

THE STRUCTURE OF GLASS

Volume 5

STRUCTURAL
TRANSFORMATIONS
IN GLASSES
AT HIGH TEMPERATURES

Edited by

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THE STRUCTURE OF GLASS
STRUCTURAL TRANSFORMATIONS IN GLASSES
AT HIGH TEMPERATURES

STEKLOOBRAZNOE SOSTOYANIE
STRUKTURNYE PREVRASHCHENIYA V STEKLAKH
PRI POVYSHENNYKH TEMPERATURAKH

СТЕКЛООБРАЗНОЕ СОСТОЯНИЕ
СТРУКТУРНЫЕ ПРЕВРАЩЕНИЯ В СТЕКЛАХ
ПРИ ПОВЫШЕННЫХ ТЕМПЕРАТУРАХ

PREFACE

A wide range of theoretical researches, laboratory experimental work, and industrial trials is necessary for the successful solution of the problem of production of high-strength and heat-resistant crystalline glass materials.

This series of investigations, conducted in a number of scientific establishments, industrial institutes, and factory laboratories, is one of the important trends in the general plan of development of new routes for creation of a variety of structural and protective materials for the national economy and the building industry. This constitutes one of the most important tasks currently facing Soviet glass scientists. Theoretical research and exploratory work on the production of glass-ceramics are concentrated mainly in the I. V. Grebenshchikov Institute of Silicate Chemistry.

In the development of an extensive series of theoretical and experimental investigations of the internal atomic and molecular structure of glass in the Institute, studies of the phenomena occurring during crystallization of glass are being conducted on a broad front. These studies include the primary structure of such glasses and the initial stages of chemical and physical differentiation of silicate melts in a strongly supercooled glassy state. The possible mechanisms of formation of crystal nuclei under these conditions are being examined theoretically and experimentally.

Much attention is being devoted to investigation of the subsequent growth of these nuclei and further development of the complex stages of formation of crystalline concretions and other structural types of crystalline glass materials.

PUBLISHER'S NOTE

The following books, frequently cited in this volume, are available in English translation:

N. V. Belov, *Crystal Chemistry of Large-Cation Silicates*, New York, Consultants Bureau, 1963.

The Structure of Glass, Volume 1: Proceedings of the Second All-Union Conference on the Glassy State, New York, Consultants Bureau, 1958 (originally published as *The Structure of Glass*, Izd. Akad. Nauk SSSR, Moscow-Leningrad, 1955).

The Structure of Glass, Volume 2: Proceedings of the Third All-Union Conference on the Glassy State, New York, Consultants Bureau, 1960 (originally published as *The Glassy State*, Izd. Akad. Nauk SSSR, Moscow-Leningrad, 1960).

The Structure of Glass, Volume 3: Proceedings of the Fourth All-Union Conference on the Glassy State, New York, Consultants Bureau, 1964 (originally published as *The Glassy State*, Izd. Akad. Nauk SSSR, Moscow-Leningrad, 1963).

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Russian Title	English Title	Publisher
Fizika tverdogo tela	Soviet Physics—Solid State	American Institute of Physics
Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics
Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America
Steklo i keramika	Glass and Ceramics	Consultants Bureau
Uspekhi khimii	Russian Chemical Reviews	Chemical Society (London)
Zavodskaya Laboratoriya	Industrial Laboratory	Instrument Society of America
Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	Chemical Society (London)
Zhurnal neorganicheskoi khimii	Journal of Inorganic Chemistry	Chemical Society (London)
Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau
Zhurnal prikladnoi khimii	Journal of Applied Chemistry	Consultants Bureau
Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau

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STRUCTURE OF GLASS AND INITIAL STAGES IN THE FORMATION OF GLASS-CERAMICS

E. A. Porai-Koshits

The discovery of new crystalline glass materials, glass-ceramics ("sitalls"), forced many physicists and chemists to investigate the nature of the glassy state and, in particular, the mechanism of glass crystallization.

