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OF MATERIALS SCIENCE AND ENG.. J D MACKENZIE MAR 88
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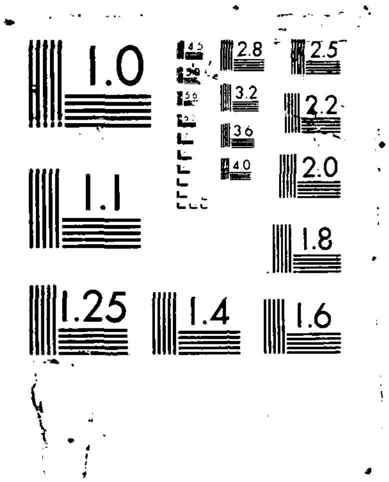
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Research has been carried out on two families of solids. This first one involves solids made by the sol-gel process and includes composites. The second one involves non-oxide glasses based on fluorides, chalcogenides and chalcohalides. The structures of oxide gels were studied by X-ray photoelectron spectroscopy, and the gelation of gels investigated as a function of temperature andcatalyst. A new theory was developed on gel transformations. A number of new composites made by the sol-gel route were examined included the using of SiC and diamond powder as fillers and some triphasic solids. The viscosity and viscoelasticity of fluorozirconate glasses and glass fibers have been studied. New chalcohalide glasses were prepared and their optical properties evaluated. Structural information was derived from Raman spectra.

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Final Technical Report

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
on project entitled

Preparation and Properties of New Inorganic Glasses and Gel-Derived Solids

Grant No: AFOSR 84-0022

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1 October 1986 to 30 September 1987

Principal Investigator:

J.D. Mackenzie
Professor of Engineering and Applied Science

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ABSTRACT

Research has been carried out on two families of solids. This first one involves solids made by the sol-gel process and includes composites. The second one involves non-oxide glasses based on fluorides, chalcogenides and chalcohalides. The structures of oxide gels were studied by X-ray photoelectron spectroscopy, and the gelation of gels investigated as a function of temperature and catalyst. A new theory was developed on gel transformations. A number of new composites made by the sol-gel route were examined including the use of SiC and diamond powder as fillers and some triphasic solids. The viscosity and viscoelasticity of fluorozirconate glasses and glass fibers have been studied. New chalcohalide glasses were prepared and their optical properties evaluated. Structural information was derived from Raman spectra.

1. INTRODUCTION

This research program, under Contract No. AFOSR-84-0022 was studied in October 1983. it is concerned with two relatively new families of solids of importance to the Air Force. The first family consists of porous oxides derived from gels and composites prepared from such porous gels. The second family is concerned with non-oxide glasses which are infrared transmitting. The broad objectives of this program are to learn how to prepare these solids, measure some important properties and understand how these properties are controlled by chemical composition, structure and microstructure.

This final technical report covers the period from 1 October 1986 to 30 September 1987.

2. Progress in Sol-Gel and Composites Research

a. Fundamental Understanding of the Sol-Gel Process

The sol-gel process for the preparation of glasses and ceramics has received a great deal of attention in the past few years.(1,2) Although this new processing route does hold promise for new materials and enhanced properties, truly successful applications are relatively few.(3) The main barrier to progress is the lack of sufficient knowledge on the process of gelation. The UCLA group has performed systematic studies on the effects of solvent, catalyst, raw materials and temperature on the rates of gelation, and the microstructure of the resulting gel. Silica was selected for the studies because of its relative simplicity. The very significant effects of all these factors were clearly demonstrated.(4)

During gelation, the viscosity of the solutions increases as a function of time. Throughout this process the molecular weight is also increasing. We have developed two theoretical models to elucidate this structural evolution utilizing data. The first one, applicable to linear gels such as SiO_2 with HCl as a catalyst is represented by the equation:

$$\ln(\eta) = \left[\ln(A) + m\ln(\Omega)\right] + m\ln(\alpha/1-\alpha) \tag{1}$$

where η = viscosity,

A = ν_0/M_0 = initial viscosity/initial molecular weight.

m = slope

Ω = $2M_0/(F-2)$ and

F = functionality

α = reduced time of gelation = t/t_{gel}

The second model, applicable to fractal growth such as HF-catalyzed SiO_2 gel, is represented by:

$$\ln(\eta_s) = \ln(QL/\rho_o) + (3 - D)q_r t \tag{2}$$

where η_s = reduced viscosity = $(\eta/\eta_o - 1)$,

Q = mass conc. of hydrolyzed monomer in solution

L = Einstein geometrical constant

D = fractal dimension

q_r = exponential constant for radius growth

ρ_o = fractal core density, and

t = time

The first model, linear growth, appears to be applicable to silica gels catalyzed by HCl as seen in Fig. 1. The complexities involving HF catalyst are illustrated by the three growth regions for a silica gel in Fig. 2. The two models developed will serve to differentiate the various growth mechanisms under different conditions. They have contributed to the understanding of gelation in the silica system. The application of these models to other gel systems will be attempted in the near future. For this purpose, research has commenced on the measurement of viscosity for the Al_2O_3 and $Al_2O_3-SiO_2$ system as for the SiO_2 system.

After gelation has occurred and the gel has been dried, two types of dense oxides can be prepared, namely, glasses and polycrystalline ceramics. The porous gel will have to be heated, of course. The difference between a melt-formed glass and a gel-derived amorphous solid is shown in Fig. 3. During this period, significant progress has been made in the understanding of what controls the ultimate structure of a gel-derived amorphous solid. The theory we have developed is based on the application of a topology concept similar to Zachariasen's rules for oxide glasses. Based on such an approach, some gel systems are more likely to give a polycrystalline ceramic (e.g., Al_2O_3, TiO_2, $BaTiO_3$ and some are more likely to give **glasses** (e.g., SiO_2, GeO_2). These two groups of oxides are shown in Tables 1 and 2, respectively. This fundamental understanding of the gel transformation process will be very useful for the preparation of all types of oxides via the sol-gel process in the future.

b. New Inorganic Composites Based on Gels

By the addition of inorganic or organic particles to sol-gel solutions and allowing the mixture to gel, a porous composite can be made. The preparation of silicon carbide-silica porous composites was successful. The porous composites were subsequently fired to give dense composites. The porous composite, however, can also be impregnated with organic polymers. We thus have a **triphasic** composite. In Fig. 4, it is seen that a triphasic composite consisting of SiO_2, SiC and PMMA exhibits yield behavior similar to that of a metal. A tentative theory has been formulated to explain this very interesting property of this new composite.

By stirring dye molecules into a sol-gel solution and allowing the solution to gel, it has been shown that the dye molecules are encased in an oxide gel.(5,6) The dyes can no longer be leached out from the oxide matrix. Such composites are potentially useful for many optical applications especially if the dye molecules are non-linear in their optical properties. These types of composites, however, are very porous and have low mechanical strengths. Further, the interconnective fine pores permit the passage of impurities which can degrade the mechanical, chemical and optical properites of the composite. We have successfully filled up the pores with PMMA, thus giving a dense composite which is still optically transparent.

Work is continuing on diamond-oxide, cubic boron nitride-oxide composites. Such new composites have unique properties and will be useful as coatings or substrate materials because of their high hardness, high electrical resistivity and low dielectric constant.

c. Ferroelectrics and Ferromagnetics by the Sol-Gel Technique

The sol-gel method for the preparation of glasses and ceramics has a number of advantages over conventional methods.(7) One is the ability to achieve homogeneity at the molecular level since liquid molecules are mixed instead of micron-size powders.(8) Another one is the ability to obtain dense polycrystalline ceramics because of the ease of sintering ultrafine particles. A third one is the ease of fabricating thick films from the liquid solutions. These advantages were exploited in the present research. Lead zirconium titanate (PZT) thick films have been successfully prepared from sol-gel solutions. Recently, by carefully control of viscosity and from an understanding of the gel transformation process, we have succeeded in the preparation of PZT ceramic fibers. Our group has pioneered research on the amorphous oxide to cryustal transformations in gel systems and have obtained the first T-T-T curves. Such a plot is shown in Fig. 5.

