

PHASE SEPARATION IN GLASS

**edited by O.V. Mazurin
and E.A. Porai-Koshits**

North-Holland

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1984

NORTH-HOLLAND

AMSTERDAM · OXFORD · NEW YORK · TOKYO



E8663985

8866001

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ISBN: 0 444 86810 0

Published by:

North-Holland Physics Publishing

a division of

Elsevier Science Publishers B.V.

P.O.Box 103

1000 AC Amsterdam

The Netherlands

Sole distributors for the U.S.A. and Canada:

Elsevier Science Publishing Company, Inc.

52 Vanderbilt Avenue

New York, N.Y. 10017

U.S.A.

Library of Congress Cataloging in Publication Data

Main entry under title:

Phase separation in glass.

Translated from Russian.

Bibliography: p.

Includes index.

1. Glass. 2. Liquation. I. Mazurin, Oleg Vsevolodovich. II. Porai-Koshits, E. A. III. Andreev, N. S.

TP858.P47 1984

666'.1042

84-10155

ISBN 0-444-86810-0

Printed in The Netherlands

PREFACE

More than twenty years ago the specific field of investigations of the vitreous state—phase separation in glasses—received a large development effort. The keen interest of the investigators in this problem was determined by several events, both coincidental in time and related to each other. Such events were the invention of glass ceramics, the fast improvement of electron microscopy, diffractational and other methods of investigating the structure of materials, the discovery of the phase inhomogeneity of fluoride and alkali silicate glasses, and the development of the theory of metastable immiscibility. During the investigations it was found that of all the structural transformations of glass-forming substances known so far (except crystallization) liquid–liquid phase separation has the most perceptible effect on their properties. One cannot but agree with Uhlmann and Kolbeck [1976] that the discovery and intensive study of metastable phase separation of liquid–liquid type had in many respects a revolutionizing effect on the investigations of the structure of glasses and glass-forming melts as a whole. No less was and is the effect, both direct and indirect, of the investigations of two-phase glasses and their properties, as well as the products of their thermal and chemical treatment, on the progress of the practical application of vitreous substances and materials based on them. Thus the discovery and study of phase separation gives an example of fast and wide practical application of structural investigations. It goes without saying that in their turn the practical needs are a spur in further development of such investigations.

At present in the world of glass investigators one cannot probably find a specialist who is not familiar with the fundamentals of the modern concepts of liquid–liquid phase separation. Several excellent reviews by Vogel [1977], Uhlmann and Kolbeck [1976] and Tomozawa [1979] also contributed to the widespread attention to the subject. The amount of theoretical and experimental data accumulated at the present time, as well as the importance of the problem, are so great that, along with review papers, a more comprehensive information source, such as a monograph, should be at the disposal of any glass specialist. Un-

doubtedly, such monograph will also attract attention of many specialists investigating the problem of phase separation in metal melts and polymers, considering that the studies on this problem made in so different fields are mutually beneficial.

The first monograph on phase separation in glasses was published in Russian in 1974 (Andreev *et al.* [1974]). Five years later one more monograph on the same problem was published in Russian (Milyukov and Kasymova [1979]).

The present edition of the former book, *Phase separation in glasses*, in English differs considerably from the Russian version by the same authors (Andreev *et al.* [1974]). The Russian edition consisted of two independent parts. The first part—*Theoretical and experimental fundamentals of metastable immiscibility*—was written by N.S. Andreev, E.A. Porai-Koshits and V.N. Filipovich; the second part—*The effect of composition of phase-separated glasses on their structure and properties*—was written by O.V. Mazurin and G.P. Roskova. The two parts are combined in the present edition in such a way as to provide a coherent approach, which will certainly help both in the search for information and its apprehension. The material of the book has been extended due to the results of numerous theoretical and experimental investigations taken from the literature of the last decade. A new chapter on the practical application of metastable immiscibility has been written for this edition at the publisher's request.

