# GLASS-CERAMICS

P. W. McMILLAN

*University of Warwick*
*Coventry, Warwickshire*
*England*

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# GLASS-CERAMICS

# NON-METALLIC SOLIDS

A SERIES OF MONOGRAPHS

*Editors*

J. P. ROBERTS
*Department of Ceramics, Glasses and Polymers,*
*University of Sheffield, England*

P. POPPER
*British Ceramic Research Association*
*Stoke-on-Trent, England*

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# PREFACE

Many developments have occurred in the field of glass-ceramics since the first edition of this monograph was published. These have included extensive research into the basic factors underlying the glass-ceramic process; studies of the relationships between the properties of glass-ceramics and their constitution; derivation of new glass-ceramic systems and substantial commercial exploitation both in specialised engineering uses and in the consumer field.

The rapid advances in the science and technology of glass-ceramics have underlined the need for an updated text. Furthermore, the great expansion of the scientific and technical literature on these materials during the intervening years provides evidence of their continuing importance and emphasises the need for an appraisal of the current state of the art.

The aim of the second edition remains essentially the same as that of the first: namely, to describe both the theoretical and practical aspects of glass-ceramics. It is hoped that the revised text will prove of value to those engaged in materials research and development, and to design engineers seeking materials with unusual and valuable combinations of properties.

Following a similar plan to that adopted in the first edition, the history of glass-ceramics is first outlined. A discussion of fundamental aspects of glass formation and structure is followed by an extensive treatment of nucleation and crystallisation processes since it is the control of these that provides the key to the successful production of high strength glass-ceramics. The important topic of metastable phase separation in glasses is discussed because of its profound influence upon crystal nucleation and growth processes. The various types of nucleating agents are discussed with regard to practical aspects and in relation to basic research on their modes of operation.

Because of their importance as tools for basic research into the materials and as aids to the control of glass-ceramic processing, methods of investigating the crystal nucleation and growth processes are discussed and illustrated by practical examples.

New information on processes for producing high strength glass-ceramics, surface-crystallised glasses and composites is included because these developments have greatly expanded the engineering potential of the materials.

The treatment of the properties of glass-ceramics has been considerably revised to include many new data and to cover additional aspects. It is believed that the relationships between properties and glass-ceramic microstructure, encompassing not only the crystal phases but also the residual glass phase, are of basic importance. For this reason, wherever possible, the properties are discussed in microstructural terms.

The discussion of the applications of glass-ceramics ranges from consideration of fields in which the materials are firmly established such as consumer products, vacumn tube envelopes and radomes to areas where the potential of the materials still awaits full exploitation, such as uses in nuclear power engineering and in the medical field.

In preparing the revised edition, discussions with my colleagues in the University and in industry have been of considerable assistance and I express appreciation of these. Appreciation is also expressed to Corning Glass Works for permission to include data on glass-ceramics Nos. 9606 and 9608 which they sell under the trademark "Pyroceram". I wish also to record my gratitude to my wife, Miss S. Callanan and Mrs P. Lewis for typing the manuscript.

Finally, I thank my wife and family for their patience and understanding throughout the period during which the revision of the monograph has been undertaken.

*February, 1979* P.W.M.

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*Chapter 1*

# INTRODUCTION

## A. Glass-ceramics: Definition and History

Glass-ceramics are polycrystalline solids prepared by the controlled crystallisation of glasses. Crystallisation is accomplished by subjecting suitable glasses to a carefully regulated heat-treatment schedule which results in the nucleation and growth of crystal phases within the glass. In many cases, the crystallisation process can be taken almost to completion but a small proportion of residual glass-phase is often present.

In glass-ceramics, the crystalline phases are entirely produced by crystal growth from a homogenous glass phase and this distinguishes these materials from traditional ceramics where most of the crystalline material is introduced when the ceramic composition is prepared although some recrystallisation may occur or new crystal types may arise due to solid state reactions. Glass-ceramics are distinguished from glasses by the presence of major amounts of crystals since glasses are amorphous or non-crystalline.

The development of practical glass-ceramics is comparatively recent although it has long been known that most glasses can be crystallised or devitrified if they are heated for a sufficient length of time at a suitable temperature. This knowledge led to the early attempts by Réaumur, a French chemist, to produce polycrystalline materials from glass. He showed that if glass bottles were packed into a mixture of sand and gypsum and subjected to red heat for several days they were converted into opaque porcelain-like objects. Although Réaumur was able to convert glass into a polycrystalline ceramic, he was unable to achieve the control of the crystallisation process which is necessary for the production of true glass-ceramics. The materials produced by his process had low mechanical strengths and distortion of the articles during the heat-treatment process could occur.

