

Volume 30

Ceramic Transactions

NUCLEATION AND
CRYSTALLIZATION IN
LIQUIDS AND GLASSES

Michael C. Weinberg

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Edited by Michael C. Weinberg,

University of Arizona

江苏工业学院图书馆

藏书章

The American Ceramic Society
Westerville, Ohio

Proceedings of the Fourth Symposium on Nucleation and Crystallization, held at the Glass and Optical Materials Division Meeting of the American Ceramic Society at Stone Mountain, GA, August 16-19, 1992.

Library of Congress Cataloging-in-Publication Data

Nucleation and crystallization in liquids and glasses / edited by
Michael C. Weinberg.

p. cm. -- (Ceramic transactions ; v.30)

Includes index.

ISBN 0-944904-57-2

1. Glass--Congresses. 2. Glass-ceramics--Congresses

3. Crystallization--Congresses. I. Weinberg, Michael C.

II. Symposium on Nucleation and Crystallization (4th : 1992 : Stone
Mountain, Ga.) III. Series

TP845.N85 1993

92-42210

666.1'042--dc20

CIP

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Printed in the United States of America.

1 2 3 4-97 96 95 94 93

ISSN 1042-1122

ISBN 0-944904-57-2

Preface

The collection of papers presented herein were presented at the Nucleation and Crystallization symposium at the Glass and Optical Materials Division Meeting of the American Ceramic Society, held August 16-19, 1992, at Stone Mountain, GA.

This symposium was the fourth in a series held approximately every ten years. It was similar to the third symposium in that a combination of review and research papers were presented. The three major topics of this meeting were nucleation, crystallization, and crystallized glass applications, as in the third symposium.

On the other hand, the present meeting had certain distinct aspects that set it apart from previous symposia. First and foremost, there was the participation of a number of scientists and engineers from diverse disciplines, such as ceramic engineering, theoretical and experimental chemistry, metallurgy, astrophysics, and glass and polymer science. Second, the outlook was somewhat broader than in previous symposia, especially with regard to the topic of nucleation. Finally, on the last day of the meeting, a panel discussion was held on the topic of nucleation. During this session, assessments were given of the experimental and theoretical triumphs and deficiencies regarding crystal nucleation from the melt.

I am grateful to all of the authors for their wonderful cooperation in the preparation of this volume. In addition, I wish to extend special gratitude to Professors D.R. Uhlmann, K. Kelton, I. Gutzow, D. Oxtoby, P. James, and J. Perepezko for their insightful contributions. I extend special gratitude to the sponsors of this symposium: the Division of Microgravity Sciences and Applications of the National Aeronautics and Space Administration, Corning Incorporated, and Heraeus Amersil. Finally, I wish to thank Lori Kozey, of the American Ceramic Society, for her help and guidance.

Michael C. Weinberg

Contents

Section I. Nucleation

Experimental Studies of Crystal Nucleation in Glasses.....3

P.F. James

Nucleation Kinetics in Undercooled Liquid Droplets.....13

J.S. Paik and J.H. Perepezko

Nucleation of Solids from the Gas Phase.....23

J.A. Nuth III and F. Ferguson

**Effect of a Distribution of Relaxation Times on Crystal
Nucleation in Glass35**

P. Harrowell and D.W. Oxtoby

Transient Nucleation in Glasses.....45

K.F. Kelton

Computer Simulations of Crystal Nucleation Processes.....55

R.D. Mountain

**Experimental Studies of Surface Nucleation and
Crystallization of Glasses.....65**

E.D. Zanotto

**Activity of Substrates in the Catalyzed Nucleation of
Glass-Forming Melts75**

A. Dobrev and I. Gutzow

Theory of Nucleation of Ice85

D.H. Rasmussen and M.-T. Liang

Section II. Crystal Growth and Crystallization

Theory of Crystal Growth from the Melt	95
K.A. Jackson	
Crystal Growth and Melting in Glass-Forming Systems— A View from 1992	109
D.R. Uhlmann and E.V. Uhlmann	
Crystal Growth in Lithium Diborate Glass	141
G.L. Smith and M.C. Weinberg	
Kinetics of Nucleation and Crystallization in Polymer Melts	151
I. Gutzow and A. Dobrev	
Gel-Crystal Nanocomposites by the Sol-Gel Process	167
L.C. Klein, S.P. Szu, A.M. Buckley, and M. Greenblatt	
Crystallization Behavior in Bi-Sr-Ca-Cu-O Glasses.....	173
R. Sato, Y. Kuken, T. Komatsu, and K. Matusita	
Ion-Exchange-Induced Crystallization of a Glass Below T_g	181
H. Takada, T. Yano, A. Yasumori, S. Shibata, and M. Yamane	
Effect of Hydroxyl Content on the Nucleation and Crystallization of Li₂O·2SiO₂ Glass	189
M.R. Heslin and J.E. Shelby	
Effect of Impurities on the Crystallization Behavior of Fluoride Glasses	197
T. Yano, M. Nakanishi, Y. Suzuki, S. Shibata, M. Yamane, and S. Inoue	