3. Progress in Non-Oxide Glass Research

a. Chalcohalide Glasses

We have maintained a world-wide leadership position in the study of chalcohalide glasses such as Ge-S-I and Ge-Se-I. The structures of these glasses are not known. We have succeeded in elucidating the structures of glasses in these systems by the use of Raman and IR studies. Recently, we have prepared new glasses based on the Ge-S-Br system. Typically Raman spectra are shown in Fig. 6. As for the iodine-containing systems, complex groups such as $GeBr_xS_{4-x}$ are formed when Br is added to GeS_2. Simultaneously, S is removed from the Ge atom to form S_8 rings. The structure of the resultant glass is shown in Fig. 7. Similar results have been obtained for glasses containing Se in place of S.

b. Chalcogenide Glasses

We have continued to use the National Science Foundation Surface Analytical Facility at Montana to examine the X-ray photoelectron emission spectra (XPS) of chalcogenide and other glasses. For chalcogenides, when Tl is added to GeSe, for instance, two types of Se atoms can be formed as shown in Fig. 8. The XPS spectra are shown in Fig. 9. Both peak positions and peak shapes are altered. Figure 10 shows the results of a best-fit curve which gave quantitative information of the concentrations of non-bridging and bridging Se atoms.

c. Viscoelasticity of Glass Fibers

Recently, a study of the viscoelastic behavior of fluorozirconate glass fibers has been initiated. It has revealed that such fibers can undergo permanent deformation at temperatures some 150°C below T_g under relatively low levels of applied stress. This result is of great importance to the future application of halide glass fibers. We have therefore performed accurate annealing temperatures on ZBLA and ZBLAN glass fibers. Figure 11 shows the length changes of a 20 cm long, 130 μm diameter fibers with $T_G \approx 300°C$. It is seen that even at 100°C, the fiber can contract appreciably and after stabilizing in 72 hrs, would contract again at 150°C. From results such as those shown in Fig. 11, the activation energy for deformation is of the order of 10 Kcal/mole. This is about one-fifth of the value for viscosity at elevated temperatures. The phenomenon of low temperature deformation is thus not related to normal viscous flow. It is most likely the result of excess **free volume** in the fiber because of rapid cooling.

e. Volumetric Changes

Because of the unexpectedly large deformations found for halide glass fibers and because of the unusually large changes in viscosity over a relatively short temperature range, it was considered essential to obtain more information on volumetric changes between the solid glass and the melt. Figure 12 shows the variation of molar volume with temperature for two fluorozirconate systems. The difference in molar volume between the melting (liquidus) temperature, T_M and T_g is large and is likely to be the cause of the large viscosity differences between T_M and T_g. Direct observations of structural changes via Raman spectroscopy of the melt are now planned.

4. Publications, 1986-87

1. *Sol-Gel Processing of Silica. I: Effects of Raw Materials*, J. Non-Cryst. Solids, **26**, 227 (1986), K.C. Chen, T. Tsychiya, J.D. Mackenzie.

2. *Applications of the Sol-Gel Method. Some Aspects of Initial Processing*, **Proc. Int. Conf. on Ultra-Structure Processing**, L.L. Hench and D.R. Ulrich, Chap. 12, Wiley and Sons (1986), J.D. Mackenzie.

3. *Comparative Corrosion Mechanism of ThF_4 and ZrF_4 Based Glasses*, J. Non-Crystalline Solids **83**, 282 (1986), with D. Tregoat and J.D. Mackenzie.

4. *Effect of Oxide Impurity on Physical Properties of Fluorozirconate Glass*, J. Non-Crystalline Solids **80**, 495 (1986), H. Hu and J.D. Mackenzie.

5. *Halide Glasses Based on Chlorides, Bromides and Iodides*, J. Non-Crystalline Solids **80**, 538 (1986), J. Lau and J.D. Mackenzie.

6. *Effects of Temperature on Formation of Silica Gel*, J. Non-Crystalline Solids **82**, 37 (1986), M. Colby, H. Osaka and J.D. Mackenzie. Chemistry II, Brinker, Clark and Ulrich, eds., Materials Res. Soc. Pittsburgh, 731 (1986).

7. *Crystallization of Oxide Films Derived from Metallo-Organic Precursors*, K.C. Chen, A. Janah, J.D. Mackenzie, **Better Ceramics Through Chemistry II, Brinker, Clark and Ulrich, eds., Materials Res. Soc. Pittsburgh, 731 (1986).**

8. *Oxide-Non Oxide Composites by Sol-Gel*,, E.J. Pope and J.D. Mackenzie, **Better Ceramics Through Chemistry II,** Brinker, Clark and Ulrich, eds., Matls Res. Soc., Pittsburgh, PA, 809 (1986).

9. *Viscoelastic Deformation of Fluoride Glass Fibers*, **Proc. 30th SPIE Meeting, 683**, 92 (1986), J.S. Sanghera, S.Y. Ryou, J.D. Mackenzie.

10. *Infrared Transmitting Chalcohalide Glasses*, **Proc. 30th SPIE Meeting, 683**, 85 (1986), J. Heo, H. Nasu, J.D. Mackenzie.

11. *Sol-Gel Processing of Silica, II: Role of the Catalyst*, J. Non-Cryst. Solids,**87**, 185 (1986), E. Pope and J.D. Mackenzie.

12. *Hot-Pressed KTN from Ultrahomogeneous Powders. I. Powders*, **Proc. 6th IEEE Int. Sym. Appl. Ferroelectrics,** 388 (1986), E. Wu, A.X. Kuang, J.D. Mackenzie.

13. *Hot-Pressed KTN from Ultrahomogeneous Powders. II. Ceramics*, **Proc. 6th IEEE Int. Sym. Appl. Ferroelectrics**, 391 (1986), E. Wu, A.X. Kuang, J.D. Mackenzie.

14. *Chloride, Bromide and Iodide Glasses*, NATO ASI Series **123, Halide Glasses for Infrared Fiberoptics,** R.M. Almeida (ed.), Martinus Nijhoff Publishers, Dordrecht,

p. 357 (1987).

15. *Viscosity Behavior of Halide Glasses and Melts,* NATO ASI Series**123, Halide Glasses for Infrared Fiberoptics,** R.M. Almeida (ed.), Martinus Nijhoff Publishers, Dordrecht, p. 139 (1987), J.D. Mackenzie, H. Nasu, J.S. Sanghera.

16. *XPS Studies of Sulfide and Selenide Glasses,* J. Non-Cryst. Solids, **95**, 351 (1987), H. Nasu, R.M. Almeida, J.D. Mackenzie.

17. *Applications of Zachariasen's Rules to Different Types of Non-Crystalline Solids,* J. Non-Crystl. Solids **95**, 441 (1987), J.D. Mackenzie.

18. *Identification of Non-Bridging Sulfur Atoms in* GeS_2-Tl_2S *Glasses,* J. Matls. Sci. Letters **6**, 701 (1987), R.M. Almeida, H. Nasu, J.D. Mackenzie.

19. *Non-linear Optical Properties of Glasses and Gel-Based Composites,* Opt. Engr. **26**, 102 (1987), H. Nasu, J.D. Mackenzie.

20. *Temperature Related Volumetric Changes in Fluorozirconate Glasses and Melts,* **Proc. 4th Int. Symp. Halide Glasses,** Monterey, CA, January (1987), J.S. Sanghera, J.D. Mackenzie.

21. *Structure and Properties of IR Transmitting Chalcohalide Glasses,* **Proc. 4th Int. Symp. Halide Glasses**, Monterey, CA, January (1987), J. Heo, J.S. Sanghera, J.D. Mackenzie.

22. Viscoelastic Deformation of Fluoride Glass Fibers, **Proc. 4th Int. Symp. Halide Glasses**, Monterey, CA, January (1987), S.Y. Ryou, J.S. Sanghera, J.D. Mackenzie.

23. *Novel Composite Materials for Space Structures and Systems,* **Proc. 32nd Int. SAMPE Symp., 32**, 760 (1987), E. Pope, J.D. Mackenzie.

24. *Incorporation of Organic Dyes in Polymer-Oxide Composites.* Mat. Res. Soc. Bull. **12**, 29 (1987), E. Pope, J.D. Mackenzie.

5. Presentation of Research Based on this Project

E.J.A. Pope and J.D. Mackenzie, *The Viscosity Relationship of Gels*, 1986 Fall Meeting, Am. Ceram. Soc., Seattle, WA, October 22 (1986).

E.J.A. Pope and J.D. Mackenzie, *Ultrafine metallic Particles in Porous and Dense Silica Glass, 1986 Fall Meeting, Materials Research Society, Boston, MA, December 4 (1986).*

H. Nasu, J. Heo, S.Y. Ryou and J.D. Mackenzie, XPS Studies of Alkali Borosilicate Glasses, Glass Division Meeting of the Ceramic Society of Japan, Nagoya, Japan, October (1986).

J.D. Mackenzie, *Current Status and Future Developments of Sol-Gel Science and Technology,* Japan Ceram. Soc. Meeting, Osaka, Japan, November (1986).

J.D. Mackenzie, *Recent Trends of Materials Development by the Sol-Gel Method*, Tokyo Inst. Technology, Tokyo, Japan, November (1986).

E.J.P. Pope and J.D. Mackenzie, *Incorporation of Organic Dyes in Polymer/Oxide Composites,* Matls Res. Soc. Fall Meeting, Boston, MA, December (1986).