The usual crystallization of glass — devitrification — is, of course, a harmful effect; a completely devitrified glass is a coarsely crystalline and fissured material of very low strength, which has lost its transparency and other useful properties of glass. Glass technologists have always sought glasses which crystallize with difficulty. The discovery of glass-ceramics was the discovery of new ways of glass crystallization, as the result of which the glass was converted into a very valuable technical material with remarkable combinations of useful properties: strength, heat resistance, lightness, transparency in various spectral regions, good dielectric properties, chemical durability, etc. The technical production of these new materials began independently in Rumania and in the United States of America (Corning Glass Works, New York), and then spread rapidly to other countries.

Searches began immediately for a satisfactory interpretation of the structural processes taking place in glass during the production of glass-ceramics, and it soon became clear that the basis of their formation is controllable catalyzed or nucleated crystallization of glass. *

A glass-ceramic is an almost ideal polycrystalline material consisting of very fine (smaller than $1\ \mu$ in ordinary glass-ceramics and about $0.1\ \mu$ in transparent materials) randomly oriented crystals of uniform size, formed into concretions or cemented by residual glass (5-10% in ordinary and up to 40% in transparent materials), without cavities or defects. The composition and structure of the crystals may be very diverse and not in accordance with the phase diagram, i.e., they may be to a certain extent metastable. Their lattice may be distorted, the unit cell unknown, and the properties may be new and undergoing a number of changes in the course of heat treatment. A glass-ceramic is nearly always a metastable crystalline glass system and a transition to a stable equilibrium state (during prolonged exposure to high temperatures) may lead to sharp worsening of its properties as the result of recrystallization with breakdown of contacts between the crystals and further crystallization of the residual glass [1].

The condition for formation of a glass-ceramic is therefore nucleated rather than ordinary crystallization of glass; this implies crystallization in the following two stages:

1. At the first stage an "intermediate product" is formed — a glass with nuclei (for example, fine crystals about $100\ \text{\AA}$ in size), which stimulate subsequent crystallization, distributed uniformly throughout its volume.
2. At the second stage, uniform and simultaneous volume crystallization of the main bulk of the glass occurs. The crystals may pass through a series of metastable forms in the process.

*A catalyst is a substance which accelerates a chemical reaction, whereas, in this case, there is no acceleration of crystallization, but rather creation of conditions ensuring uniform and simultaneous crystallization around the nuclei or crystallization centers; therefore, the term "nucleated crystallization" is to be preferred to the more common Russian term "catalyzed crystallization."

Two main ways of obtaining the "intermediate product," preparatory to general volume crystallization, are now known. One consists of introduction of additives which stimulate formation of disperse metal particles with linear lattice parameters (regardless of the crystal system) approximating to within 10-15% to the linear parameters of the "future" crystals; their angular parameters should also be close (the epitaxy effect). The second involves utilization or creation of a chemically heterogeneous glass structure with heterogeneity regions of submicroscopic size (of the order of 100 Å), where one of the "submicrophases" must crystallize more readily than the rest. The first way has been examined in detail by É. M. Rabinovich [2]. With regard to the second, it was shown earlier, in the case of sodium borosilicate glasses [3], that the chemically heterogeneous structure can itself be controlled (regions of different sizes and different compositions can be produced by appropriate heat treatments); other examples of the possibility of such control are given in the present collection [4-6].

Of course, it is also possible to combine the two ways of obtaining the intermediate product, for example, when additives stimulate crystallization of one of the "submicrophases" of chemically heterogeneous glass.

Independently of intermediate product formation, many investigators have demonstrated a clear dependence of the course of volume crystallization (at the second stage) and of the properties of the final product, the glass-ceramic, on the structural changes taking place in the glass during heat treatment in the precrystallization period (before formation of the intermediate product). According to I. I. Kitaigorodskii and R. Ya. Khodakovskaya [7], such heat treatment alters the nature of the crystallization process sharply, produces radical changes in the phase composition of the glass-ceramics and in the sequence in which the crystalline phases are deposited, and influences changes in a number of properties during crystallization; in particular, it affects the possibility of formation of transparent glass-ceramics.

