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Preface

I should like to thank very much indeed all contributors who spared their valuable time submitting their papers to the special issue of *Thermochimica Acta* dedicated to Professor Hiroshi Suga. This invitation to authors was received with unanimously positive enthusiasm and has resulted in a collection of over 60 manuscripts. While I was pleased with such a large number of excellent papers the editors were faced with a practical problem: it would be difficult to include more than about 40 papers in one issue. Therefore I have to apologize for the fact that it was not possible to publish all the received papers in the same issue. In consultation with Prof. Suga, my co-editor Prof. Sorai and the editors-in-chief of *Thermochimica Acta*, Drs. Hemminger and Whiting, it was decided to publish the contributions in two parts: the first part entitled "*Transition Phenomena in Condensed Matter*" was already published in Volume 266 (1995). The remaining papers were suggested to form another special issue of *Thermochimica Acta* covering a more specific and "hot" topic of formation, transformation and crystallization of glasses having in mind the idea of its completion by inviting other distinguished authors well known in the various fields of glass science. At the same time I felt it should be dedicated to the protagonists of nonisothermal study of glasses showing the essential role of Prof. Suga. I was happy to undertake such an editorship to create this second part, containing over 30 papers to prepare it for consequent publication as another monothematic compendium avoiding the somewhat unusual situation of having two honor issues dedicated to the same person.

The tremendous potential impact of the general area of crystal growth and crystallization kinetics has resulted in the publication of several thousand papers, where over one thousand studies were addressed to the entire area of crystallization of glasses. The longest tradition is in the field of oxide glasses with its own congresses originating in the 1930s, already putting emphasis on the formation and crystallization of vitreous media (J. Frenkel or W.T. Richards). In the 1950s this was followed by the extended theory of crystal growth in undercooled liquids (e.g. W.D. Hillig and J. Frankel), measurements of devitrification characteristics (A.J. Milue), use of DTA (the Indian school of T.S. Das, H.H. Gupta and R.L. Tharkur in the 1960s) and the detailed analysis of nucleation-growth processes in glasses (amongst others, C.A. Angell, J.D. Mackenzie, P.W. McMillan, P.F. James, I. Gutzow or D.R. Uhlmann). The other types of inorganic glasses have created their own history, in the first period, typically not interacting with the other fields creating their own crystallization systematics. Namely it is the field of chalcogenides (e.g. D.W. Henderson) which followed the boom of amorphous semiconductors starting their symposia in the 1960s. Even more effectively, the field of metallic glasses has appeared starting their symposia in the 1970s and presenting valuable contributions to crystal-growth theories (for example F. Spaepen, H.A. Davies, F.E. Luborsky, A.L. Greer or U. Koester). Glassy (melt quenching) or amorphous (disinteg-

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ration) states have become essential precursors for the preparation of many advanced materials such as magnetics, solid electrolytes, oxide superconductors or generally low-dimensional systems (e.g. semiconductor quantum dots). Moreover, the sol-gel method has succesfully competed to become one of the most progressive techniques in preparing the various inorganic, organic and mixed glasses not attainable by other techniques. Certainly we should not forget the traditional field of organic glasses, having their important past in polymer science (e.g. J.H. Flynn) and recently in cryogenics (e.g. P. Bourton). Progress in various aspects of solidification should also be noted as carried out in the areas of nucleation (B. Mutaftschiev), stability (J.J. Favier) and growth (A.A. Chernov).

The theory development has proceeded in various stages using different means in order to study general processes of formation of solids upon cooling; recently based on the extended capabilities of large computers. It can be roughly ranked into two general groups:

(i) Molecular dynamics and Monte Carlo methods involving the determination of coordinates impulses in the so-called mechanical approach. It deals with equations of motion or potential interactions and evaluation is controlled by kinetic equations based on single and/or multiple particle behaviour characterized by three-dimensional distribution functions.