J.D. Mackenzie, *Amorphous Oxide from Gels,* **3rd Int. Conf. on Ultrastructure Processing of Ceramics, Glasses and Composites,** San Diego, CA, February (1987).

E.J.A. Pope and J.D. Mackenzie, *Novel Composite Materials for Space Structures and Systems*, **32nd Int. SAMPE Symp.,** Anaheim, CA, April (1987).

J.S. Sanghera, C.J. Chu and J.D. Mackenzie, *Temperature Related Volumetric Changes in Fluorozirconate Glasses and Melts,* **4th Int. Sym. Halide Glasses**, Monterey, CA, January (1987).

J. Heo, J.S. Sanghera and J.D. Mackenzie, *Structure and Properties of IR Transmitting Chalcohalide Glasses,* **4th Int. Sym. Halide Glasses**, Monterey, CA, January (1987).

S.Y. Ryou, J.S. Sanghera and J.D. Mackenzie, *Viscoelastic Deformation of Fluoride Glass Fibers,* **4th Int. Sym. Halide Glasses,** Monterey, CA, January (1987).

E.J.A. Pope and J.D. Mackenzie, *Predicting the Evolution of Gel Microstructures from Viscosity-Time Relations,* **3rd Int. Conf. on Ultrastructure Processing,** San Diego, CA, February (1987).

J.D. Mackenzie, *Applications of Zachariasen's Rules to Different Types of Non-Crystalline Solids*, **Int. Conf. Physics of Non-Cryst. Solids**, Kyoto, Japan, July (1987).

H. Nasu and J.D. Mackenzie, *XPS Studies of Sulfide and Selenide Glasses*, **Int. Conf. Physics of Non-Cryst. Solids,** Kyoto, Japan, July (1987).

J.D. Mackenzie, *Applications of the Sol-Gel Process*, **Int. Workshop on Glasses and Glass-Ceramics from Gels**, Kyoto, Japan, July (1987).

T. Tsuchiya and J.D. Mackenzie, *Synthesis of CuO-Al sub 2 O sub 3 -SiO sub 2# Glasses from Gels*, **Int. Workshop on Glasses and Glass-Ceramics from Gels**, Kyoto, Japan, July (1987).

6. Personnel

During this period the following people had participated and made contributions to the progress reported.

Dr. J.D. Mackenzie	Principal Investigator
Dr. R. Almeida	Visiting Research Felow
Dr. J.S. Sanghera	Postdoctoral Scholar
Dr. K. Chemseddine	Postdoctoral Scholar
Dr. Florence Babonneau	Postdoctoral Scholar
Ms. Mary Colby	Research Assistant
Ms. Azar Nezeri-Eshghi	Research Assistant
Mr. Edward Pope	Research Assistant
Mr. Jong Heo	Research Assistant
Mr. Joseph Yuen	Research Assistant
Mr. K.C. Chen	Research Assistant
Mr. S.Y. Ryou	Research Assistant
Mr. H.X. Zheng	Research Assistant

In addition, a number of undergraduate laboratory assistants were employed to assist in this research program.

7. References

1. L.L. Hench and D.R. Ulrich, *Ultrastructure Processing of Glasses, Ceramics and Composites*, John Wiley and Sons (1984).

2. C.J. Brinker, D.E. Clark and D.R. Ulrich, **Better Ceramics Through Chemistry,** North-Holland Publication (1984).

3. J.D. Mackenzie, J. Non-Cryst. Solids, **73**, 7 (1985).

4. J.D. Mackenzie, **Proc. 2nd Int. Conf. on Ultrastructure Processing of Glasses, Ceramics and Composites**, Florida, February (1985).

5. D. Avnir, D. Levy, R. Reisfeld, J. Phys. Chem., **88**, 5956 (1984).

6. T. Tani, et al., J. Appl. Phys, **58**, 9 (1985).

7. J.D. Mackenzie, J. Non-Cryst. Solids, **48**, 1 (1982).

8. E. Wu, K.C. Chen and J.D. Mackenzie, pp. 169-174 in ref. (2).

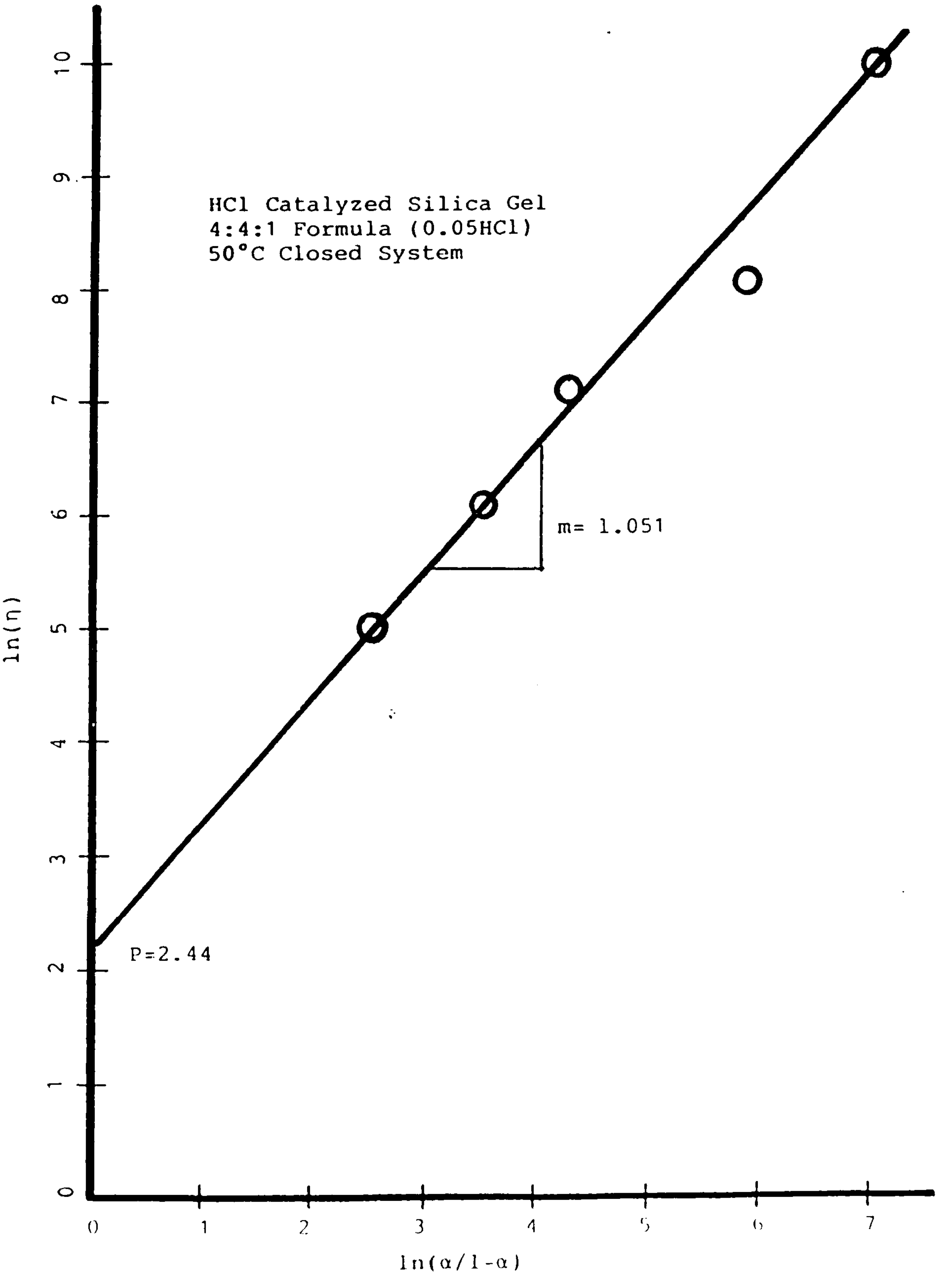


Fig. 1 Viscosity of silica gel illustrating nearly linear growth model.