About 200 years after Réaumur's work, research carried out at Corning Glass Works in the United States led to the development of glass-ceramics in their present form. The first important step was the discovery of photosensitive glasses. These contain small amounts of copper, silver or gold which can be precipitated in the form of very small crystals during heat-treatment of the glasses. The precipitation process occurs much more readily if the glasses are irradiated with ultraviolet light before heat-treatment and, by selective irradiation using a suitable mask or negative, a photographic image can be produced in the glass.

In later developments, it was shown that photosensitive glasses could be opacified in the irradiated regions by the precipitation of further crystals upon the original metallic crystals. Materials made in this way would not however be considered to be glass-ceramics since the crystalline material present constitutes only a minor proportion of the final material.

S. D. Stookey of Corning Glass Works made an important basic discovery when he heated a photosensitively opacified glass to a higher temperature than that normally employed in the heat-treatment process. He found that instead of melting, the glass was converted to an opaque polycrystalline ceramic material. This material had a much higher mechanical strength than the original glass and other properties such as the electrical insulation characteristics were markedly improved. The conversion from the glass to the ceramic form was accomplished without distortion of the articles and with only minor changes of dimensions. This material represented the first true glass-ceramic. Evidently, the small metallic crystals acted as nucleation sites for the crystallisation of major phases from the glass. The large number of nuclei present and their uniform distribution throughout the glass ensured that crystal growth proceeded uniformly and that a skeleton of crystals was produced to maintain the rigidity of the glass article as its temperature was raised.

The successful application of photosensitive metals as nucleation catalysts for the controlled crystallisation of glasses opened the way for the development of other types of nucleation catalysts which did not require irradiation of the glasses as a necessary step. These later methods usually depend upon the precipitation of colloidal particles within the glass to act as nucleation sites. S. D. Stookey developed a wide range of glass compositions which contained titanium dioxide as the nucleating agent. The use of metallic phosphates to promote the controlled crystallisation of glasses was discovered by McMillan and co-workers in Great Britain. Later researches by workers in a number of countries have led to the discovery of many different types of nucleating agents for glass-ceramics production.

## B. The Scientific Importance of Glass-ceramics

The investigation and development of glass-ceramics are closely related to studies of nucleation and crystallisation of supercooled liquids and are therefore of general interest in this field. Glass is a very convenient medium for fundamental studies of this type because glass-like liquids have high viscosities so that the diffusion processes and atomic rearrangements which control nucleation and crystal growth occur relatively slowly. Because of the rapid increase of viscosity which occurs when the temperature falls, it is possible to arrest the crystallisation process by rapid cooling. Thus various stages in crystal growth and development can be "frozen in" permitting the use of convenient methods of examination.

Closely related to crystal nucleation and growth studies are investigations of amorphous phase separation. This subject is of interest both from the viewpoint of the basic phenomena involved and with regard to modifications of glass properties that accompany the structural change. Furthermore, the influence of prior phase separation upon glass crystallisation processes is of prime importance both with regard to glass-ceramics formation and in relation to the stability of glasses.

The wide range of compositions that can be produced in the vitreous state is particularly valuable since it allows phase transformations to be investigated in widely differing chemical environments. The development of many crystal types, including metastable and stable phases and the formation of solid solutions, can be investigated under controlled conditions. Because molten glass is a good solvent for most oxides, for certain metals and for some halides and other compounds, the effects of these, present as minor constituents, upon crystal nucleation and growth processes can be investigated. Such studies, in addition to their basic importance, are of considerable interest in relation to the development of glass-ceramic microstructures.

In addition to their value for the study of physico-chemical effects, glass-ceramics are also valuable for fundamental investigations of certain physical properties. One important field concerns the investigation of mechanical strength and fracture processes for brittle solids. Glass-ceramics are especially valuable in such studies because they can be produced to have a very fine microstructure and in addition can contain a wide variety of crystal types. A further valuable possibility is that for identical chemical compositions, the degree of crystallinity can be varied from the amorphous glass at one extreme to the almost completely crystalline glass-ceramic at the other. This latter possibility is of interest not only in studies of mechanical failure but also in the investigation of properties which are dependent on diffusion processes, such as ionic conductivity.

