to 1×10^8 Pa. All the above hydrothermal methods use seeds in order to obtain large crystals. The crystals synthesized hydrothermally without any seeds can only attain a size of several tens of micrometers.³²

CONCLUSION

The hydrothermal method is the preferred method for the synthesis of either zircon powders or single crystals. It is superior to other methods because of the low temperatures involved and the purity of the resulting zircon phase.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge financial support for this work by Johnson Matthey Technology Center.

REFERENCES

1. W.A. Deer, R.A. Howie, and J. Zussman, "Rock-Forming Minerals," Vol. 1, Longmans, London, p. 59 (1962).
2. A.J. Hathaway and J.B. Munro, "Zircon and Zirconia," Am. Ceram. Soc. Bull. 63[5], 690-691 (1984).
3. P. Robyn, J. Moreau, and G. Soumoy, "Selection of Zircon Bricks for the Superstructure of Container-Glass Furnaces by Laboratory Simulative Testing," Interceram., Special Issue (1986).
4. R.J. O'Brien and E. Tauber, "The Use of Zircon in Steel Ladle Lining," 2nd Ind. Miner. Int'l. Cong., Munich, West Germany, 245-249 (1977).
5. T. Kawakami, "Properties of Zircon-Roseki Bricks for Steel Ladles," Taikabutsu Overseas 1[2], 29-36 (1981).
6. W.C. Butterman and W.R. Foster, "Zircon Stability and the ZrO_2 - SiO_2 Phase Diagram," Am. Mineral. 52, 880-885 (1967).
7. E.W. Washburn and E.E. Libman, "An Approximate Determination of the Melting Point Diagram of the System Zirconia-Silica," J. Am. Ceram. Soc. 3[8], 634-640 (1920).
8. N. Zhirnowa, "Melting Diagram of System ZrO_2 - SiO_2 ," Z. Anorg. Allgem. Chem., 218:192-300 (1934).
9. R.F. Geller and S.M. Lang, "System SiO_2 - ZrO_2 ," J. Am. Ceram. Soc. 32[12], 157 (1949).
10. A. Cocco and N. Schromek, "Stability of $ZrSiO_4$ at High Temperatures," Ceramica (Milan) 12:45-48 (1958).
11. C.E. Curtis and H.G. Sowman, "Investigation of the Thermal Dissociation, Reassociation, and Synthesis of Zircon," J. Am. Cer. Soc. 36[6], 190-193 (1953).
12. F.R. Glasser, I. Warshaw, and R. Roy, "Liquid Immisibility in Silicate Systems," Phys. Chem. Glasses 1:39-45 (1960).
13. B. Brezny and R. Engel, "Evaluation of Zircon Brick for Steel Ladle Slag Lines," Am. Ceram. Soc. Bull. 63[7], 880-883 (1984).
14. E.M. Levin, C.R. Robbins, and H.F. McMurdie, "Phase Diagrams for Ceramists," Am. Ceram. Soc., Columbus, OH, pp. 601 (1964).
15. C. Frondel and R.L. Collette, "Hydrothermal Synthesis of Zircon, Thorite, and Huttonite," Am. Mineral. 42[6], 759-765 (1957).
16. H.S.C. Deville and H. Caron, "New Method of Synthesis of Crystals of Various Substances," C.R. 46, 764; Ann. Chim. Phys. 5:109 (1865).
17. G.L. Clark and D.H. Reynolds, "Chemistry of Zirconium Dioxide; X-ray Diffraction Studies," Ind. Eng. Chem. 29[6], 711-715 (1937).