The role of heat treatment of the glass during the precrystallization period has been stressed by I. M. Buzhinskii, E. I. Sabaev, and A. N. Khomyakov [8], Hintz and Kunth [9], Vogel and Gerth [10], Roy [11], Ohlberg, Golob, and Strickler [12], and others. Vogel and Roy consider that separation of a second glassy submicrophase within the glass during such heat treatment is probably the sole cause of highly disperse homogeneous crystallization. Vogel states that glassy submicrophases are nuclei catalyzing subsequent volume crystallization and refers to "spontaneous crystallization of microphases." This problem is examined theoretically in articles by V. N. Filipovich published in the present collection.

All these recent investigations, as well as numerous others, show convincingly that the problem of glass structure, of the existence of geometrical and chemical order (i.e., crystallites or regions of different compositions) in the glass, of the possible effects of this structure of heat treatment, chemical modification, or irradiation; in other words, the problem of the structural life of glass, is a problem which was almost entirely of purely academic interest before the appearance of glass-ceramics, but is now of great practical significance, associated with selection of compositions of glass-ceramics and development of technological processes for their production.

A crucial year in this respect was 1958. Before 1958, there was virtually no theoretical or experimental material to provide a basis for a theory of glass-ceramic formation, while the hypothesis of chemically heterogeneous structure of complex glasses lacked direct structural proof. The idea that chemical interaction of atoms of different kinds has a significant influence on the structure of glass now seems trivial. However, remarkable intuition was necessary to notice on the basis of the first systematic studies of the dependence of various physical properties of silicate glasses (coefficient of thermal expansion, refractive index, birefringence, etc.) on heat treatment that this dependence cannot be explained by development of internal stresses in structurally homogeneous glasses, and to suggest structural transformations as the cause.

This was done 43 years ago by A. A. Lebedev, who put forward in 1921 the "crystallite hypothesis" of glass structure, which was the cause of excitement and controversy among chemists and physicists studying the glassy state for several decades. Even though modern views on the nature of the glassy state have long abandoned the suggestion that glass is "an ordinary melt consisting of highly disperse crystallites" [13], the main merit of the remarkable researches of A. A. Lebedev must incontestably lie in the fact that they first established the connection between the properties of glass and its geometrical structure.

The same may be said about the views of I. V. Grebenshchikov on chemical separation in complex silicate glasses, which stemmed from his work on leaching and chemical durability of silicate glasses, and from his theory