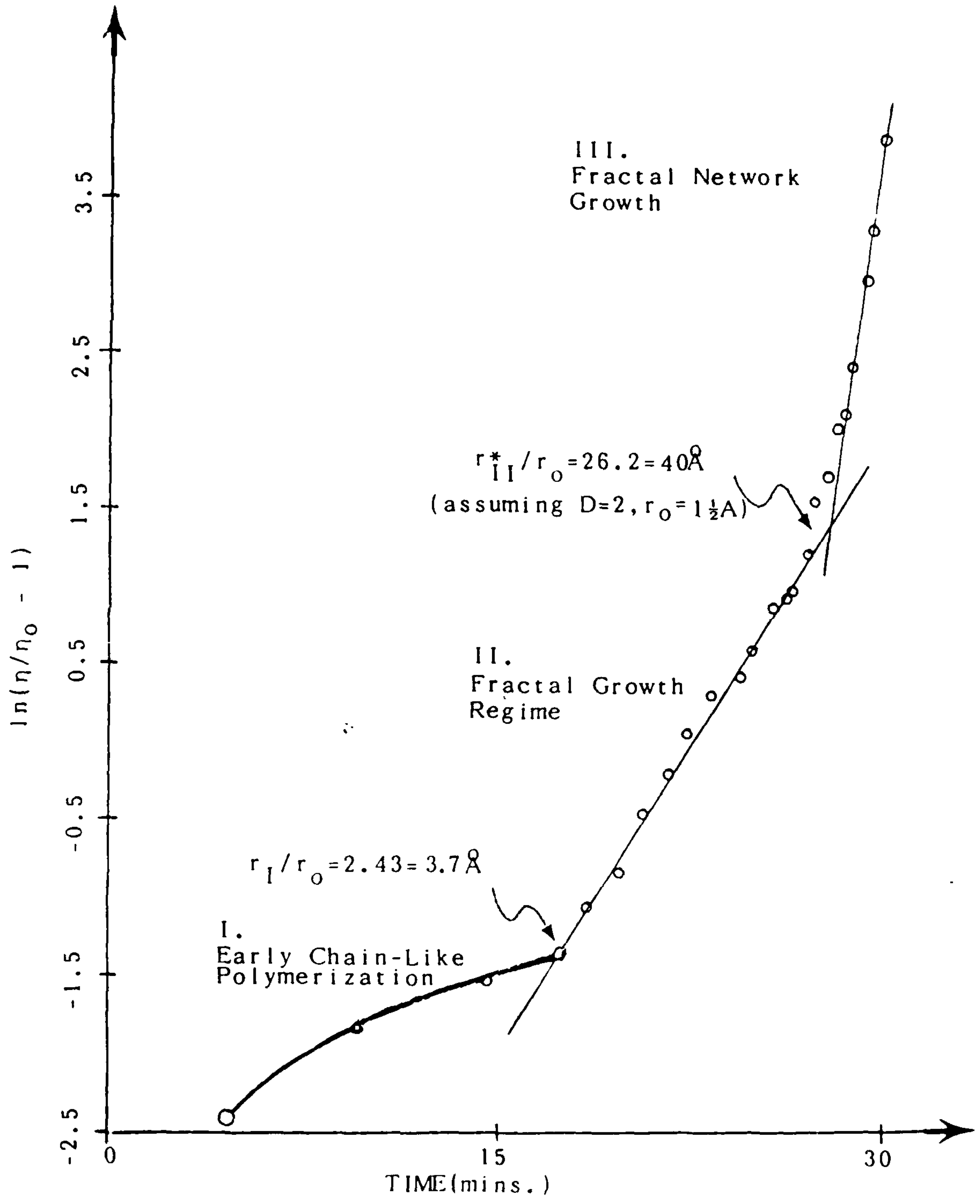
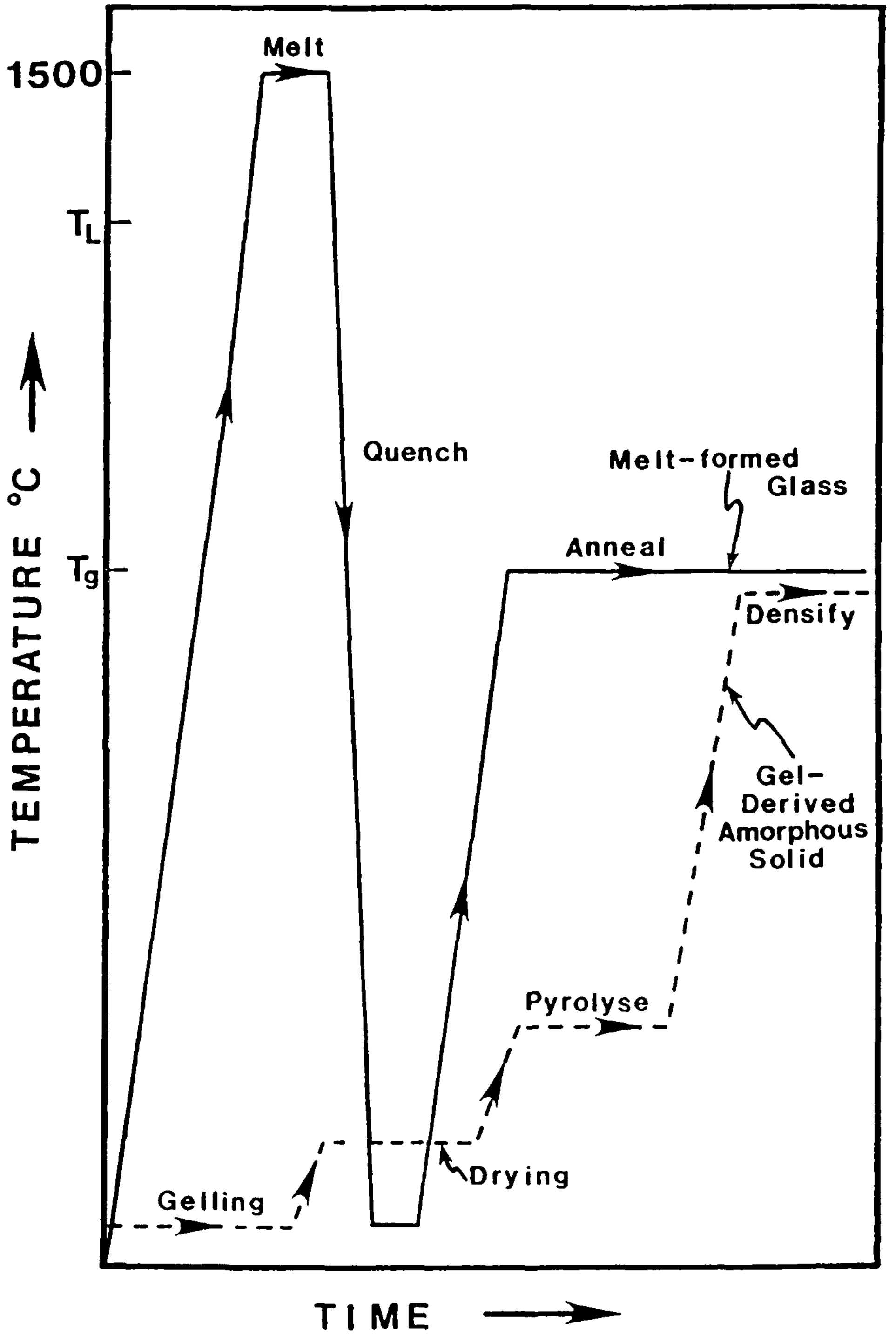


Fig. 2 Viscosity data for HF-catalyzed silica gel.



Fi.g 3 Comparison of preparation processes of melt-formed glass and gel-derived amorphous solid.