Section III. Crystallization and Glass-Ceramics

Nucleation and Crystallization in Glasses as Determined by DTA	207
C.S. Ray and D.E. Day	
Relation Between Nucleation and Growth and Its Effect on Bulk Crystallization Kinetics	225
V.A. Shneidman and M.C. Weinberg	
Controlled Nucleation and Crystallization of Fluorozirconate Glasses	233
G.H. Frischat	
Glass-Ceramics: Recent Developments and Applications....	241
G.H. Beall	
Low-Expansion Glass-Ceramics—Review of the Glass-Ceramics Ceran and Zerodur and Their Applications.....	267
W. Pannhorst	
Porous Glass-Ceramics with a Skeleton of High-Performance Titanium Phosphate Crystal—Preparation, Modification, and Application	277
H. Hosono and Y. Abe	
Optimization of a Glass-Ceramic Heat Treatment Schedule Through Thermal Analysis	285
D. Parsell	
In Situ Reinforced Glass-Ceramic in the Lithia-Alumina-Silica System	293
K.H. Lee, D.A. Hirschfield, and J.J. Brown, Jr.	
Nucleation and Crystallization in Fluoroindate Glasses	303
Y. Messadeq, A. Delben, M.A. Aegerter, and M. Poulain	

Crystallization Behavior of $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ Glass and Microstructure Dependence of Its Thermal Structure	311
B. Ryu and I. Yasui	

Section IV. Poster Presentations

Raman Spectroscopy of $2\text{Na}_2\text{O} \cdot 1\text{CaO} \cdot 3\text{SiO}_2$ Glass and Glass-Ceramics	319
E.C. Ziemath and M.A. Aegerter	

Sintering and Crystallization Behavior of Glass Powder with a Composition of Anorthite, $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	323
I. Yasui, B. Ryu, and T. Kawarazaki	

Suppression of Crystallization of $\text{BaO} \cdot \text{TiO}_2 \cdot \text{SiO}_2$ Gel During Densification Treatment	327
M. Iwasaki, A. Yasumori, S. Shibata, and M. Yamane	

Microstructural Characterization of Gel-Derived Thin Films	331
K. Miyazawa, K. Itoi, K. Higuchi, T. Sakuma, and K. Suzuki	

Numerical Approach to Adiabatic Nucleation in Oxide Glasses.....	335
M.F. da Silveira and E. Meyer	

Test of the Adiabatic Nucleation Model in Chalcogenide Glasses.....	339
V. de Barros Brasil and E. Meyer	

Kinetic Competition During Duplex Partitionless Crystallization.....	343
D.R. Allen, S. Das, and J.H. Perepezko	

Kinetics of Cristobalite Formation in Binary Borosilicate/High-Silica Glass Composite	347
J.-H. Jean and T.K. Gupta	

Experimental Studies of Nucleation in Undercooled Metal Melts by Fluxing Technique.....	355
F. Politi, T.T. Ishikawa, and C.S. Kiminami	

Effect of Hydroxyl Concentration on the Crystallization of a Lithium Silicate Glass-Ceramic.....	359
V.R. Stenshorn, M.R. Heslin, and J.E. Shelby	
Sintering and Crystallization of BaO•SiO₂ System Glass-ZrO₂ Powder Mixtures	363
S. Sridharan and M. Tomozawa	
Impact of Heat Treatment on the Chemical Stability of Nuclear Waste Glasses Produced at the West Valley Demonstration Project	367
V. Jain, S.M. Barnes, I. Joseph, L.D. Pye, I.L. Pegg, and P.B. Macedo	
Phase Stability Determinations of DWPF Waste Glasses	371
M.K. Andrews, C.A. Cicero, S.L. Marra, D.C. Beam, and C.M. Jantzen	
Theory of Transient Nucleation As a Tool To Process Experimental Data.....	375
V.A. Shneidman and M.C. Weinberg	
Crystal Nucleation on the Surface of Cordierite Glass	379
N.S. Yuritsin, V.M. Fokin, A.M. Kalinina, and V.N. Filipovich	
Index	383