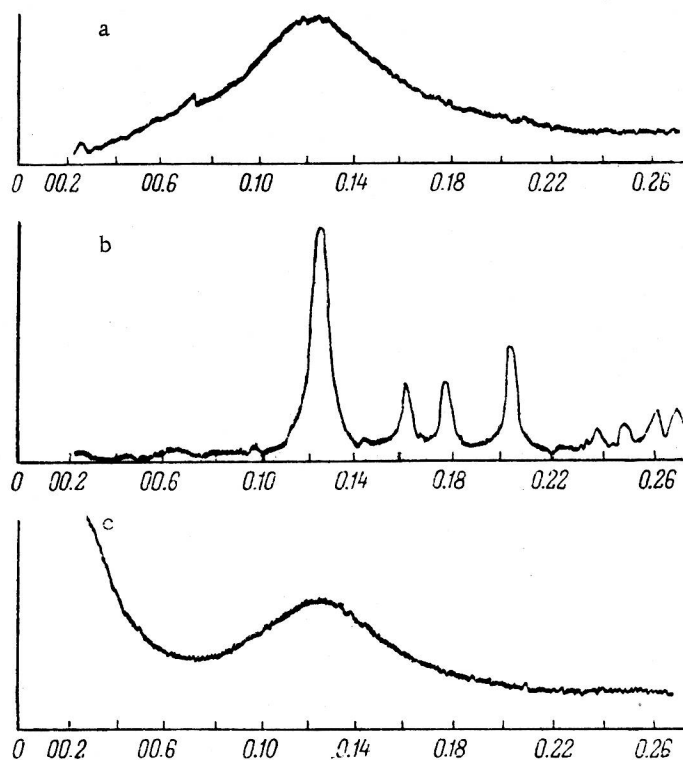


Fig. 1. Microphotometric traces of x-ray diffraction patterns of glassy silica (a), cristobalite (b), and dry silica gel (c).

of surface film formation [14]. These views, which mutually supplemented each other, were essentially concerned with geometrical and chemical order in glasses, and both opposed the existing view that glass is an indefinite chemical compound, completely amorphous, i.e., uniformly random at all points.

The development of views on chemical order in glasses is significant for elucidation of the problem of glass-ceramic formation. First, it must be remembered that not only the investigators of I. V. Grebenshchikov's school, but many other Soviet physical chemists [15], have long considered the possibility of existence of different chemical compounds (regardless of their structural form) in complex glasses. They were later joined by a number of foreign scientists [16]. However, direct structural methods were not in general used in these investigations.

The first attempts to identify the presence of chemical compounds in glass by x-ray phase analysis (as is done for polycrystalline substances) were made as long ago as 1936 by N. N. Valenkov and E. A. Porai-Koshits for sodium silicate glasses [17], and somewhat later by Porai-Koshits for a number of other silicate glasses [18]. This was done by comparison of the x-ray patterns of complex glasses with the x-ray patterns of their components; it was found that these components had independent scattering, i.e., that they retained their individual structures in the complex glass. However, at that time, the authors identified these chemically heterogeneous "submicrophases" with crystallites, i.e., chemical order in glasses was reduced to geometrical order. This was partly due to the impossibility of determining experimentally the dimensions of chemically heterogeneous regions.

It was only after the discovery and development of a new method of x-ray structural analysis, small-angle x-ray scattering, that the submicroscopic structure of various substances, so significant for interpretation of many important technical properties, ceased to be a "blank spot" [19]. However, in the case of glasses the situation was more complex. The view that glasses never give small-angle scattering and are therefore structurally homogeneous, passed from Warren's facile pen into many articles and important monographs, such as Morey's "Properties of glass" or James's "Optical principles of the diffraction of x-rays." The microphotometric curves shown in

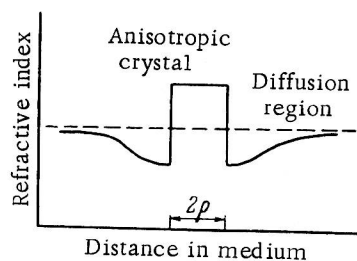


Fig. 2. Schematic diagram of the change of refractive index in passage through a spherical crystal of radius ρ .

Fig. 1 were usually cited as proof. In fact, all subsequent attempts to obtain small-angle scattering in glasses either ended in failure or the results were rejected as spurious: they were attributed to parasitic scattering by the slits, to air, dust, surface of the grains in the powder specimen, etc. [21].

It is therefore natural that the first objects of investigation by the new method were porous glasses, obtained by leaching from sodium borosilicate glasses of certain compositions [3]. These investigations showed at once that the pore dimensions, which were identified with the dimensions of the sodium borate components of the original glass, were too large for chemically heterogeneous crystallites. These investigations therefore led to the hypothesis of the existence of chemically heterogeneous regions, of chemical order.