(ii) Phenomenological methods covering the typically hydrodynamic approaches which use balanced equations of heat and mass transfers and fluid convection, as well as the kinetics of phase transitions through statistical physics and thermodynamics.

I concentrated my efforts on the second group (ii) hoping that most of the important aspects have been addressed in this volume by the carefully selected authors and themes. My original studies were started in this sense by proposing how to formally separate the activation energies of elementary processes of nucleation, growth and diffusion out of the apparent value of overall activation energy obtained from DTA/DSC measurements of crystallization of glasses (*Phys. Chem. Glasses* 15 (1974) 137). It matured in extended studies and review works carried out within our home Institute of Physics and can be viewed in the framework of our book "Kinetic Phase Diagrams; Nonequilibrium Phase Transitions" (Elsevier, 1991). The combination of boundary layer theory with Green's function technique (e.g. *Phys. Rev. B*48 (1993) 3620 or *Mater. Sci. Tech.* A173 (1993) 41) has further been developed here as an approximate analytical solution of phase transition dynamics. It is seemingly a most applicable high theory being transparent for technologists which, after slight modification, can be used in such surprisingly divergent fields of science as environmental (air pollution due to smog or cloud formation), nuclear energy (cavity formation in the reactor mantle under stress due to heavy irradiation) and/or biology (nucleation of satellite tobacco mosaic virus or rupture and permeation of bilayer films and lipid membranes). Last but not least, the general reference "Handbook of Crystal Growth" is worth noting (edited by D.T.J. Hurle, North-Holland, Amsterdam 1993).

As already noted the scope of the present collection is preferentially directed to a more easily understandable and utilizable area of a more formal (phenomenological) treatment, stressing a correlation between the theoretical description, measured data and their practical interpretation. Such an approach has been investigated within the framework of the Oxide Glass Conferences and recently continued by the Technical Committee "TC7" headed by Prof. Wolfram Höland (IVOVLAR, Schaan, Liechtenstein), Past chairman Dr. Wolfgang Pannhorst (Schott Glaswerke Mainz, Germany) and consisting of the members I. Donald (Reading, UK), V. Fokin (St. Petersburg, Russia), K. Heide (Jena, Germany), P.F. James (Sheffield, UK),T. Kokubo (Kyoto, Japan), R. Müller (Berlin, Germany), J. Šesták (Prague, Czech Republic), I.Szabo (Veszprem, Hungary), M.Weinberg (Tucson, USA) and E. D. Zanotto (S. Carlos, Brazil). Their interest is currently focused on the surface nucleation phenomena.

It is clear that such a vast amount of data on crystallization has required a certain classification, leading to the formation of specific journals and symposia devoted to crystal growth viewed from both limiting sides: on one hand it is the growth of single crystals upon a slow cooling of melts (e.g. *Journal of Crystal Growth*) and on the other hand the crystallization of quenched melts (e.g. *Journal of Non-crystalline Solids*). Recently it also became a frequent subject of publications in *Thermochimica Acta* and was traditionally covered by specialized sections of most material and thermoanalytical symposia. The best efforts, however, have been made in the field of oxide glasses where the traditional symposia on advances in nucleation and crystal growth were held every ten years resulting in the valuable proceedings: "Advances in nucleation and crystallization of glasses" L.L. Hench and S.W. Freiman(Eds) (Amer.Cer. Soc., Columbus, Ohio 1972); "Nucleation and crystallization of glasses" J.H. Simmons, D.R. Uhlmann and G.H. Beall(Eds) in "Advances of Ceramics" Amer. Cer.Soc., Columbus, Ohio 1982) and "Nucleation and crystallization in liquids and glasses" M.C. Weinberg(Ed.) (in "Ceramic Transactions" Amer. Cer. Soc., Westerville, Ohio 1993).