18. H.B. Barlett, "X-ray and Microscopic Studies of Silicate Melts Containing ZrO_2 ," J. Am. Ceram. Soc. 14[11], 837-843 (1931).
19. V.H. Stott and A. Hilliard, "Variation in the Structure of Zircon," Min. Mag. 27, 198-203 (1945).
20. R.F. Geller and P.J. Yavorsky, "Effects of Some Oxide Additions on Thermal-Length Changes of Zirconia," J. Res. Natl. Bur. Standards 35[1], 87-110 (1945).
21. F.A. Mumpton and R. Roy, "Hydrothermal Stability Studies of the Zircon-Thorite Group," Geochimica et Cosmochimica Acta 21, 217-238 (1961).
22. O.D. Maurice, "Transport and Deposition of the Non-Sulphide Vein Minerals: V. Zirconium Minerals," Econ. Geol. 44:721-731 (1949).
23. R. Caruba, A. Baumer, and G. Turco, "Nouvelles Synthèses Hydrothermales du Zircon: Substitutions Isomorphiques; Relation Morphologie-Milieu de Croissance," Geochimica et Cosmochimica Acta 39[1], 11-26 (1975).
24. G. Vilmin, S. Komarneni, and R. Roy, "Lowering Crystallization Temperature of Zircon by Nanoheterogeneous Sol-Gel Processing," J. Mat. Sci. 22:3556-3560 (1987).
25. K. Yukihiro and Y. Yamate, "Synthesis of Zircon by the Sol-Gel Method," Yogyo-Kyokai-shi, 93[6], 74-76 (1985).
26. S. Komarneni, R. Roy, E. Breval, M. Ollinen, and Y. Suwa, "Hydrothermal Route to Ultrafine Powders Utilizing Single and Diphasic Gels," Advanced Ceramic Materials 1[1], 87-92 (1986).
27. V.O. Nicolai, "Light Polarizing Prism of Zircon," U.S. Patent 3,700,308, October 24, 1972.
28. A.A. Ballman and R.A. Laudise, "Crystallization and Solubility of Zircon and Phenacite in Certain Molten Salts," J. Am. Ceram. Soc., 48[3], 130-133 (1965).
29. A.B. Chase and J.A. Osmer, "Growth and Preferential Doping of Zircon and Thorite," J. Electrochem. Soc. 113:198-199 (1966).
30. R. Dharmarajan, R.F. Belt, and R.C. Puttbach, "Hydrothermal and Flux Growth of Zircon Crystals," Journal of Crystal Growth 13/14, 535-539 (1972).
31. R. Uhrin, R.F. Belt, and R.C. Puttbach, "The Hydrothermal Growth of Zircon," Journal of Crystal Growth 21, 65-68 (1974).
32. R. Caruba, A. Baumer, and P. Hartman, "Crystal Growth of Synthetic Zircon Round Natural Seeds," J. Crystal Growth, 88:297-302 (1988).

TABLE I.
Data on the Thermal Stability of ZrSiO₄*

Investigators Temperature	Year	Manner of Breakdown	
Washburn and Libman	1920	congruent melting	2550°C
Zhirnowa	1934	congruent melting	2430°C
Geller and Lang	1949	incongruent melting	1775°C
Curtis and Sowman	1953	solid state decomposition	1540°C
Cocco and Schromek	1957	incongruent melting	1720°C

*After Buttermann and Foster⁶

TABLE II.
Hydrothermal Synthesis of Zircon*

Temperature	Pressure in Bars	Duration in Hours	Reagents	Results
700°C	1000	48	ZrO ₂ , SiO ₂ , mixed gels	Zircon
400°C	1000	168	ZrO ₂ , SiO ₂ , gels	Zircon
350°C	165	48	ZrO ₂ , SiO ₂ , gels	Zircon
325°C	121	240	ZrO ₂ , SiO ₂ , gels	Zircon
300°C	86	120	ZrO ₂ , SiO ₂ , gels, NaCl	Zircon
240°C	34	72	ZrO ₂ , SiO ₂ , gels, ZrF ₄	Zircon
150°C	4.8	500	ZrO ₂ , SiO ₂ , gels, ZrF ₄	Zircon

*After Frondel and Collette¹⁵

TABLE III.
**Lowest Temperature at Which Zircon Formed in Different
Mono- and Diphasic Precursors***

Structural Diphasicity	Compositional Diphasicity	
	No	Yes
No	1325°C	1175°C
Yes	1100°C	1075°C

*After Vilmin et al., (1987)²⁴

TABLE IV.
**XRD and TEM Analyses of Single-Phase and Diphasic Zircon
Gels After Hydrothermal Treatment with Deionized Water.***

Sample	Hydrothermal treatment	Reaction products by XRD	Morphology by TEM
Single-phase gel	450°C/100 MPa/4 h	Zircon	
Single-phase gel	500°C/100 MPa/12 h	Zircon	Vermicular aggregates (≈75-nm crystals)
Single-phase gel	600°C/100 MPa/12 h	Zircon	
Diphasic gel	450°C/100 MPa/4 h	Zircon + baddeleyite	
Diphasic gel	500°C/100 MPa/12 h	Zircon + baddeleyite	Platy crystals (≈75 nm)
Diphasic gel	600°C/100 MPa/12 h	Zircon	