Soon after this (again in 1958), the first small-angle x-ray diffraction patterns of the original sodium borosilicate glasses were obtained, followed by those of glasses of other compositions [22]. The failures of earlier attempts to obtain small-angle scattering by glasses — they were due to the extremely small difference between the electron densities of different "submicrophases" ($0.03 \text{ el}/\text{\AA}^3$ in sodium borosilicate glasses).

The chemically heterogeneous structure of many complex glasses gained general acceptance at the Third All-Union Conference on the Glassy State in 1959. Academician N. V. Belov, who had been one of the main opponents [23], not only agreed completely with the arguments put forward by the supporters of this structure [24], but developed some very interesting views explaining the causes of the tendency to chemical differentiation on glasses. Several quotations from the paper by N. V. Belov [25] must be given in this connection. N. V. Belov considers that "the structural basis of silicates consists not of silica or of silicon-oxygen radicals, but of cations," that "silicon-oxygen radicals — chains, bands, networks, and even rings — are fairly stable but not rigid and are easily deformed, adapting themselves to various conditions imposed by the concentrations of the principal cations, and often merely by the enforced geometry of their arrangement." He then concludes that "in all 'crystallochemical' interpretations or, more correctly, conjectures, of the processes taking place in glasses it must be taken into account that the fundamental 'form factors' are not silicon-oxygen chains but rather rods consisting of the Ca and Na octahedrons which are so characteristic of most of the structures determined in the second chapter of the crystal chemistry of silicates, and stable but far from rigid silicon-oxygen radicals are adapted to them."

There is no doubt about the similarity of these statements to the views of Academician I. V. Grebenshchikov, who repeatedly put forward the idea of a silicon-oxygen spongelike framework in silicate glasses, which may be deformed under the influence of silicates permeating it.

Thus, during the last five years, owing to the discovery of glass-ceramics and the direct proof of the chemically heterogeneous structure of a number of complex glasses, new views on the structure of glass have been adopted everywhere. These views were confirmed independently and almost simultaneously by the electron-microscopic investigations of Vogel [10], Watanabe and Moriya [26], Ohlberg, Golob, and Strickler [12], and others.

In 1962, two symposia were held. One was arranged by the American Ceramic Society [27] and the other, convened by the I. V. Grebenshchikov Institute of Silicate Chemistry of the Academy of Sciences of the USSR, the S. I. Vavilov State Optical Institute, the Art Glass Factory, and the V. I. Ul'yanov-Lenin Leningrad Electrotechnical Institute, was held in Leningrad. Mainly the experimental principles of glass-ceramic formation were discussed at both symposia. The two collections of proceedings are remarkable in the similarity of ideas, techniques, certain experimental results, and suggested further investigations. There is also a tendency to avoid primitive indirect confirmation of various viewpoints by a purely phenomenological comparison of the results, and to justify them by direct structural methods or calculations which permit quantitative verification and are based on the nature of the observed effects and on the physical laws governing them.

For example, Maurer [28] applied the modern theories of visible light and x-ray scattering to his model of formation of a primary crystal nucleus in glass, surrounded by a region poor in the ions entering the glass (Fig. 2),

i.e., a region with refractive index n different from the refractive index n before formation of the crystal nucleus. By measuring the intensity of horizontally polarized light, which should be proportional to NV^2 (N is the number of crystals per unit volume, and V is the average volume of a crystal), and the integral intensity of the strongest Debye line, proportional to NV , Maurer found the absolute average values of N and V separately, and from them he calculated the average sizes of the crystals at the various stages of heat treatment stimulating the growth of crystal nuclei. The composition of the glass used by him was: 56% SiO_2 , 20% Al_2O_3 , 15% MgO , 9% TiO_2 , and a few tenths of 1% of As_2O_3 . The crystal size increased from 57 Å at the end of heat treatment at 742° to 110 Å (756°), 154 Å (771°), and 210 Å (791°). Polarization of visible light made it possible to observe conversion of isotropic into anisotropic regions, i.e., crystallization of droplets in the glass nucleated by "emulsification," during the heat treatment.