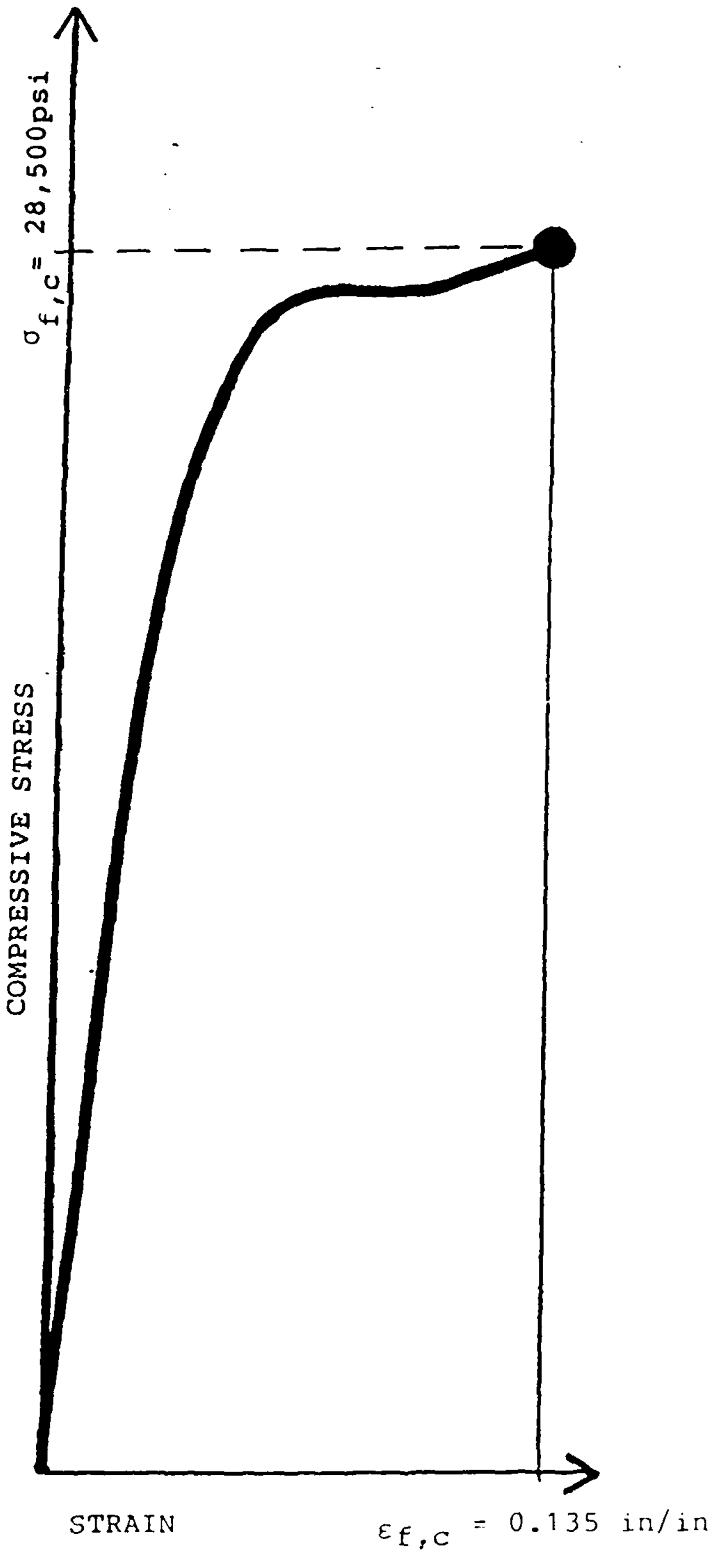


Fig. 4 Yield behavior of a **triphasic** composite.

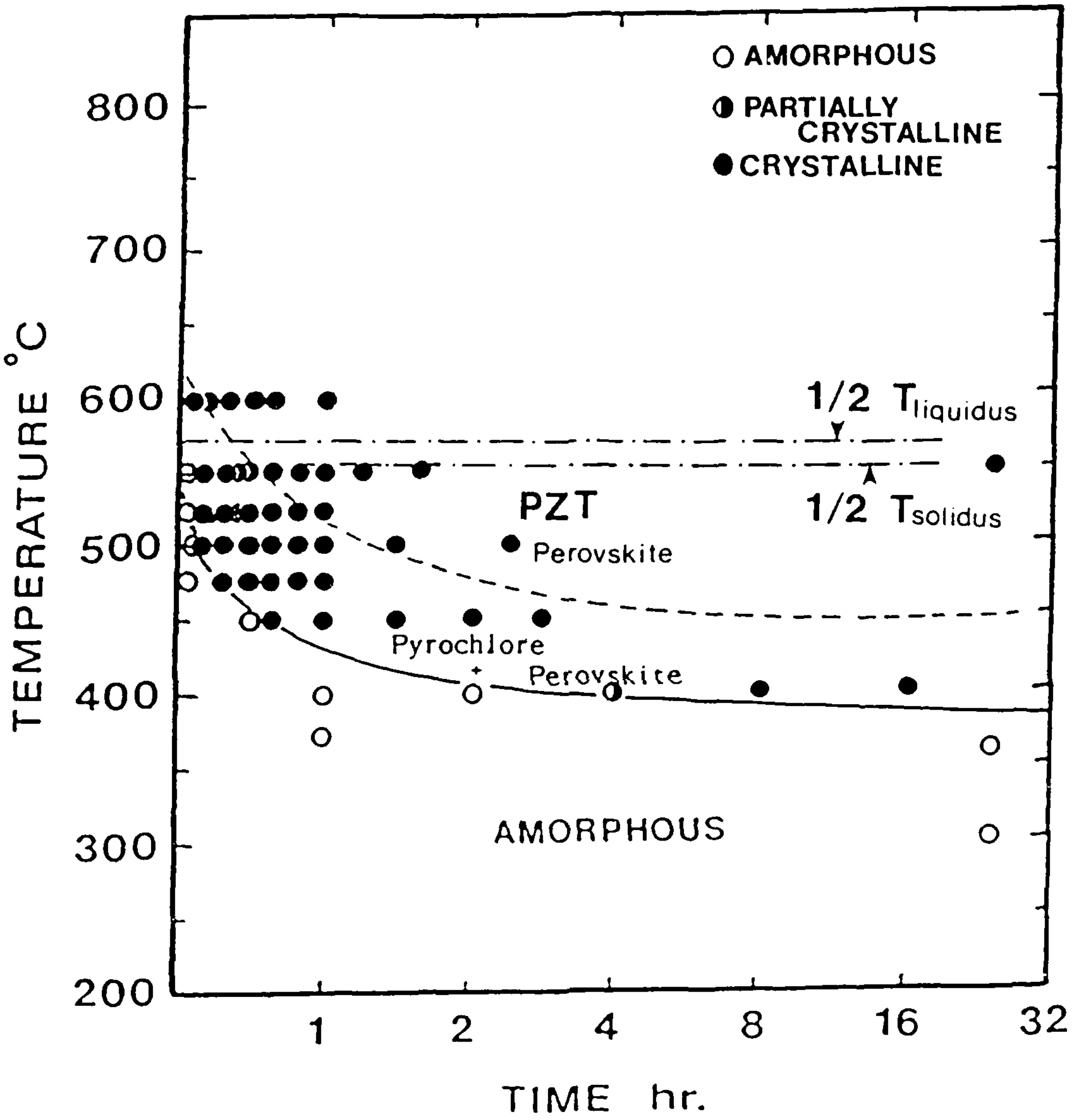
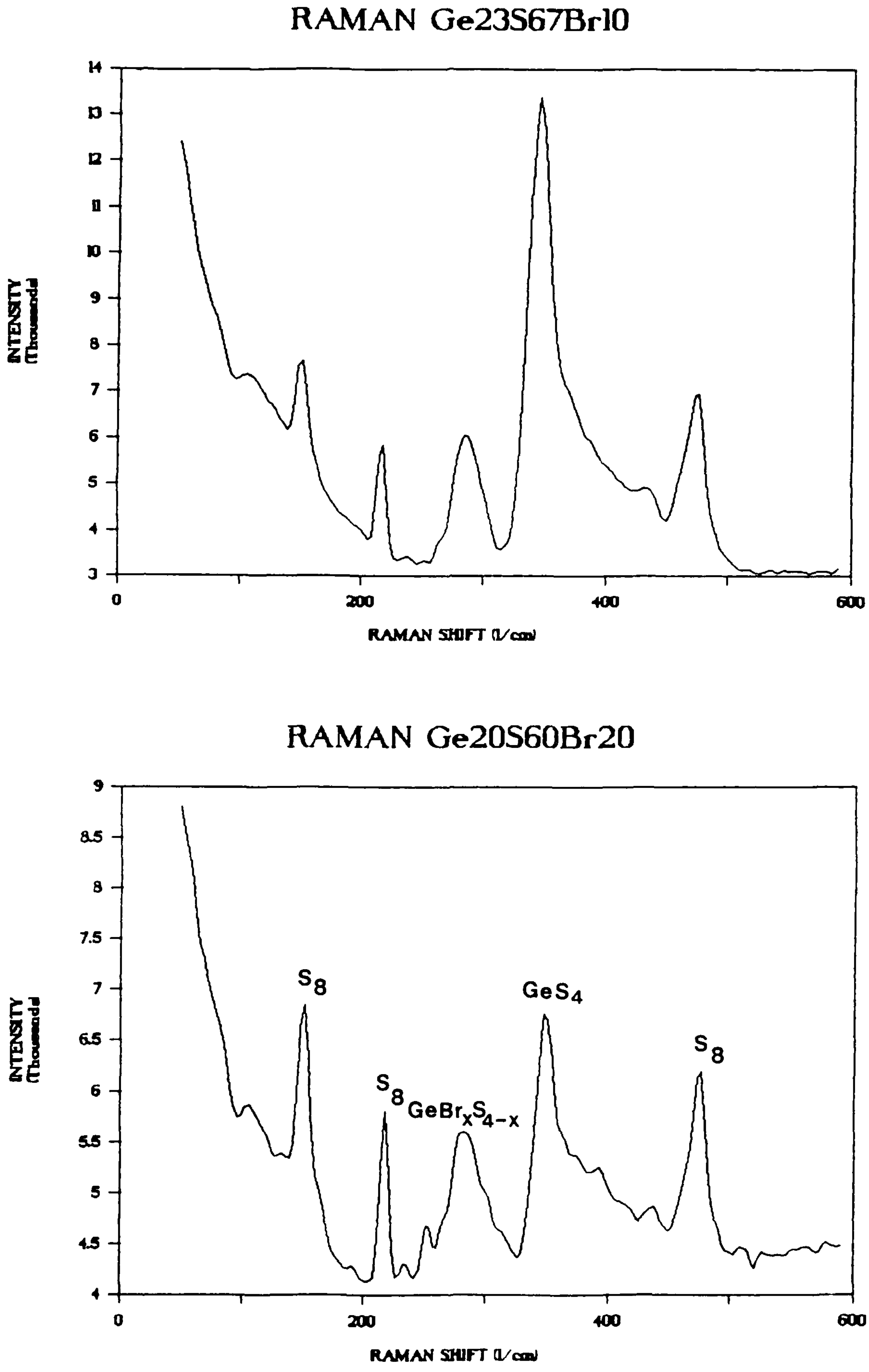


Fig. 5 T-T-T plots for PZT from gels


RAMAN Ge23S67Br10

RAMAN Ge20S60Br20

Fig. 6 Raman spectra of chalcohalide glasses.