Basic studies on glass-ceramic systems are of interest in connection with other areas of Materials Science. In the general field they are of importance because they offer combinations of physical properties not available with other classes of materials. To the glass technologist, the development of glass-ceramics is of great interest not only because they extend the possible applications of glass-making techniques but also because the search for new glass-ceramics stimulates research into glass compositions and the relative stabilities of various types of glass. Many of these data can be of value in the development of conventional glasses and manufacturing processes. In the field of conventional ceramics it is of interest to study the relationship crystallographic constitution and physical properties. Investigations of glass-ceramics may be particularly valuable because the crystal phases present can be varied in a controlled manner and materials having identical chemical compositions but different crystallographic compositions can be prepared. The possibility of investigating the effects of variations in the proportion and chemical composition of the vitreous phase in glass-ceramics is also of value since in some conventional ceramics the vitreous phase plays an important part in determining certain properties.

Finally, the investigation of glass-ceramics is of interest to the mineralogist since materials containing unusual combinations of known crystals are possible and in addition there is the possibility of developing entirely new crystal phases which are not formed except by the devitrification of unusual glass compositions.

## C. The Technological Significance of Glass-Ceramics

The process of manufacturing a glass-ceramic involves the preparation first of a glass which is shaped in its molten or plastic state to produce articles of the required form. The glass-ware is next subjected to a controlled heat-treatment cycle which brings about nucleation and crystallisation of various phases so that the final product is a polycrystalline ceramic. This method of making a ceramic material represents a radical departure from conventional ceramic manufacturing processes and it offers a number of important advantages.

Since molten glass can be obtained in a homogeneous condition, uniformity of chemical composition can easily be achieved for glass-ceramics. The homogeneity of the parent glass together with the controlled manner in which the crystals are developed results in ceramic materials having a very fine grained uniform structure free from porosity. This is beneficial in a number of ways since it favours the development of high mechanical strength and also results in good electrical insulating characteristics.

An important feature of the glass-ceramic process is that it is applicable to a wide range of compositions and this, together with the variations which can be applied in the heat-treatment process, means that various crystal types can be developed in controlled proportions. As a result, the physical characteristics of glass-ceramics can be varied in a controlled manner and this fact has an important bearing upon the practical applications of glass-ceramics. For example, the thermal expansion coefficients of glass-ceramics can be varied over a very wide range so that at one extreme materials possessing low expansion coefficients and having very good resistance to thermal shock are possible while at the other extreme materials possessing very high thermal expansion coefficients closely matched to those of common metals can be obtained.

The use of glass-working processes such as pressing, blowing or drawing offers certain advantages over the techniques available for shaping conventional ceramics since glass lends itself to the use of high-speed automatic machinery. In general, the techniques used for shaping conventional ceramics, such as extrusion, jolleying or slip-casting, are slower than glass-shaping methods and a further point is that the ceramic ware usually requires extended drying and firing periods to avoid distortion and cracking. The advantages of the glass-ceramic process are particularly apparent in the production of thin-walled hollow-ware and other shapes where the section of the material is small since unfired conventional ceramic articles of this type are fragile, while the parent glass articles in the glass-ceramic process are relatively strong.

During conversion of the glass to the glass-ceramic form, a change in dimension occurs. However, this change is small and is controllable so that control of the shape and dimensions of the glass-ceramic article can be achieved without too much difficulty. With conventional ceramics, relatively large shrinkages (40 to 50 per cent by volume) occur during the drying and firing operations and these dimensional changes may be accompanied by distortion. Consequently, control of the final dimensions is more difficult for conventional ceramics than for glass-ceramics.

The glass-ceramic process has certain special characteristics which allow new processes to be applied. Since the materials originate as glasses they can be bonded to metals by relatively simple processes based on the fact that glass in its molten state will "wet" other materials. Thus it is possible to seal the parent glass to a suitable metal and to heat-treat the composite article to convert the glass into a polycrystalline glass-ceramic. This method of producing a ceramic-to-metal seal has many advantages over the processes available for conventional ceramics which involve complicated and expensive pre-treatment and furnacing procedures.

In recent years, important advances have taken place in the control of glass-ceramic microstructures resulting, for example, in the development of machinable glass-ceramics and in the production of bulk and fibrous glass-ceramics having orientated microstructures.

Glass-ceramics have become established as commercially important materials in fields such as consumer products, vacuum tube envelopes, telescope mirror blanks, radomes for the aerospace industry and protective coatings for metals.

