Table 1. High-temperature polymerization of alkynes and diynes.

monomer	electric conductivity of polymer film [a] [S/cm] undoped	doped with I_2
propyne	10^{-8}	10^{-1}
1-hexyne	10^{-9}	10^{-2}
butadiyne	10^{-8}	10
1,5-hexadiyne	10^{-6}	60

[a] Determined with the four-probe technique [4]

The reaction time of the polymerization experiments may be reduced considerably (8 h) by carrying out the above thermal processes in the presence of small amounts of various Lewis acids such as $FeCl_3$ or $MoCl_5$.

The undoped polymer films are insoluble in common solvents, possess up to 10% sp^3-hybridized carbon atoms as determined by ^{13}C NMR spectroscopy, and are more stable to air than a Shirakawa-polymer film. The oxygen-uptake of the latter amounts to 6% after 1 hour (in air, room temperature, humidity 50%) and reaches 14% after 24 hours under the same conditions. A polyene film prepared from propyne by our approach only absorbed 1.5 and 2.7% of oxygen after 1 and 24 hours respectively.

The simplicity of this new approach to conducting organic polymers makes it amenable to other highly unsaturated systems (other allenes, cumulenes, alkylacetylenes) and the results of presently performed experiments along these lines will be published in due course.

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[1] For recent summaries of the vast literature see a) C. Kröhnke, G. Wegner, *Houben-Weyl-Müller E20/2* (1986) 1312, Thieme Verlag, Stuttgart, 1986; b) H. J. Mair, S. Roth (Eds.): *Elektrisch leitende Kunststoffe*, C. Hanser Verlag, Munich 1986; c) M. G. Chauser, Yu. M. Rodionov, V. M. Misin, M. I. Cherkasin, *Russ. Chem. Rev. 45* (1976) 348.
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Research News/Inorganic Materials I

Glass-Ceramics in the Scheme of Inorganic Materials

By Graham Partridge [*]

1. Introduction

Glass and ceramic materials have been known for several thousands of years, the technology of preparation and diversity of composition and properties increasing, perhaps relatively slowly at first, but latterly much faster leading to the advanced materials which are becoming established in todays technology and which are expected to form the backbone of developments into the 21st century.

Originally it was considered that the various materials should be classed as insulating, and were distinct in composition and properties. However, these distinctions have become very blurred at the edges, for example, conducting ceramics such as silicon carbide and the superconducting materials such as yttrium–barium–copper oxide have appeared together with semiconducting glasses of the chalcogenide type. Indeed the blurring has gone even further with the advent of such materials as amorphous metals or metallic glasses. How should these be classified—as special glasses or special metals?

A further type of material which bridges the original gap between glasses and ceramics are glass-ceramics. These are much more recent in concept and possess many of the useful properties of the earlier materials. Essentially, they help to extend the overall range of materials and provide the technologist and materials designer with more opportunities to meet the increasing technological demands of today.

The present article, intended to form part of a series describing and discussing recent developments in these materials is aimed at introducing the materials and outlining their properties and general position in the overall scheme of inorganic materials. By way of introduction it is useful to consider what is meant by the various terms used for these materials.

2. Description of the Materials

2.1. Ceramics

The definition of ceramics provided by *Kingery*; "the art and science of making and using solid articles which have as their essential component, and are composed in large part of

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inorganic, non-metallic materials"[1], covers not only porcelains and refractories, which are normally considered to be ceramics, but also glasses and glass-ceramics. More specifically, however, ceramics are polycrystalline materials, generally with some interstitial glassy phase present, the material being a product of high temperature solid and/or liquid phase reactions occurring between the initial inorganic crystal forms resulting in regrowth and restructuring of the crystal phases present.

Many of the earlier ceramics, such as porcelains and refractories, were essentially silicate-based materials, but many other types now exist which have been developed as the technological demands increase. These include pure oxide ceramics, for example alumina (Al_2O_3) and zirconia (ZrO_2) ceramics, nitrides such as silicon nitride (Si_3N_4) and boron nitride (BN), and carbides such as silicon carbide (SiC). All these are polycrystalline materials and can truly be considered as ceramics which are made by the sintering of powder precursors.

2.2. Glasses

There have been a number of attempts to provide a satisfactory definition of glass which would enable this type of material to be differentiated from the "all embracing" ceramic definition given above. These attempts have tried to take into account the fact that glasses are essentially supercooled, high viscosity liquids, possess an amorphous structure and can be obtained from a wide range of both inorganic and organic compositions.[2] Perhaps the most satisfactory definition is "glass is a non-crystalline solid"[3], since this includes all solid materials which are non-crystalline regardless of their composition and mode of formation. This latter definition comes closest to overcoming the great difficulty of attempting a broad classification of such widely diverse substances.