Structural Model $Ge_{20}S_{60}Br_{20}$

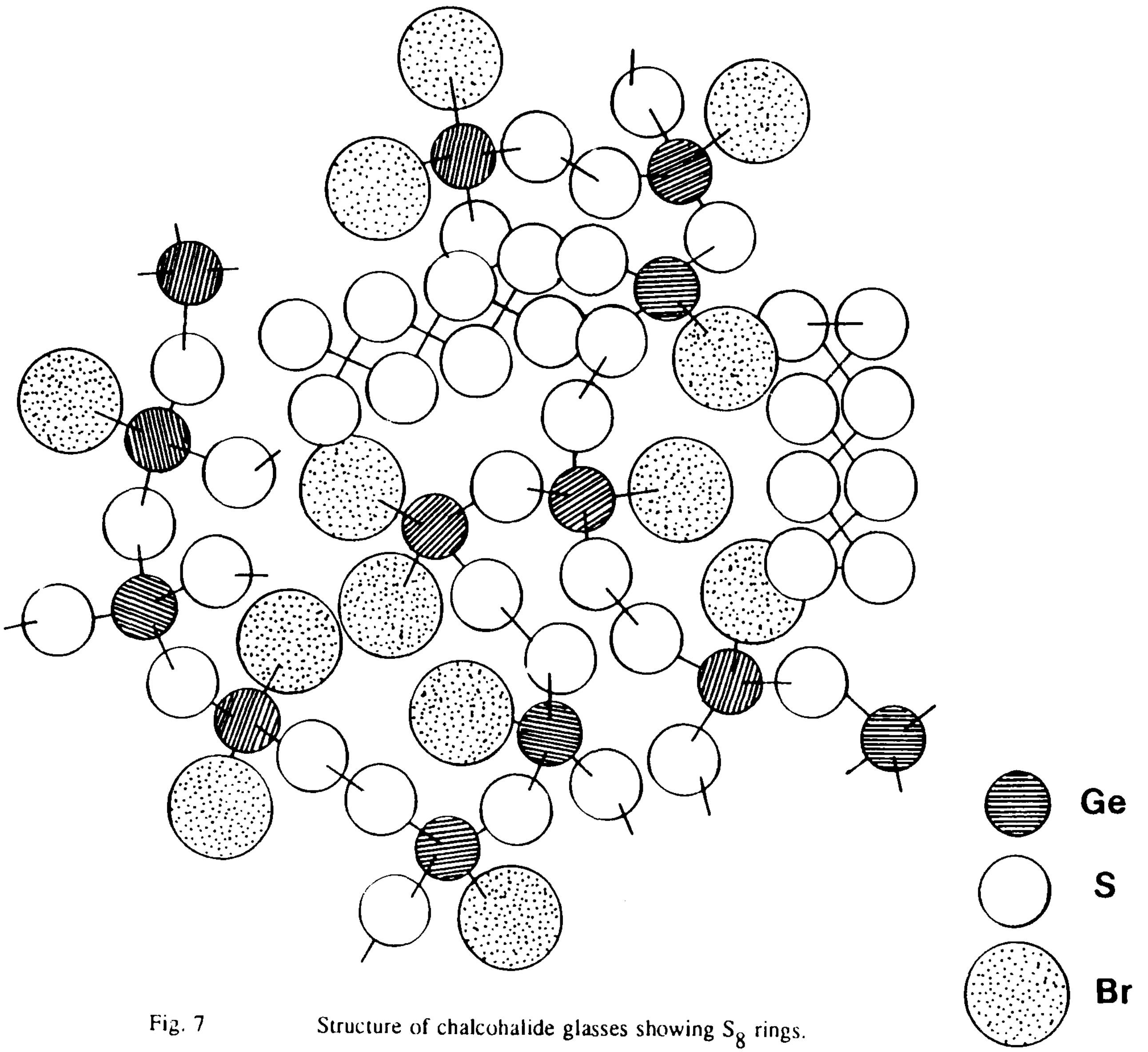


Fig. 7 Structure of chalcohalide glasses showing S_8 rings.