Section I. Nucleation

EXPERIMENTAL STUDIES OF CRYSTAL NUCLEATION IN GLASSES

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ABSTRACT

Recent studies of nucleation kinetics in oxide glasses are briefly discussed, including the following topics; Volume and surface nucleation, trends in homogeneous nucleation in stoichiometric compositions, nucleating agents in silicate and phosphate systems, and nucleation in melt-derived and sol-gel derived glasses.

INTRODUCTION

Nucleation and growth govern the glass forming tendencies of melts and so are of practical importance in the manufacture of a wide range of stable glass compositions. These processes are also essential steps in the conversion of glasses into fine grain crystalline glass-ceramics, materials with a variety of well established applications. In melts that do not require extremely high cooling rates to form glasses, the rates of nucleation and growth are relatively low. Thus in high viscosity oxide systems crystallization at high temperatures can be 'frozen in' by fast cooling and the kinetics conveniently determined. Hence glasses are ideal media for fundamental quantitative studies and provide a unique opportunity to test many of the predictions of classical theories. The topic of the present paper is nucleation. Although significant advances have been made since the last Symposium in this series in 1981 [1] many important questions remain unresolved. Here some recent studies are highlighted. Various important topics such as the effects of amorphous phase separation on crystal nucleation have been recently reviewed elsewhere [2-4].

SUMMARY OF CLASSICAL NUCLEATION THEORY

It is helpful to summarize the relevant theory to aid later discussion.

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The rate of homogeneous steady state nucleation (I) at absolute temperature T in a one-component supercooled liquid is given, according to classical theory [5] by

$$I = A \exp - [(W^* + \Delta G_D)/kT] \quad \dots (1)$$

where W^* and ΔG_D are the thermodynamic and kinetic free energy barriers respectively and k the Boltzmann constant. The pre-exponential factor A is given to a good approximation by

$$A = n_v (kT/h) \quad \dots (2)$$

where n_v is the number of atoms, or strictly, 'formula units' of the crystallizing component phase per unit volume of liquid and h is Planck's constant. A is typically $10^{41} - 10^{42} \text{ m}^{-3} \text{ s}^{-1}$ and is effectively constant over the observed temperature range of nucleation. For a spherical nucleus

$$W^* = 16\pi\sigma^3 V_m^2 / 3\Delta G^2 \quad \dots (3)$$

where σ is the crystal-liquid interfacial free energy per unit area, V_m the molar volume of the crystal phase and ΔG the bulk free energy change per mole in crystallization. ΔG_D can be expressed in terms of an effective diffusion coefficient D by

$$D = (kT\lambda^2/h) \exp(-\Delta G_D/kT) \quad \dots (4)$$

where λ , the 'jump distance' is of the order of atomic dimensions. D may be related to Viscosity η by the Stokes-Einstein relation

$$D = kT/3\pi\lambda\eta \quad \dots (5)$$

or obtained from crystal growth measurements, assuming the kinetic barriers for nucleation and growth are the same [1-3].

EXPERIMENTAL METHODS

The two stage method of measuring nucleation rates involving heat treatments at the nucleation temperature T_N for a given time and then at a higher (growth) temperature T_G to develop the crystal nuclei to observable dimensions is discussed elsewhere [1]. The number of crystals per unit volume N_V may be determined by reflection optical microscopy of polished and etched sections through the glass, and from plots of N_V against time the nucleation rate I at a given temperature obtained. For higher nucleation rates scanning electron microscopy (SEM) may be employed. It is essential to ensure that during heat treatment at T_N a large proportion of the nuclei have time to grow into small crystals and

will not redissolve on heating up to, and holding, at T_G , i.e. the nuclei will attain a size larger than the critical nucleus size at T_G . The measured N_V will then closely approximate the number of nuclei formed at T_N . The choices of both nucleation time and T_G are important. To minimise dissolution effects the difference between T_G and T_N should be as small as possible, consistent with a reasonable growth rate and negligible nucleation rate at T_G . When correctly employed the method gives accurate and reproducible results [1]. It has the advantages that it is direct, is an absolute method, and can readily distinguish between nucleation in the volume and at the surface of the glass, but is time consuming. In some cases it is possible to dispense with the second stage growth treatment provided the growth rate is high enough at the nucleation temperature, for example at temperatures well above the nucleation maximum. A thorough discussion of the errors in the determination of N_V by optical microscopy has recently been given [6]. Other methods, faster than microscopy techniques, for determining information on nucleation rates have been developed using differential thermal analysis (DTA) [7,8]. These methods, based on measurements of the temperature and height of the DTA crystallization peak, should prove particularly useful, for example for rapid comparisons of the nucleation behaviour of compositions and determining the effectiveness of nucleating agents. The validity of these techniques has been analysed theoretically [9].