Glass-ceramics can be regarded as a most valuable addition to the materials available to the design engineer. Being inorganic and non-metallic they combine useful high temperature capabilities with a high degree of chemical stability and corrosion resistance. Their unique combination of properties is likely to make them attractive for a number of specialised engineering applications.

*Chapter 2*

# CRYSTALLISATION AND DEVITRIFICATION

## A. The Glassy State

### 1. *Glasses and Crystals*

Glass might be described as a transparent substance possessing the properties of hardness, rigidity and brittleness. Thus, with the possible exception of transparency, the properties usually thought of as characterising glass are those normally associated with solids. As we shall see, however, glass possesses a number of properties which are characteristic of the liquid state and the classification of glass as a liquid of very high viscosity rather than as a solid would be in accordance with modern views.

Various definitions of glass have been put forward but one which is widely accepted is that proposed by the A.S.T.M.: *glass is an inorganic product of fusion which has cooled to a rigid condition without crystallising*.

This definition would exclude certain organic substances such as glucose or glycerol which can be supercooled to a rigid condition without crystallising and which in this form would possess many of the characteristics of glasses. In the present volume we are chiefly concerned with inorganic glasses and their crystallisation although it is not the intention to deny the usefulness of studies of supercooling and crystallisation of organic glasses as a means of obtaining fundamental information.

The foregoing definition would also exclude amorphous substances prepared by methods other than melt cooling: for example, by vacuum evaporation techniques. Some of these materials have structures and properties that closely resemble those of glasses as defined above and therefore it may be thought artificial to exclude them from the general definition of the vitreous state.

A definition that would embrace this further class of materials is: *An amorphous substance is one in which long range order in the atomic arrangement does not exist over distances greater than 10 nm.*

According to this definition, polycrystalline solids made up of crystallines of sizes less than 10 nm would be amorphous as would a "crystalline" solid containing more than $10^{19}$ point defects per $cm^3$.

Although there is no *a priori* reason why a glass-ceramic could not be formed by the controlled crystallisation of an amorphous material prepared by one of the alternatives to melt cooling this is rarely, if ever, done in practice and we shall not therefore be concerned with this possibility.

It is useful at this point to consider the relationship between the solid and liquid states in order to obtain a clearer understanding of the type of structure exhibited by a glass. X-ray diffraction measurements for liquids show that a certain degree of regularity exists in the liquid state since the diffraction patterns consist of one or more diffuse haloes. This result implies that a liquid cannot be structureless in the same sense as a gas but that there must be some sort of grouping or arrangement of the molecules in the liquid related to that which occurs in the solid state. The units of structure (atomic or molecular groupings) are the same in the liquid as in the crystalline solid but in the liquid these units are not arranged in a regular manner. Thus the liquid possesses short-range order but not long-range order whereas the crystalline solid possesses both short-range and long-range order leading to complete regularity throughout the solid.

If a melt of a pure substance is cooled, it is generally observed that there is a definite freezing point at which solidification occurs due to the formation of crystals. However, it is sometimes possible to continue the cooling of a liquid below its freezing point without encountering crystal formation. In this case the liquid is stated to be supercooled. Supercooling is not a rare phenomenon and is especially likely if precautions are taken to exclude anything (eg dust) which can act as nuclei upon which crystals can grow. A supercooled liquid represents a metastable state since its free energy is higher than that of the corresponding crystal but the structure of the supercooled liquid has a lower free energy than any immediately neighbouring structure.

The relationship between the glassy state and the normal solid and liquid states can be understood on the basis of what happens during the cooling of melts. For a substance which crystallises, it is observed that there is a closely defined temperature at which solidification occurs and at this temperature a discontinuous volume change (often a contraction) occurs. In addition heat is evolved when solidification takes place. For a substance which can be cooled to the glass state on the other hand, no discontinuous volume change is found and there is no exothermic effect corresponding with the change from the liquid to the solid state. Instead, the viscosity of the melt increases progressively as the temperature falls and eventually the viscosity attains values which are so high that for all practical purposes the substance behaves as a rigid solid. Thus the glassy state is continuous with the liquid state and is distinguished from the normal liquid state by the high magnitude of the viscosity. On this basis, it is clear that glass may be regarded as a supercooled liquid since the melt is cooled through the temperature zone in which crystallisation might occur but the liquid-like structure is retained. With increasing degrees of supercooling, there is an increasing difference in free