The majority of glasses which are known and made on a commercial scale consist of glass-forming systems based on silica (SiO_2) and boric oxide (B_2O_3). However, many other glass forming systems are known within the overall range of technical glasses based on oxides such as phosphorus pentoxide (P_2O_5) and alumina (Al_2O_3) and non-oxide glasses such as the chalcogenides (glasses based on sulphur, selenium or tellurium)[3b] and indeed elemental glasses, for example amorphous alloys. With these, as with all glass-forming systems, the range of compositions which will form glasses is influenced to some degree by the rates of cooling which may be employed from temperatures above the liquidus: fast rates extend the composition range. Limits are imposed, however, by what is achievable in practice, being influenced by the size of the article and constraints such as thermal stress build-up and resistance to thermal shock.

2.3. Glass-Ceramics

Glass-ceramics are essentially polycrystalline solids prepared by the controlled crystallization of what is now a wide range of glass compositions.[4, 5] These technologically important materials may perhaps be described as "wonder materials", and the first wonder may be that they exist at all. Glass is essentially a meta-stable material, with a disordered liquid-like structure, and would prefer to exist in a more ordered, crystallized condition. Nevertheless, for many glass compositions, particularly those which are produced commercially in large quantities, the emphasis over the years has been to prevent devitrification occurring. If the glass can be cooled successfully through the temperatures at which crystallization occurs, the high viscosity of the material prevents the structural reorganization which would develop crystals, and the product possesses an amorphous structure.

Devitrification, as it is normally understood in the glass industry, is an uncontrolled process which has a harmful effect since it can lead to sudden and unpredictable changes in viscosity which interfere with the working of glass making machinery. Additionally, localized high stresses can be generated arising from differential contraction between glass and crystal phases formed, resulting in a mechanically weak product.

It has been appreciated, for some time, however, that if crystallization could be controlled then useful materials

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might be produced. Indeed, *Reaumur*,[6] in 1739 tried to produce a polycrystalline material by heating articles of a soda-lime-silica composition immersed in a mixture of sand and gypsum. However, crystallization occurred from the surface, resulting in weak and brittle articles. Although surface crystallization in certain glass compositions can now be controlled to provide high mechanical strength materials,[7] in the context of the discussion on bulk derived glass-ceramics this is an undesirable form of crystallization.

In the 1950's, research at Corning Glass Works in the USA led to the realization (it is claimed by serendipity) that, under suitable conditions and (at that time) in a restricted range of compositions, it was possible to produce a usable polycrystalline material by the controlled devitrification of a glass provided that sufficient nuclei were developed within the bulk of the glass on which crystals could subsequently grow.

The glass-ceramic process may thus be essentially divided into two parts. In the first, nuclei are developed in the glass body either by phase separation of the glass or by precipitation of a primary crystal phase during the first stages of a heat-treatment process as depicted in Figure 1. In order to develop the required quantity of nuclei it is usual to incorporate in the glass composition a nucleating agent. There have been many and varied such agents over the years of glass-ceramic development but the ones that are generally preferred in current developments are the oxides P_2O_5, TiO_2, and ZrO_2. Further heat-treatment to higher temperatures causes crystals to grow on the nuclei to form a closely interlocking crystal structure, with crystal sizes generally in the region of 1 μm, with a small proportion of interstitial residual glassy phase. In many cases, the crystallization processes can be very complex and the simple heat-treatment schedule depicted has to be modified to incorporate further holding stages in order to produce the desired materials and properties.

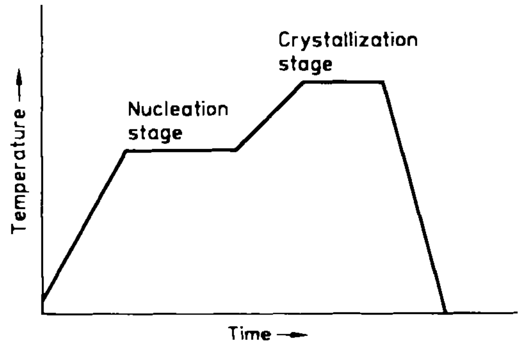

Fig. 1. Typical heat-treatment schedule for the production of glass-ceramics showing nucleation and crystallization holding stages.

Alternatively, the glass may be reduced to powder and then processed in a similar manner to that discussed above for sintered ceramics. In this case the glass powder particles react together and because of the highly damaged state of the particles, surface crystallization may become dominant over bulk crystallization. Two possibilities exist in the use and development of sintered glass-ceramic materials. In the first, the compacted material is sintered to a vitreous body and is then subsequently heat-treated as in the case of the bulk materials above. Alternatively, nucleation and bulk crystallization occur during the same firing cycle as that used for the sintering step and this is to be preferred from an economic point of view.

The majority of glass-ceramic compositions are silicate based, although a number are known based on aluminate compositions. The many and varied compositions which can now be prepared as glass-ceramics the materials possess very different properties from those of the glasses from which they are derived. Mechanical properties are often improved and the linear thermal expansion characteristics of a glass-ceramic can be considerably different to those of its parent glass. Good electrical, particularly dielectric, properties are also produced as a result of the conversion of glass to glass-ceramic.