VOLUME AND SURFACE NUCLEATION

Most glasses show only surface nucleation on heat treatment. In many cases volume nucleation may be produced by adding a suitable nucleating agent but for certain compositions no such additions are required. Most of the glasses in Table 1 are 'simple' stoichiometric, compositions, the crystallizing phase having the same composition as the parent glass. Typical nucleation curves in Figure 1 demonstrate the large variation in maximum nucleation rates (from $1.9 \times 10^{12} \text{ m}^{-3}\text{s}^{-1}$ for BS_2 to only $1.7 \times 10^6 \text{ m}^{-3}\text{s}^{-1}$ for CS). The maximum nucleation temperatures (T_M) are all close to T_g (taken here as corresponding to a viscosity of 10^{12} Pas). Striking trends are evident from Table 1. The consistent set of seven T_M/T_m values in the narrow range 0.54-0.58, for the stoichiometric compositions showing volume nucleation, and the high undercoolings involved, suggest homogeneous nucleation. Moreover, the systems showing volume nucleation tend to exhibit, with one exception, lower values of T_g/T_m (less than 0.6) than in the systems showing only surface nucleation (T_g/T_m more than 0.6). This trend can be understood from theory. As T_g is defined here in terms of a fixed viscosity, D and ΔG_D are essentially constant at T_g and the driving force at T_g is given approximately [1] by

Table 1. Examples of glasses having (a) volume and surface or (b) only surface nucleation; Temperatures (K) of maximum nucleation rate (T_M), liquidus (T_m) and glass transformation (T_g).

Key: Ba(BaO), B(B_2O_3), C(CaO), K(K_2O), L(Li_2O), M(MgO), N(Na_2O), P(P_2O_5), S(SiO_2), Sr(SrO).

Data from [2] and [10-12] as indicated.

Composition	T_M/T_m	T_g/T_m	W^*/kT (at T_M)
(a) <u>Volume and surface nucleation</u>			
BaS ₂	0.58	0.57	27
Ba ₃ S ₅	0.58	0.56	
CS	0.58	0.57	45
LB ₂ [10,12]	0.65	0.64	
LS ₂	0.56	0.56	32
40L.60S (mole %) [10]	0.53	0.51	
45L.55S (mole %) [10]	-	0.49	
48L.52S (mole %) [10]	-	0.48	
NC ₂ S ₃	0.56	0.54	30
N ₂ CS ₃	0.54	0.51	25
NS	0.54	0.50	32
SrS	≈0.55	0.55	
(b) <u>Surface nucleation only</u>			
BaB [10]		0.61	
BaC ₂ S ₃ [10]		0.63	
BaP [10]		0.65	
CMS ₂ [10]		0.61	
CP [11]		0.61	
KS ₂		0.58	
NS ₂		0.64	
LB [10]		0.62	

$$\Delta G = -\Delta H_f [1 - (T_g/T_m)] \quad \dots\dots(6)$$

where ΔH_f is the heat of fusion per mole. Thus a low ratio T_g/T_m implies a higher nucleation rate and a greater tendency towards volume nucleation. As the ratio increases volume nucleation becomes less probable until only surface nucleation is detectable for certain systems. This simple argument neglects variations in other factors between compositions such as σ , ΔH_f