The idea of a collection devoted to broader viewpoints of the formation and devitrification of glasses, particularly aimed at the confrontation of various aspects of descriptive theories and evaluation treatments applied to all sorts of inorganic and organic materials, was mentioned during Kreidl's symposium on Advances of glasses (proceedings by D.R. Uhlmann and W. Höland) held in Liechtenstein 1994 and

Fig. 1. Top row from left to right: M.C. Weimberg, P.F. James, C.T. Moynihan, D.R. Uhlmann and S. Sakka. Bottom row: J. Šesták, I. Gutzow and E. Zanotto

supported by the members of the TC7 group (see fig.1). It took a great effort to contact various interested scientists all over the world to create a platform for such a multinational monograph realization. I was sorry to miss the other articles first promised but later unsubmitted due to various reasons: C.A. Angell (Tempe, Arizona) "Relaxation transition and ergodicity breaking within the fluid state" (vol. 266, p. 1), M.T. Clavaguera–Mora (Bellaterra, Spain) "About the meaning of activation energy of crystallization measured by DTA/DSC",J. Colmenero (San Sebastian, Spain) "Kinetics of crystallization in glasses; nonequilibrium behaviour around the glassy transition", M.H. Fernandes (Aveiro, Portugal) "Kinetics of crystallization in the Mgo-3CaO-P_2O_5-SiO_2 system by DTA", M. Harmelin (Vittry, France) "On evaluation of activation energies for nucleation and growth in metallic glasses", N. Koga (Hiroshima, Japan) "Accomodation of an actual crystallization process in the kinetic model functions" (to be published in the forthcoming Ozawa TCA special issue), J. Mimkes (Paderborn, Germany): Diffusion, phase diagrams and precipitation in binary alloys (to be published in the forthcoming Ozawa TCA special issue), S. Nemilov (St. Petersburg, Russia) "On definition of the concept of vitreous state", S. Sakka (Kyoto, Japan) "Crystallization in the sol-gel precursor glasses". F.L. Cumbrere (Badjoz, Spain) "Use of the JMAYK kinetic equation for the analysis of Solid-state reactions" (Vol 266, p. 315), T. Mitsuhashi and J. Málek "Nanocrystallization kinetics of amorphous RhO_2" (to be published in the forthcoming Ozawa TCA special issue), A. Bezjak and E. Tkalčec "Separation of overlapping DTA peaks and determination of kinetic parameters for crystallization of multicomponent systems" and J. Málek "Applicability of JMA model in the thermal analysis of crystallization kinetics of glasses" (Vol. 267, p. 61).

In conclusion it is my privilege to mention here three distinguished people to whom I owe my appreciation and who also represent the three regions (Czech republic, Japan and USA) most essentially involved in creating this collection. In particular this is to mark the 70th birthday of Prof. Dr. Vladimír Šatava (Emeritus Professor of the Institute of Chemical Technology in Prague) who brought me to the field of science during my early studies;the 65th birthday of Prof. Dr. Hiroshi Suga (Emeritus Professor of Osaka University and the 60th of Prof. Dr. Donald R.Uhlmann (Professor and Department Head at Arizona University in Tucson) who gave me enthusiasm to study crystallization while I was a post-doctorate assistant in the University of Missouri at Rolla, enjoying the leadership of the late Professor Norbert J. Kreidl together with Drs. Peter Schultz, Edward Boulos, Jürgen Mimkes and Larry Hanch.

In the former Czechoslovakia, Professor V. Šatava (fig. 2) represented a deeply recognised protagonist of the advanced science of glass, cements and ceramics, having established his position similar to Kingery's in the USA. Similarly, he wrote a basic book called "Introduction to the physical chemistry of silicates and ceramics" published as early as 1965 and it has since, served as the bible for scientific generations. He, unfortunately, did not belong to those scientists favored by the past communist regime, so he was not allowed to have the book translated nor was he able to travel abroad. Nevertheless he had a significant role in the development of the Czech scientific school of nonisothermal studies of materials and understanding of nonequilibrium processes, having educated quite a few recognized scientists such as Drs. Pavel Hrma, (Richmond,

Fig. 2.