3. Properties

The general properties of the three types of inorganic materials discussed above are reviewed in this section. Detailed properties of materials relating to specific applications will be reviewed in future articles. Table 1 provides limited data for a number of inorganic materials.

3.1. Mechanical Properties

Although glass in its pristine state, for example newly drawn fiber, can possess very high mechanical strength with moduli of rupture above 7000 MPa, in practice, owing to surface damage, this is not realized and the practical moduli of rupture of glasses are in the range 50–120 MPa. Glass-ceramics are somewhat stronger and moduli of rupture up to 750 MPa have been realized. However, by far the strongest ceramic materials are derived from the sintered type of material with high strengths being obtained in oxide, carbide and nitride materials and particularly in materials such as yttria stabilized zirconia.

3.2. Electrical Properties

Owing to the presence of closed pores in sintered ceramics, their dielectric breakdown strengths are usually no higher than 20–25 $kV mm^{-1}$ whereas both glasses and glass-ceramics which do not contain closed pores can show dielectric breakdown strengths of 40–50 $kV mm^{-1}$. The dielectric properties of sintered ceramics and glass-ceramics cover sim-

Table 1. Properties of typical inorganic materials.

Property		Ceramics					Glasses			Glass-ceramics [8]			
		Al_2O_3	SiC	Si_3N_4	ZrO_2/ Y_2O_3	SiO_2	Na_2O-CaO-SiO_2	B_2O_3-SiO_2	Li_2O-Al_2O_3-SiO_2	Li_2O-Al_2O_3-SiO_2	Li_2O-ZnO-SiO_2	MgO-Al_2O_3-SiO_2	ZnO-Al_2O_3-SiO_2
									low α	med α			
Modulus of rupture at RT	MPa	250–350	400–600	250–700	650–2000	50	120	90	100	255	200	350	95
Elastic modulus at RT	GPa	250	360	160–300	300	70	60	70	90	80	97		
Density	$kg \cdot m^{-3}$	360–390		240–310		220	220	255	255	244	260	265	370
Dielectric breakdown strength	$kV mm^{-1}$	20–25					25–30	44		45	50		
Volume resistivity	ohm cm	$>10^{16}$					10^{10}	10^{12}					
Dielectric constant	1 MHz	8.6–10					5	7			5.4		
	10 GHz	8.8–9.2		9		3.4			5.9	5.6		5.7	6.8
Loss angle, $\tan\delta \times 10^4$	1 MHz	5–8					38	40		22			
	10 GHz	1–10				4			1300	106		3	5
Linear thermal expansion coefficient, α, 20–500 °C $\times 10^7$ °C^{-1}		78				5	92	32	~0	52	145	53	30
Thermal conductivity	$Wm^{-1}K^{-1}$	26	300	34	2	3			1	2	3	3	3

ilar ranges, the properties being strongly dependent on the crystal phases (and interstitial glass phase) present in the material. In general, glasses show higher dielectric losses than crystalline materials at high frequencies although fused silica (SiO_2) is very good in this respect.

3.3. Thermal Properties

The linear thermal expansion characteristics of sintered ceramics and glasses cover similar ranges although it is difficult to obtain a satisfactory sintered material which possesses a very low expansion comparable to that of fused silica. At the high expansion end, linear thermal expansion coefficients greater than about 140×10^7 °C^{-1} can be obtained for sintered ceramics but the materials possessing such expansions are generally poor in terms of strength and resistance to attack by atmospheric moisture. Glass-ceramic materials, however, enable the overall expansion range to be extended and usable materials with linear thermal expansion coefficients ranging from negative to as high as 180×10^{-7} °C^{-1} can readily be obtained. The thermal conductivities of glasses and glass-ceramics are low, comparable with those of zirconia ceramics. High thermal conductivities can only be obtained in selected sintered ceramics, for example, Al_2O_3, BeO, SiC.

In addition, in terms of increasing resistance to high temperatures, the order is glass, glass-ceramics, ceramics. Many glasses cannot withstand temperatures in excess of 500–600 °C for long periods although fused silica may be used to temperatures in the region of 1000 °C before devitrification becomes a problem. Glass-ceramics can operate for extended periods at temperatures of 700 °C to over 1200 °C. Sintered ceramics, however, can provide operational capability to temperatures of 2000 °C although protection by means of a neutral or reducing atmosphere may be necessary to achieve this.

4. Selection

The selection of an inorganic material depends, perhaps obviously it could be argued, on the properties specified for a particular application. Often the properties are interactive so that whilst it is relatively easy to optimize one or two properties required, the problem becomes increasingly more severe when three or more properties must be optimized. However, properties are not always the overriding criteria and attention frequently has to be paid to fabrication routes. A fabrication route necessary for the highest strength material may not be practical in a specific application and compromises have to be made. Thus selection of a material for a given application may be guided, perhaps on economic terms, and the materials expert then has to obtain the best properties possible with the designated material. Examples of selection will be given in future articles and reasons discussed.

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