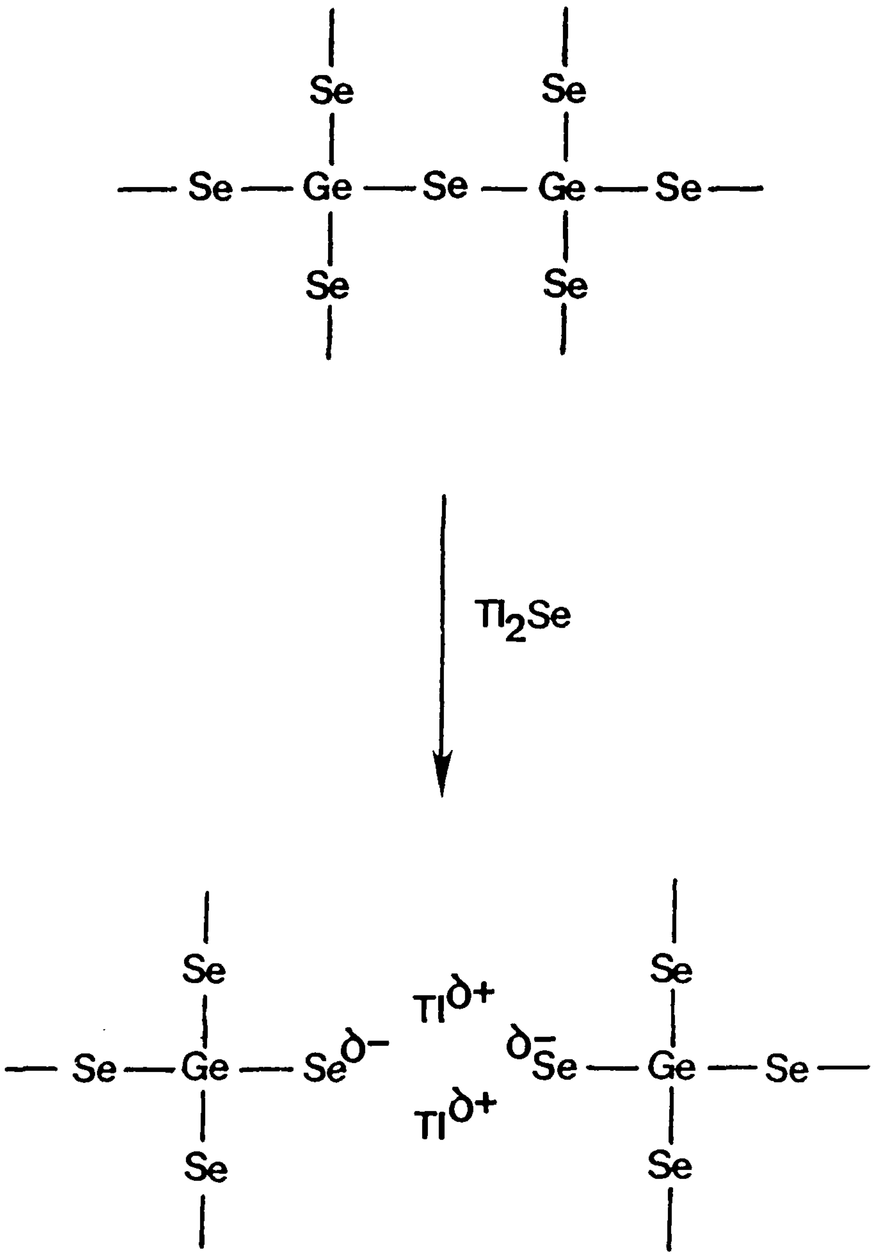


Fig. 8 Formation of non-bridging Se atoms in GeSe glass

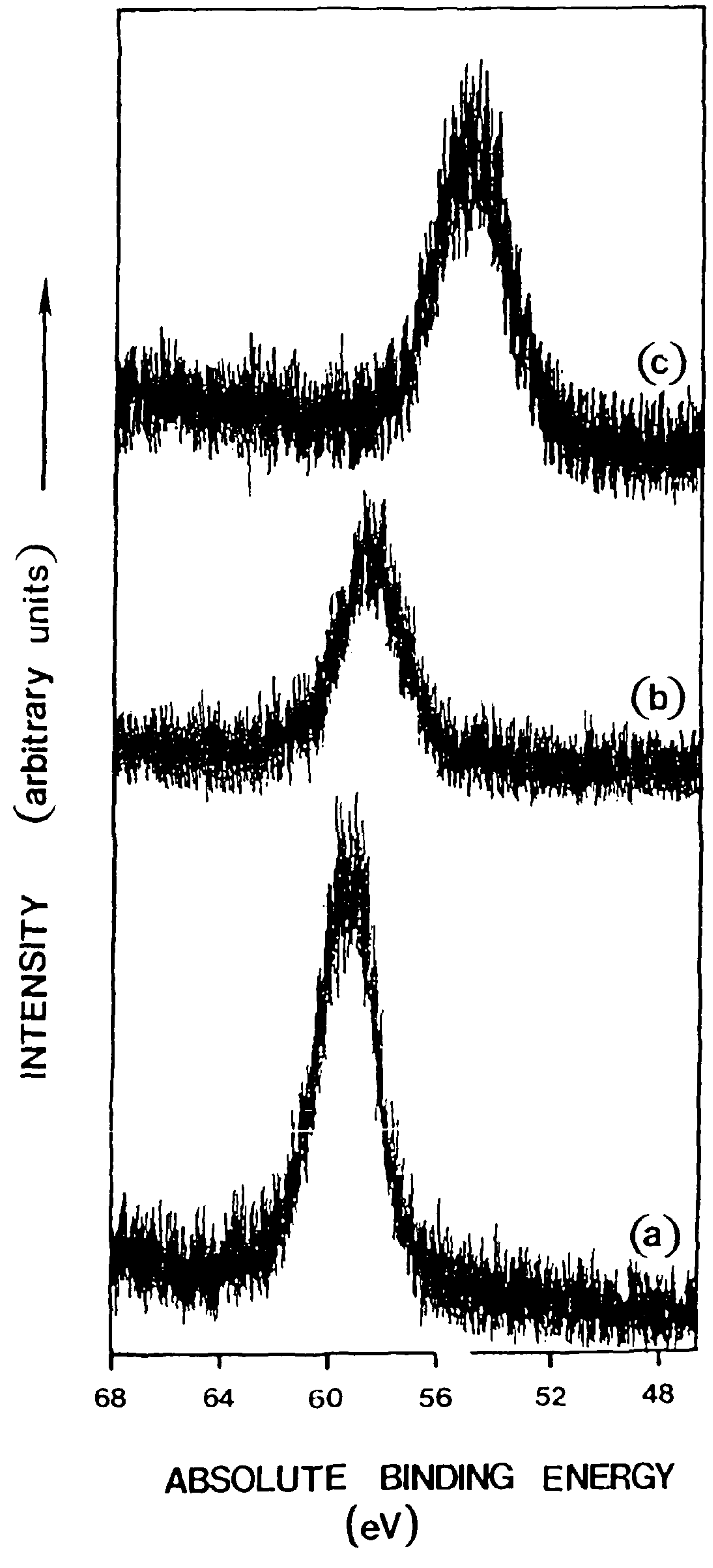


Fig. 9 XPS spectra of $GeSe_2$ and $GeSe_2$ containing Tl_2Se (b and c).

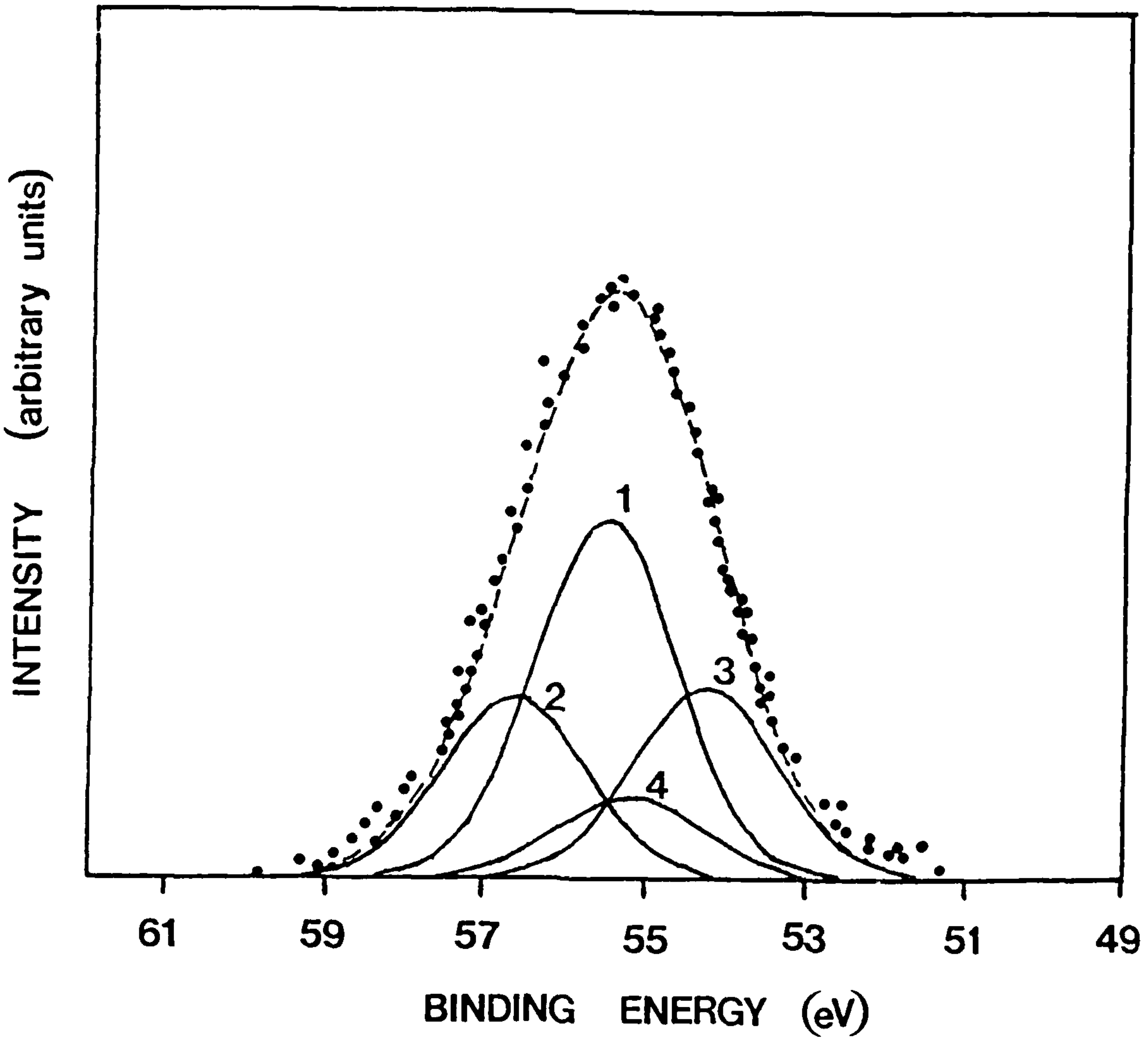


Fig. 10 Selenium 3d XPS spectra of 70GeSe$_2$-30Tl$_2$Se: (•••) raw spectrum after smoothing; (- - -) convoluted spectrum; (——) 4-peak gaussian fit. 1,2,3 and 4 refer to the Se$_b$ 3d$_{5/2}$, Se$_b$ 3d$_{3/2}$, Se$_{nb}$ 3d$_{5/2}$ and Se$_{nb}$ 3d$_{3/2}$ peaks, respectively.