WA), Luboš Němec and Jiří Matěj (Prague) and Jana Volavka (Newark, NJ). Beside the authorship of over 300 scientific papers, his name is associated with Satava's method of evaluation of nonisothermal kinetic data (1971) and further it is worth noting his advanced textbooks on rational thermodynamics, solid-state chemistry and physics published in the 1970s. He was cofounder of a prestigious Czech scientific journal "*Silicaty/Ceramics*" (started in 1957 by the late Professor R. Bárta) having served as the Editor-in-chief until recently. He was also the director of the Joint Laboratory for Ceramic and Glass Research under the Prague Technical University

Fig. 3.

and the Academy of Sciences until his suspension enforced by the communist leadership. He is an excellent pianist, a skillfull painter and is always full of progressive ideas in many scientific fields, and is always ready to distribute them freely to his coworkers; governing politically his Institute department for more than 40 years.

The curriculum vitae of Professor H. Suga (fig. 3) was published in greater detail in Volume 266. I would like to stress his significant role in searching the validity of the third law of thermodynamics through the observation of ordering processes in disordered systems. He discovered the class of glassy crystals (1970), confirming that the glass transition is not only the characteristic property of liquids, but also condensed matters in relation to the freezing process of some degree of freedom. In this sense he played an important role in maintaining "unfrozen" world contacts with the Czech thermodynamic society during the strict period of its communist control, confirming the humorous abbreviation of his name H (Enthalpy), S (Entropy) U (Internal), G (Gibbs) and A (Helmholtz energy). He is well-known as a cofounder and director of the Osaka Chemical Thermodynamic Laboratory and later the famous Microcalorimetry Research Centre. He was awarded memorial medals by Huffman and Kurnakov, the Japanese Academy Prize 1995 and served as the Chief Editor of *Journal of Calorimetry and Thermal Analysis*. He enjoys listening to classical music, from Bach to modern Prokofiev, and collects natural minerals and stones. He is a recognised philosopher/theologian.

Professor D.R. Uhlmann (fig. 4) is a well-known professor of ceramics and polymers originally associated with M. I. T., presently serving as the Head of the Department of Material Science and Engineering at the University of Arizona and as the Director of the Arizona Materials Laboratory in Tucson. His name is associated with the derivation of nucleation—growth equation applied to the crystallization of glasses (1972). He is the coauthor of the second edition of Kingery's famous book "Introduc-

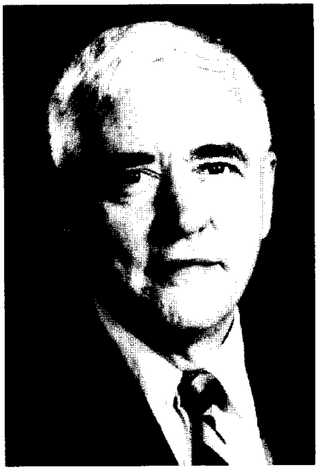

Fig. 4.

tion to Ceramics" and Associate Editor of the journals "*Sol-Gel Science and Technology*" and "*Materials Science and Engineering*". He has published over 300 technical papers and served with N.J. Kreidl as a General Editor of multivolume "Treatise on Glass: Science and Technology". He is a member of the American Ceramic Society (Glass and Optics), American Physical Society (Polymers), Technical Committee on Material Processing in Space of the American Institute of Aeronautics and Astronautics, and has served on the Material Advisory Board of the National Academy of Sciences. Among others, he has received Norton and Morey awards, a Guggenheim fellowship and is a fellow of the American Ceramic Society and the U.K. Society of Glass Technology. He is known as a charming person smoking big cigars.

I truly hope that the present special issue of *Thermochimica Acta* will provide our readers with a useful compendium to highlight modern aspects of formation and devitrification of glasses, as brought from the different geographical areas and carried out by recognized specialists in order to provide an authoritative description of the current state of research in the various fields of their activities.

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