*After Komarneni et al.²⁶

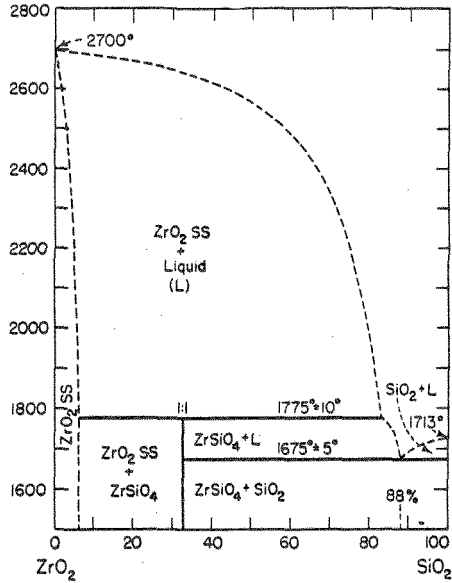


Figure 1. System $\text{SiO}_2\text{-ZrO}_2$ Revised and corrected phase diagram after Levin et al., (1964).¹⁴

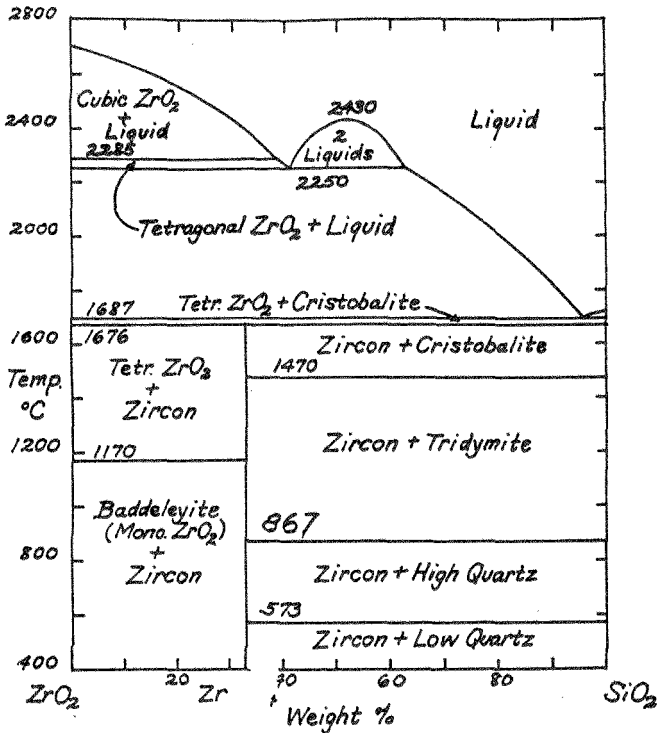


Figure 2. Phase diagram for $\text{ZrO}_2\text{-SiO}_2$ system after Buttermann and Foster.⁶