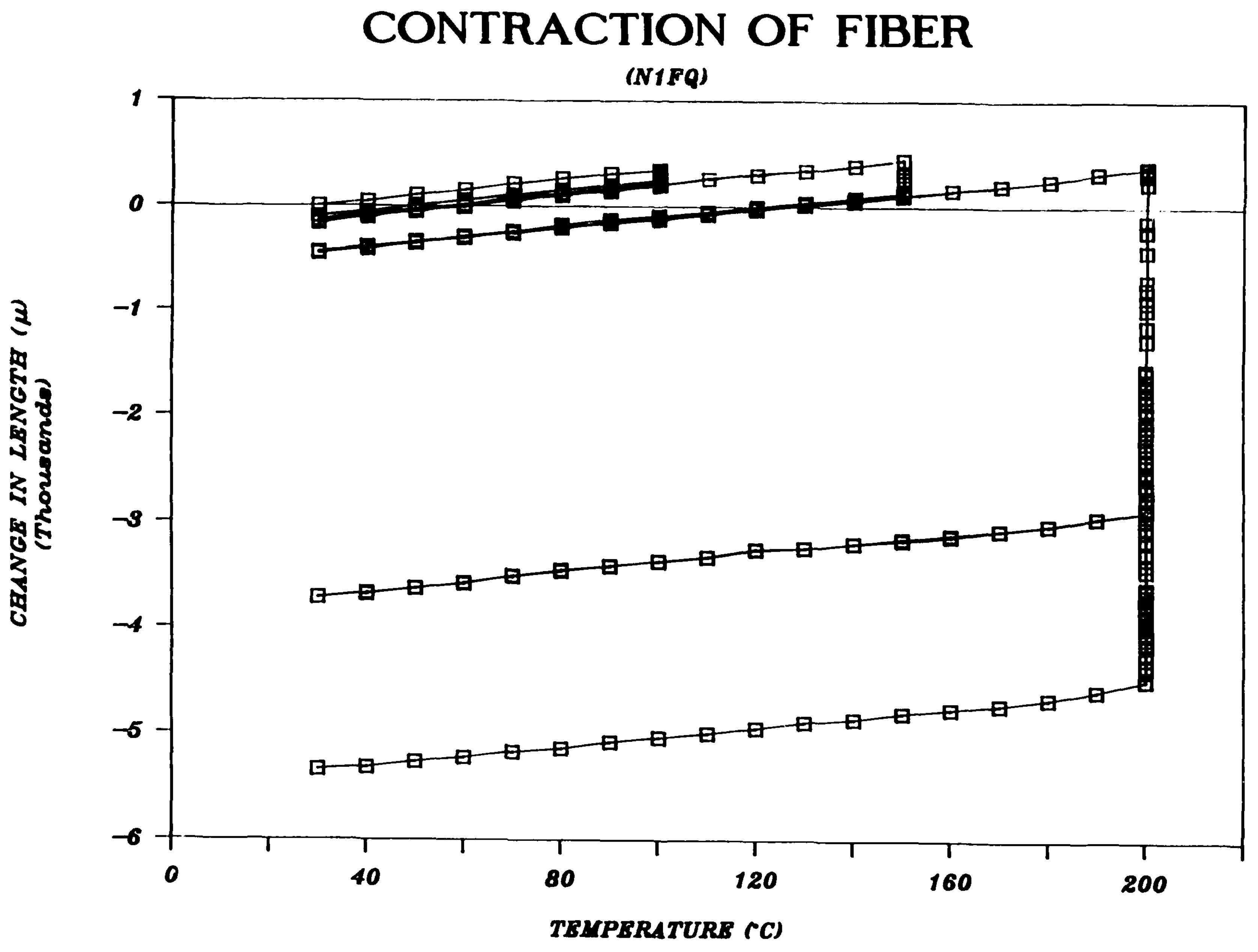


Fig. 11 Low temperature deformation of halide glass fibers.

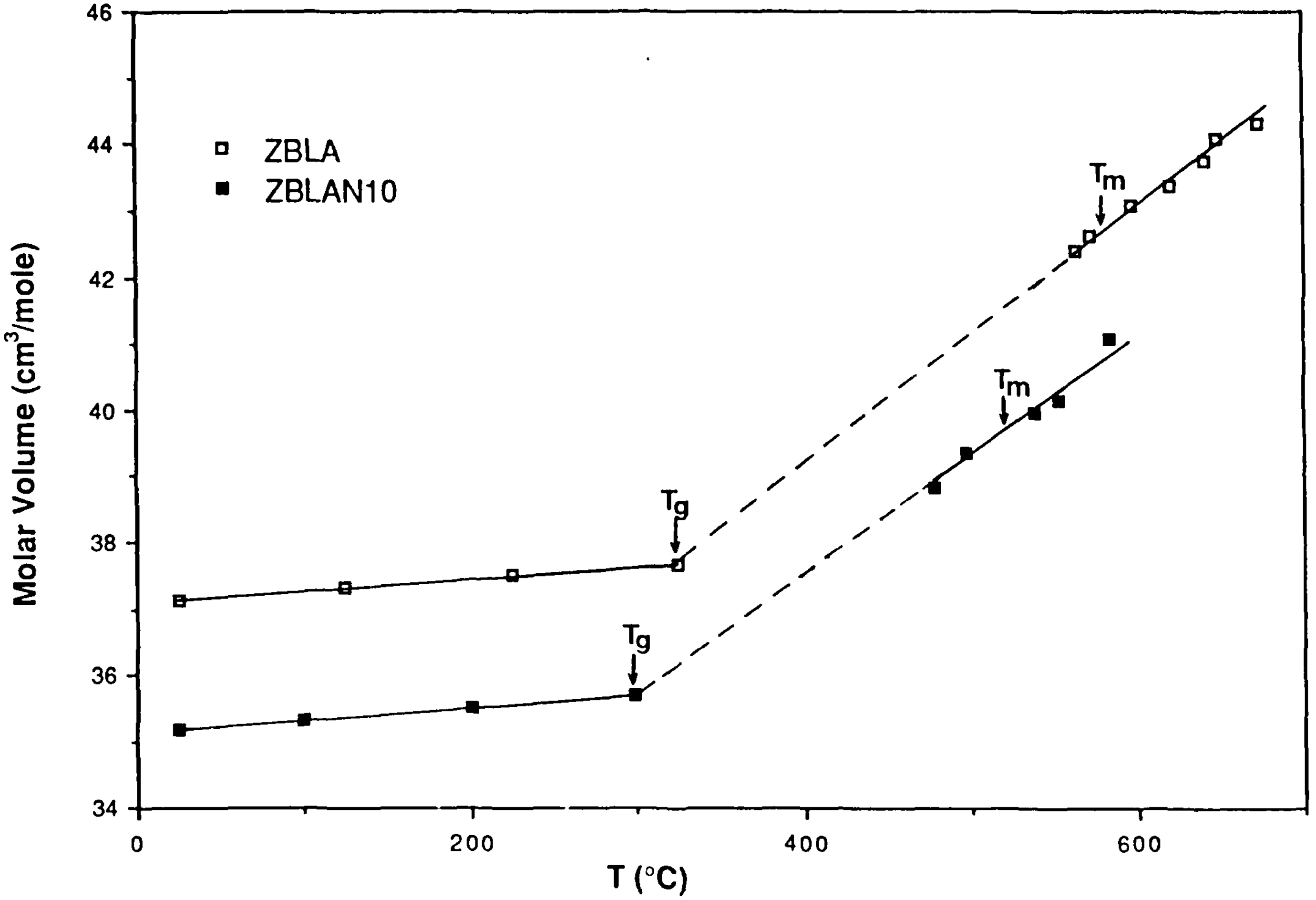


Fig. 12 Variation of molar volume with temperature for two fluorozirconates.

Table 1

Vitrifiable Oxides from Gels

System	T_g(°C)	T_c(°C)	T_L(°C)	Ref.
SiO_2	1070	1400	1728	26
$20B_2O_3$–$80SiO_2$	490	1000	1050	27
$15P_2O_5$–$85SiO_2$	510	980	1030	28
$20Na_2O$–$80SiO_2$	460	620	1100	29
$34Li_2O$–$66B_2O_3$	280	550	920	30
GeO_2	600	695	1116	31
$10PbO$–$90GeO_2$	462	540	1040	32
$25CaO$–$25Al_2O_3$–$50SOi_2$	875	1060	1550	33

Table 2

Easily Crystallized Oxides from Gels

System	T_c(°K)	0.5 T_L(°K)	T_L(°K)	Ref.
Al_2O_3	748	1162	2323	34
$4Y_2O_3-6Al_2O_3$	1083	1087	2173	35
TiO_2	473	1072	2143	36
$BaTiO_3$	873	943	1885	37
$SrTiO_3$	773	1157	2313	38
$PbTiO_3$	723	722	1443	37
$PbZr_{0.5}Ti_{0.5}O_3$	803	847	1693	39
ZrO_2	773	1497	2993	40
ZrO_2-2SiO_2	673	1350	2700	41
$CoFeO_4$	880	950	1900	42
$Li_2O-Fe_2O_3$	573	950	1900	43
$KTa_{0.6}Nb_{0.4}O_3$	773	772	1543	44
V_2O_5	453	482	963	45
Ta_2O_5 (bulk)	623	1062	2123	46
(film)	908	1062	2123	
$2TiO_2-5Nb_2O_5$	1083	874	1748	47

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