During many years the authors of the present edition have been actively working in the field of liquid-liquid phase separation in glasses. Being different in their professions and scientific interests they worked in different provinces of this expansive problem. Nevertheless, as fellow workers of the Institute of Silicate Chemistry of the Academy of Sciences of the USSR, they associated with each other trying to combine their knowledge and experience for better insight into the problem under study. The authors hope that their association has made it possible to cover equally competently the greater parts of the scientific and applied aspects of the problem.

It should be noted that both in their research on phase separation in glasses and in their actual work on the first and second editions of the book the authors were constantly encouraged and supported by the help of the prominent specialists of the Institute of Silicate Chemistry, such as academician M.M. Shultz (who was the editor of the first edition of the monograph and was very helpful with his valuable comments concerning the second edition), professors F.Y. Galakhov and S.P. Zhdanov, doctors

V.I. Averjanov, B.I. Venzel, T.S. Tsekhomskaya and many others, as well as professor B.G. Varshal of the State Institute of Glass. The authors would like to express appreciation to all of them for stimulating discussions and helpful comments on the manuscript.

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CHAPTER I

HISTORICAL REVIEW

E.A. PORAI-KOSHITS

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0. Introduction

For many hundreds and even thousands of years glass has been sparkling for humanity in all its fascinating brilliancy. The best museums of the world are proud to exhibit such masterpieces as the necklace of Hashepset, the Queen of Egypt (made 3450 years ago), the famous Ajudgio vase, Venetian goblets, jugs and beakers made by unknown prisoners of the island of Murano.

But when physicists and chemists turned to glass it lost all its brilliancy and appeared as a tedious, internally amorphous and completely homogeneous indefinite chemical compound, the so-called "ideal glass". A wealth of experimental data concerning a great variety of simple and complex, organic and inorganic, oxide and non-oxide glasses was accumulated by the middle of our century. Nevertheless different new definitions of such concepts as "glass", "vitreous substance" and "vitreous state" are still appearing in the literature.

During recent decades, a demand arose for the development of glasses with unusual and sometimes almost fantastic properties; new approaches to the investigation and synthesis of glasses have been worked out, the range of practical glasses has been immensely extended and new attempts have been made to reveal the indefinite structure and the "tedious" nature of the vitreous state. New glass-ceramic materials were developed (Stookey [1954, 1957]) and this was a rather surprising display of new behaviour of the ancient material which under specific crystallization conditions transformed into the tough engineering material, Pyroceram. An explanation of these properties was needed, but notwithstanding the existence of well-developed solid-state theory, a theory of the vitreous state was practically nonexistent. The problem of the vitreous state has attracted the attention of physicists and chemists, both experimenters and theorists. According to Stookey [1962] a rapid and "drastic progress of the investigations" of structure, properties and crystallization of glasses became evident. The progress of the theory of structural methods and their techniques has resulted in new publications experimentally verifying many (sometimes purely speculative or based on rather indirect data) hypotheses on glass structure. And now we are experiencing a

period when physicists and chemists make glass sparkle again, referring not only to its exterior but also to its inner essence.

In the present review we shall briefly deal with the evolution of views on glass structure and the nature of the vitreous state and separate, with the greatest possible thoroughness, controversial from reliable information. We shall not discuss shades of meanings of different definitions of the fundamental concepts (see, for example, Huggins [1943], Secrist and Mackenzie [1964], Porai-Koshits [1966], Solomin [1971], Kreidl [1973]), since they will be subject to repeated refinements as new data on the structure and properties of non-crystalline solids in general and glasses in particular are accumulated. With reference to this we shall define our use of the main terms, in §II.1.1. We only wish to emphasize the fact that the development of a general theory of the vitreous state is impossible without reliable data on the structure of vitreous substances.