Vogel and Gerth [10] presented some excellent electron micrographs of a crystallizing glass during gradual conversion into a glass-ceramic [lithium aluminosilicate glass with titanium oxide, magnesium oxide (3%), zinc oxide, and traces of Na_2O , K_2O , CaO , Fe_2O_3 , and As_2O_3], and of model fluoroberyllate glasses. On the basis of essentially only one method, they overestimated somewhat the role of formation of heterogeneity regions in the glass, regarding them as the first stage of crystallization. Moreover, in interpreting the results of investigations of glasses of definite compositions, the authors concluded that droplets always crystallize in glass-ceramics, and the matrix in model glasses; this contradicts the electron-microscopic investigations of the influence of chemically heterogeneous glass structure on crystallization, reported in the present collection [5].

Watanabe and Moriya [26] published an extensive investigation in which an interesting attempt was made to establish a relation between the mechanism of glass destruction and its submicroheterogeneous structure. Modifying Griffith's theory of "incipient flaws" in the light of the "microphase theory" of glass, and using the "microphase" dimensions determined with the electron microscope for the calculations, they obtained very good agreement between the theoretical and experimental relationships for viscosities of sodium calcium silicate and borosilicate glasses as functions of the loading time with constant and supplementary loads, at various temperatures. In another article, Watanabe, Caporali, and Mould [29] studied the effect of heat treatment on the mechanical properties of crystallizing glasses.

Ohlberg, Golob, and Strickler [12] used x-ray phase analysis and electron and optical microscopy for investigating crystallization of the following glasses: magnesium aluminosilicate with added titanium dioxide, lithium calcium silicate with added titanium dioxide, and lithium magnesium aluminosilicate. They concluded that internal nucleation in these glasses is the result of phase separation occurring when the glass is cooled from the melt: growth of the heterogeneity regions formed to a critical size (about 500 Å) when the glass is heated leads to crystallization, which spreads from the "drop" surface either inward or into the matrix. This course of crystallization is consistent with [5].

Hilling [30] investigated the formation of glass-ceramics theoretically with the aid of the Tilton pentagonal-dodecahedral model of silicate glasses [31] and concluded that a glass-ceramic may be formed from a glass of homogeneous structure without preliminary nucleation.

Hintz, Kunth, and Roy, like Galakhov, approached the problem of glass-ceramic formation from the standpoint of the theory of heterogeneous equilibria, and gave similar recommendations concerning the use of phase diagrams for selection of glass compositions with the most favorable structure for formation of glass-ceramics.

Hintz and Kunth [9] consider that only crystallization which begins on the basis of previous phase separation creates uniform distribution of the primary nuclei and results in subsequent uniform growth of the crystals of the main phase. An appreciable difference between the crystallization rates of the phases formed is a necessary condition.

Roy [11] found that glass with the structure of an ideal supercooled liquid is a rare special case. Every real supercooled liquid deviates to a greater or lesser extent from an ideal supercooled liquid with regard to composition, viscosity, rate of cooling, heat treatment, etc. A glass of a given composition can, according to Roy, have a number of structures with different, although similar regions of short-range order. If the glass passes through a metastable region of coexistence of two liquids on cooling, it may retain the separated structure. Roy concluded that separation into two glasses is probably the only cause of possible highly disperse nucleation and subsequent formation of glass-ceramic.

According to F. Ya. Galakhov [32], a special type of phase separation: microseparation (or "submicroseparation"), when the coexisting liquids or glasses differ little in composition, may be identified. Within the region of the phase diagram where these microseparation effects occur, there is not a single general separation region, but a number of separate, "partial" microseparation regions; as a rule, they are by the side of the separation "dome" and not within it. In this case, heterogeneity regions are not capable of growth during heat treatment of the glass.