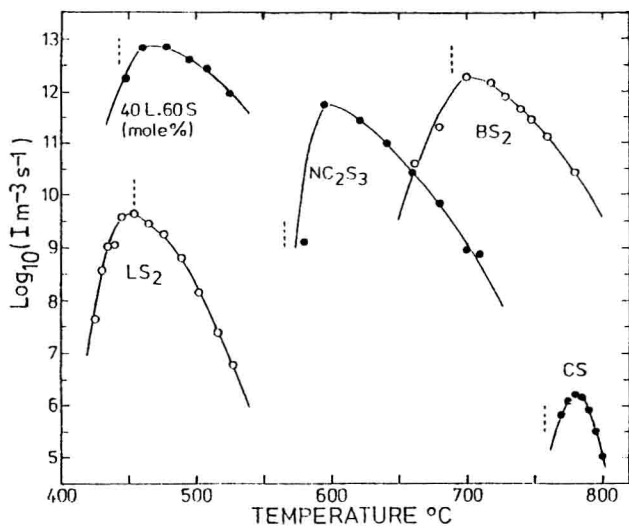


Figure 1: $\text{Log}_{10}(\text{I m}^{-3}\text{s}^{-1})$ vs temperature ($^{\circ}\text{C}$) for various compositions (see Table 1). Dashed lines indicate T_g values.

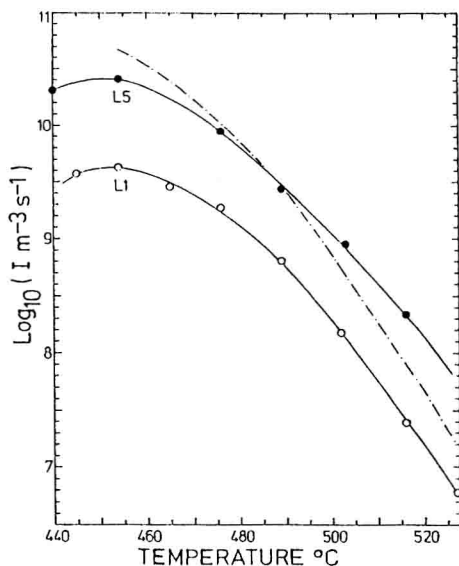


Figure 2: $\text{Log}_{10}(\text{I m}^{-3}\text{s}^{-1})$ vs temperature ($^{\circ}\text{C}$) for LS_2 glasses; L5, 0.136 wt% H_2O (O), L1, 0.02 wt% H_2O (O).

and ΔC_p , the difference in specific heats between crystal and liquid, but the general trend is clear from Table 1. A more general criterion for observable volume nucleation depends on W^* (equation (3)). Calculation using equations (1), (2), (4) and (5) indicates that $W^*/kT \leq 40$ is required for a 'just detectable' nucleation rate of $10^6 \text{ m}^{-3}\text{s}^{-1}$ at $T = T_g$ [2]. The variations in the calculated (Table 1) values of W^*/kT at T_M for the different compositions reflect the large differences in nucleation rates.

Most of the nucleation rates plotted in Figure 1 represent steady state values. In practice a steady state (constant) nucleation rate is approached gradually, the kinetics of the process being governed by an induction time, which increases with fall in temperature. Non-steady state effects [1] become of increasing importance near and below T_g .

Detailed comparison has been made of measured steady state I values with theory (equations (1) to (5)) for lithium disilicate glass because thermodynamic (ΔG) and viscosity data are available [1-3]. Assuming a constant interfacial energy (σ) yielded a value of A much higher than expected by theory. However, setting A at the theoretical value, the value of σ required to give agreement with theory varied with temperature from 147 mJm^{-2} at 454°C to 158 mJm^{-2} at 527°C , an increase of 7%. Similar behaviour has been observed with other compositions [2,3]. Unfortunately, little further progress can be achieved until an independent means of determining σ is available to test this possibility. It has been shown recently that the apparent temperature variation of σ for lithium disilicate may reflect the dependence of σ on the radius of the crystal embryo [13].

NUCLEATING AGENTS

Nucleating agents are constituents added to a glass which promote volume nucleation and glass ceramic formation. Examples are metallic particles, oxides (such as TiO_2 , ZrO_2 and P_2O_5) commonly used in silicate compositions and non-oxides (such as fluorides and water [3]). Their various possible roles include increasing homogeneous nucleation of a stable or metastable phase by increasing ΔG and reducing σ or ΔG_D [1,3], but most commonly the agent precipitates, often in combination with another component, initiating heterogeneous nucleation of a major phase [14]. The role of water is particularly interesting in relation to the crystallization of sol-gel derived glasses, which often contain higher hydroxyl levels than melted glasses. Small concentrations of water can increase nucleation and growth kinetics and reduce the viscosity of oxide glasses [1]. For example, nucleation rates in a lithium disilicate glass (L5) containing 0.136 wt% H_2O were about six times greater than those in a similar glass (L1) containing 0.02 wt% H_2O .