1. Structural inhomogeneity of glass

The nature and extent of structural inhomogeneity in glass is one of the principal subjects of the general problem of glass structure (Porai-Koshits [1974], Mazurin and Porai-Koshits [1974]). Historically the first indication of an inhomogeneous glass structure was the assumption that there are crystallites in glass, that is, the finest local geometrically ordered regions in which the distribution of structural elements (e.g. SiO_4 tetrahedra in silicate glasses) or atoms (ions) is characterized by a greater ordering (approaching the crystalline one) than the disordered deviations from the mean statistic distribution. This kind of inhomogeneity was later called “physical inhomogeneity”, as distinguished from “chemical inhomogeneity” of glass, that is, local deviations from the mean glass composition. It is more proper to speak about *structural* and *chemical inhomogeneity* which we shall hold to in this book. Naturally, different order extent (i.e. the difference of structural inhomogeneity) at different points in glass inevitably leads to composition variations, but these are too small to take into account. It is clear that a specific region of chemical ordering can consist in principle of structurally inhomogeneous regions (but not vice versa). If we disregard for the moment the internal structure of chemically ordered regions and consider them as elementary structural formations, we can see that these regions are distributed in glass to a certain degree of structural ordering.

It is obvious that the only possible inhomogeneity region in one-component glasses is a structural one.

Sixty years ago Lebedev [1921] suggested the "crystallite hypothesis" of glass structure, the subject having been disputed for several decades. Lebedev made systematic investigations concerning the dependency of various physical properties of silicate glasses (such as thermal expansion coefficient, refractive index, etc.) on heat treatment. Earlier these dependencies were explained by the development of internal stresses in structurally homogeneous glass during its chilling. An astonishing foresight was necessary in 1921 to detect the inadequacy of this interpretation and to relate these dependencies to the structural transformations in glasses. And though nobody today considers glass as "an ordinary melt consisting of highly dispersed crystals" (Lebedev [1924]), it was Lebedev's idea of the interrelation between the properties and internal structure of a glass that was proposed long before the first results of X-ray structural methods in glass investigations (Lebedev [1921, 1924, 1926, 1933]).

Fifty years ago a well-known paper by Zachariasen [1932] appeared, in which, based on the concepts of crystal chemistry, he drew the following conclusion concerning glass structure:

"...the atomic arrangement in glass is characterized by an extended three-dimension network which lacks symmetry and periodicity. The interatomic forces, we concluded, had to be essentially the same as in crystals".

Without interpreting glass structure on the basis of the relative positions of atoms, ions or complexes in melts, i.e., on the basis of liquid structure just as unknown, Zachariasen related the vitreous to the crystalline state, both in terms of the distances between nearest neighbours and in terms of complete homogeneity in both states and the impossibility of isolating discrete molecules, crystallites or more expanded regions in a glass network.

Similar hypotheses concerning liquid structure were set up at that time. Stewart's hypothesis of cybotaxis (Stewart [1930]), in which cybotactic groups acted as crystallites, was similar to the crystallite hypothesis, whereas Prins's quasicrystalline hypothesis (Prins [1929]) was analogous to the hypothesis of a disordered network, which compared a liquid to a crystal in which all the interatomic distances and bond angles are slightly distorted. Naturally, the distortion increases as we move away from any "central" atom or ion.

X-ray diffraction investigations of glasses and liquids carried out at that time were interpreted in favour of either the crystallite hypothesis (Randall [1934], p. 175) and the cybotaxis hypothesis (numerous papers by Stewart, see references in Randall [1934], p. 115) or the hypothesis of

a disordered network (numerous papers of Warren and his associates: Kruter *et al.* [1936], Warren and Biscoe [1938], Biscoe and Warren [1938a, b], Warren *et al.* [1939], and others) and the quasi-crystalline hypothesis (papers by Prins [1929, 1937a], and others).

Discussions between the supporters of these two hypotheses continued throughout the investigations of glass or liquid structure. In the course of the discussions the strong and weak points of the hypotheses were cleared up and general concepts were developed and modified. Thus the crystallite and the cybotaxic group ceased to be considered as geometrically regular formations with clearly defined boundaries and became regions of the highest ordering, bonded to each other by their external, most distorted parts into one continuous network, whereas the definition of glass as a disordered network was acknowledged only as a mean statistical pattern averaging possible regions of higher ordering. Evidently in this case, bearing in mind that crystalline boundary positions are completely indistinct, the problem of a crystallite volume fraction in a glass becomes senseless.