V. N. Filipovich [33], on the other hand, considers that there is no difference in principle between micro- and macroseparation, and that the first is a purely fluctuational effect, the initial stage of the second. In this way, Filipovich classifies as fluctuational the numerous heterogeneity regions from 200-300 Å to 0.5 μ in size, reported in [4,5] and [32], and considers that in a one-component glass "the degree of order may be different in different nucleation regions of the fluctuation type. For example, it is reasonable to assume that it diminishes from the center of the nucleus to its periphery. This region of order fluctuation can, if desired, be called a crystallite."

Goganov and Porai-Koshits [6], who applied the small-angle x-ray scattering method to investigations of the submicroscopic structure of glass, observed that under certain conditions very small heterogeneity regions (with radius of the order of 50 Å) are formed in certain optically transparent glasses; the size of these regions, as in the case of Galakhov's microseparation regions, does not alter during heat treatment. Similar observations are reported in [4] and [5]. It is very probable that these structural investigations may provide an interpretation for an experimental fact reported by many investigators: for uniform highly disperse crystallization of glass, the glass compositions chosen should be close to the "separation dome" of the phase diagram, but not within the dome itself.

Owing to the possibility of measuring integral intensities of small-angle scattering, a method was used in [34] and [6] for experimental determination of the root mean square fluctuation of electron density, which is a satisfactory quantitative measure of the degree of chemical heterogeneity of glasses. By determination of its variation during heat treatment, it is possible to control the preparation of the glass structure for nucleated crystallization.

Mention should also be made of a recent publication by I. I. Kitaigorodskii, É. M. Rabinovich, and V. I. Shelyubskii [35], containing an analysis of the general relationships in the initial stages of formation of glass-ceramics. A fairly detailed description of the possible routes of the process, based on general thermodynamic considerations, is supported by electron micrographs merely in illustration.

This brief survey of the principal work on glass structure and the theory of glass-ceramic formation is intended to demonstrate the close connection between chemically heterogeneous glass structure and the possible formation of crystalline glass materials, the important technical properties of which are determined by their almost ideally polycrystalline structure. It does not touch upon the numerous special problems relating to the physical nature of individual remarkable properties of glass-ceramics, as these problems can be solved only on the basis of more detailed information on nucleated crystallization of glass. Some of these special problems are discussed in separate articles of the present collection; they include the phase composition of the crystals at various stages of heat treatment, determination of the degree of crystallinity of crystallized glasses and glass-ceramics, the persistence or breakdown of the anion framework during crystallization of glasses of stoichiometric composition, the phenomenological relation between the mechanical properties and structure of crystallizing glasses, searches of methods for production of a flexible inorganic polymer, problem of crystallization on the basis of rock melts, etc.

In distinction from the two collections on catalyzed (nucleated) crystallization of glass, published in the USSR and the USA in 1962, the experimental investigations of the structure of glass and studies of the initial stages of crystallization published in the present collection were conducted in accordance with a general plan, supplement each other, and are elucidated by the common statistical thermodynamic theory presented in four articles of the theoretical section. Of course, not nearly all the problems even of this plan have been solved or reduced to a satisfactory unity. The attempts at quantitative calculations in the theoretical papers are in the nature of very approximate estimates. As an example, we may refer to calculations of the number of composition

fluctuations and of the sizes of heterogeneity regions of fluctuational origin, carried out by Filippovich in [33] and [36]. The question whether a special kind of precrystallizational nucleated phase separation exists remains undecided [36, 37]. Thus, in its present general form the theory is used primarily for qualitative interpretation of new results of structural investigations; the next step must be experimental verification of quantitative relationships which follow from the theory and are applied to actual compositions, temperatures, and experimental conditions.

These are apparently the future paths for the development of the theory of glass-ceramic formation, its verification by direct structural methods, establishment of the relations between structure, composition, and properties of glass-ceramics, and the possibility of regulating the formation of glass-ceramics at all stages of the process. The papers published in the present collection therefore represent merely a necessary intermediate stage.

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