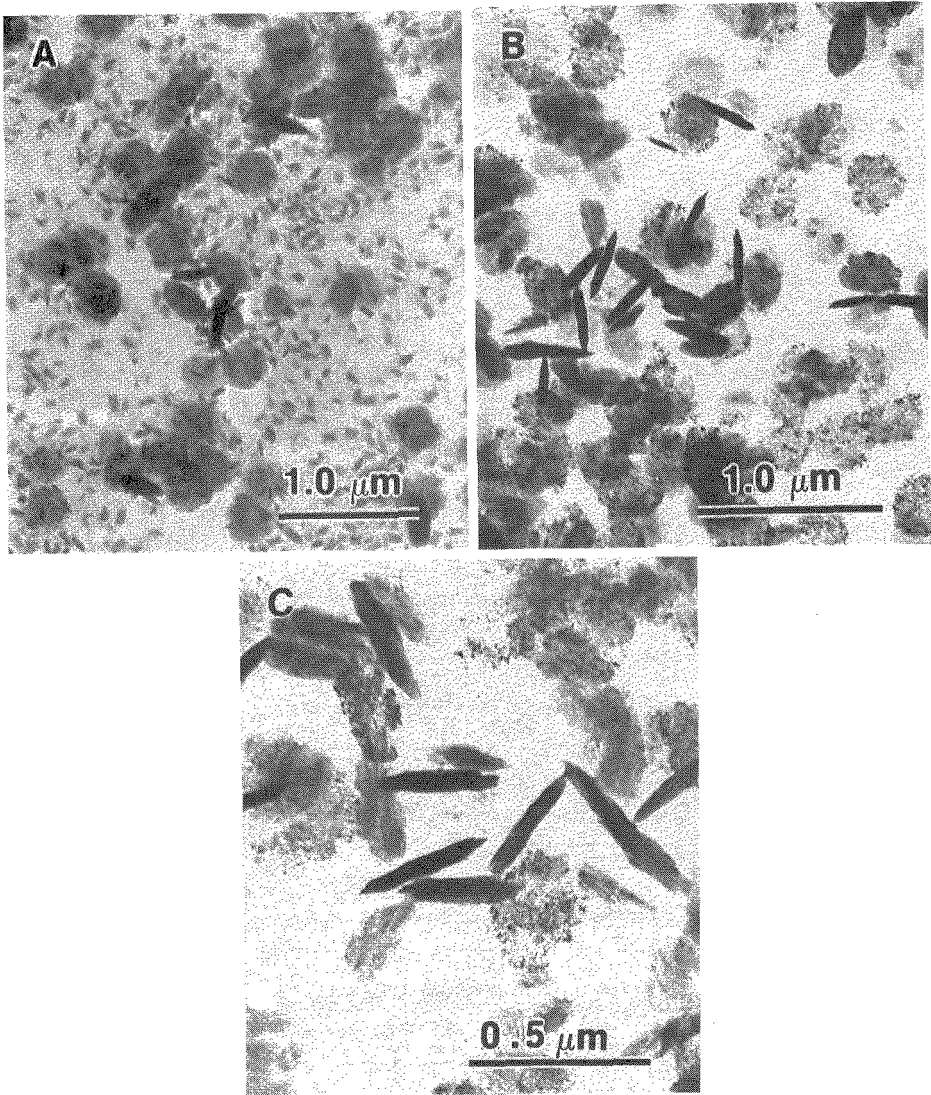


Figure 3. Transmission electron micrographs of hydrothermally prepared ZrSiO_4 powders: (a) non-uniform crystallites at 175°C ; (b) uniform crystallites at 200°C ; (c) same as in (b) but at a higher magnification (after Vilmin et al., 1987²⁴).

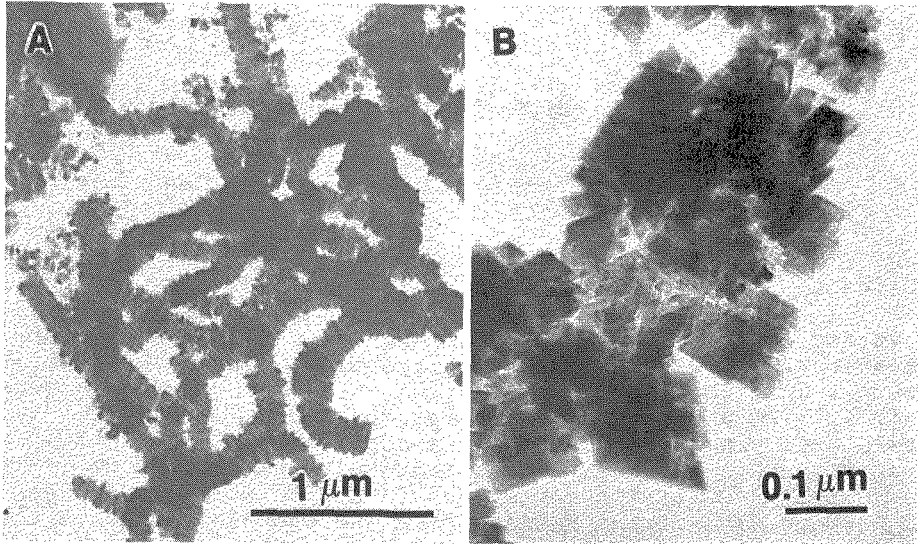


Figure 4. Transmission electron micrographs of ZrSiO_4 powders prepared hydrothermally at 500°C and 100 MPa: (a) vermicular form of ZrSiO_4 made from single phase gel; (b) platy ZrSiO_4 crystals made from diphasic gel (after Komarneni et al., 1986²⁶).