Thus, the contradictions between the hypotheses were gradually smoothed and any further discussion was assumed to be useless. This was acknowledged at the Faraday Society discussions concerning fluids in 1936 (Prins [1937a, b, c], Stewart [1937]), and emphasized regarding the vitreous state at the 2nd All-Union Conference on glass structure in 1953. The first point of the Conference Resolution, worked out with the direct assistance of the author of the crystallite hypothesis, Lebedev ([1955] p. 364), runs:

"The Conference believes that at present the advancement of the crystallite hypothesis and the short-range order hypothesis * has resulted in a common point of view on the space ordering in atom distribution in glasses revealing the existence of chemical bonds".

Nevertheless, a number of investigators (Florinskaya [1965], Pozubenkov and Florinskaya [1965], Chebotareva [1965], Pozubenkov [1971], and others) still kept holding to the initial (microcrystalline) version of the crystallite hypothesis. Relative volumes occupied by crystallites in glasses were estimated (16%, according to Vlasov [1960] and 90%, according to Pozubenkov [1971]). At the same time the steadily increasing evidence confirmed the correct choice in the dilemma "crystallites or a disordered network". Thus at the 3rd All-Union Conference Porai-Koshits

* "Short-range order hypothesis" is a short version of the term "the Zachariasen-Warren hypothesis of a continuous disordered atomic (ionic) network".

[1960] indicated possible ordering fluctuations in glasses and admitted that highly ordered regions can be referred to as crystallites. In the same paper the author noted the impossibility of revealing such regions by large-angle X-ray scattering and reported that in principle these regions can be revealed by small-angle X-ray scattering, though at that time the sensitivity of this method was inadequate. The i's were finally dotted during the discussion on the same problem held in 1971 which stated that all the structural and structure-sensitive methods, "despite their extensive development in recent years, do not permit, for some reason or other, to reveal the regions of increased order in glass" (Evstropiev and Porai-Koshits [1972]).

And though the dilemma "crystallites or a disordered network" seems to have been finally solved, new investigations during the seventies have confirmed the law of Hegel's dialectics of the spiral development of human society, that is, the dilemma "crystallites or a disordered network" has suddenly reappeared on a new level of modern mathematical and experimental achievements.

Thus Patel *et al.* [1972] inferred that there are ordered silica regions with a density of 2.32 g/cm^3 in glasses; Konnert and Karle [1973a, b] reported the existence of low-temperature tridymite microcrystallites in silica glass; Zarzycki [1974, 1978] advanced the hypothesis of a "domain structure" of vitreous silica and boric anhydride; using the paracrystalline model of Hosemann and Bagchi ([1962] p. 120), Nucui *et al.* [1978] inferred that there are quartz-like and cristobalite-like regions in silica glass, the proportions of which change with temperature. All these conclusions have much in common with Lebedev's crystallite hypothesis though certainly at a higher level of Hegel's spiral.

On the other hand Zachariasen's disordered network hypothesis found a response forty years later in the paper "The structure of vitreous silica: validity of random-network theory" (Bell and Dean [1972]) in which the authors suggested a disordered-network model for vitreous silica. The model is in agreement with the new X-ray diffraction investigation by Mozzi and Warren [1969], the latter being confirmed by the studies of Uhlmann and Wicks [1979] who refined the disordered-network model of silica glass. Other disordered-network models have been suggested by Evans and King [1966], Weinstein and Davis [1973], and Leadbetter and Wright [1972a, b].

All the above papers initiated a new wave of discussions (see, for instance, Evans *et al.* [1973], Konnert *et al.* [1973]). It is interesting to note that those investigators who developed disordered-network models

and related them to the data of direct structural methods (with radial distribution curves) inferred the validity of the disordered-network hypothesis, whereas those who favoured quasi-crystalline models detected crystallites or crystalline regions in glasses.

As early as 1960 the idea was conceived (Porai-Koshits [1960]) that the question of the existence of any ordering outside the short-range order regions in glasses characterized by radial distribution curves should be tackled by using small-angle X-ray (or neutron) scattering (SAXS). To be more precise, applying this method to one-component glasses (SiO_2 , GeO_2 , B_2O_3 and others) one must deal with medium-angle X-ray scattering (MAXS), the angles being intermediate between small and large. Several studies have been carried out during the last decade (their results are given in the reviews of Porai-Koshits [1976, 1977], Wright and Leadbetter [1976], and others). At present these methods indicate conclusively that in one-component glasses there are no inhomogeneous structures other than deviations from the regularity in the short-range order ones and the structural part of thermal density fluctuations "frozen" at about the glass transition temperature T_g (the level of these fluctuations is in good quantitative agreement with thermodynamic calculations). One can add here that it is impossible to indicate now any phenomena which for their interpretation would compulsory demand the existence of highly ordered regions in one-component glasses.

It is somewhat different with the structures of multicomponent glasses.

2. Chemically inhomogeneous glass structure

As early as 1936 an X-ray diffraction investigation of sodium silicate glasses resulted in the conclusion that chemical compounds possibly exist in sodium silicate glasses (Valenkov and Porai-Koshits [1936]). Later these conclusions were extended to a number of other silicate glasses by Hartleif [1938] and Porai-Koshits [1942a, b, 1943]. By comparing the X-ray diffraction patterns of complex glasses with the diffraction patterns of their constituent components the independence of scattering by these various components was established, that is, they preserved their individual structures in a complex glass. At that time most scientists, however, identified these chemically heterogeneous "submicrophases" with crystallites, that is, they reduced chemical inhomogeneity in glasses to a structural inhomogeneity. This can partially account for the impossibility in those years to experimentally define the sizes of chemically heterogeneous regions.

The reference to a possible existence of both structural and chemical inhomogeneity in glasses was first encountered in one of the early papers by Lebedev [1924]. The idea was developed by Porai-Koshits [1953]. Let us dwell at some length on the investigations of chemically inhomogeneous glass structures because liquid-liquid phase separation (which is the subject of the present book) is one of its main manifestations. It will be recalled that concurrent with the first X-ray diffraction investigations of glass (Valenkov and Porai-Koshits [1936]) the hypothesis of its chemically inhomogeneous structure was developed from the interpretation of concentration and temperature dependences of some glass properties (see Vainstein and Myuller [1936], Myuller [1932, 1936, 1940]). In connection with this we should refer to colloid (Turner [1925]) and aggregative (Botvinkin [1955]) hypotheses of glass structure. The former was confirmed experimentally by Grebenshchikov and Favorskaya [1931]. According to the colloid hypothesis the silicate glass is a rigid silica "sponge" impregnated by silicates, which now can be regarded as a prototype of phase-separated glasses.

Systematic and long-term investigations of "anomalous" sodium borosilicate glasses forming porous glasses on leaching have played a significant role in developing the hypothesis of chemically inhomogeneous glass structure (Grebenshchikov and Favorskaya [1931], Grebenshchikov and Molchanova [1942], Grebenshchikov et al. [1946]). These investigations gained in scope particularly in the fifties (Molchanova and Serebryakova [1953], Zhdanov [1955], Porai-Koshits [1955]). It has been suggested that chemically inhomogeneous regions develop on cooling or heat treatment of the above glasses and this is responsible for the possibility of their selective leaching.

A large series of papers "On the structure of sodium borosilicate glasses in view of an opalescence phenomenon" (Levin *et al.* [1955], Zhdanov *et al.* [1955], Porai-Koshits *et al.* [1955, 1956], Andreev *et al.* [1960]) and some other papers in which the authors investigated structural dependence of porous glasses on composition, heat and chemical treatments of initial sodium borosilicate glasses incontrovertibly confirmed the above assumption. In all cases there is a definite relation between pore sizes in leached glasses and the intensity of Rayleigh scattering by initial glasses as well as a fully identical influence of heat treatment or initial glass composition on these factors (Porai-Koshits [1955]). In these investigations, visible light scattering (VLS) has been used for initial glasses, whereas sorption, electron microscopy (EM) (Zhdanov [1955]) as well as small-angle X-ray scattering (SAXS) (Porai-