

Pennsylvania Glass Sand Corp.) supplied at -200 mesh particle size.

The hot-pressing apparatus consists of a $3\frac{1}{4}$ in. (84 mm) graphite cylinder with a concentric $\frac{13}{16}$ in. (21 mm) cylindrical hole. The sample is compressed between $\frac{13}{16}$ in. (21 mm) pistons on a standard press. The graphite reactor is inductively heated; temperature is monitored with a thermocouple recessed into the reactor. The hot-pressing is performed in air so that the graphite reactor must be replaced periodically.

In a typical experiment equal weights of simulated waste and matrix material are mixed, pre-formed into a $\frac{3}{8}$ in. (19 mm) pellet, and placed in the graphite reactor. The sample is surrounded by graphite powder to prevent sticking to the reactor and to facilitate removal. The required temperature is achieved in 10 to 20 min. After hot pressing for a selected time the power is shut off and the reactor cools in 1 to 2 h.

Good results were obtained when the sample was heated at 1000°C under 2500 psi (176 kg cm⁻²) for 10 min. The product was a well consolidated disc, harder than stainless steel, which proved to be denser than expected. An approximate theoretical density for the product is an average of the density of PW-4m hot-pressed under the same conditions (4.01 g cm⁻³) and of quartz (2.65 g cm⁻³). The measured density (3.42 g cm⁻³) was slightly higher than this theoretical value (3.34 g cm⁻³). X-ray diffraction analysis indicated that although the major crystalline phases present in the product were quartz and the components of PW-4m, a small amount of one or more other unknown phases(s) was also present. These density and X-ray results demonstrate that partial reaction had occurred between the PW-4m and quartz during hot-pressing. In fact, this reaction is necessary in order to obtain a hard dense product. When PW-4m and quartz are hot-pressed separately, the pellets produced are easily crumpled to a powder.

Other important properties of these hot-pressed discs include thermal stability and low leachability. The discs showed no deterioration in properties after heating at 600°C for 2 weeks. Also, no deterioration of the discs or measurable weight loss was recorded after distilled water treatment at 100°C for 2 h and at 45°C for 2 weeks. Of course, long term leachability tests will have to be performed in order to fully evaluate the solubility characteristics of the products.

The equipment necessary for this process is not a great deal more complex than that of the melt processes. The devitrification and phase separation problems with the melt process are eliminated. The matrix material, quartz, is one of least expensive and most available substances. Hot-pressing, although costly, is becoming a routine processing technique in the ceramic industry, especially in the production of ultra-hard materials, and, if its use leads to increased stability of stored radioactive wastes its cost may be justified.

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Preparation of iron sesquioxide glasses by ultra-fast quenching from the melt ("splat-cooling")

The technique of ultra-fast quenching materials from the melt ("splat-cooling"), developed in 1960 by Duwez [1] has been extensively applied to metals and alloys [2-4]. The very high cooling rates available with this technique (as high as

10⁷ to 10⁸°C sec⁻¹) have led to the formation of new metastable crystalline phases [4] as well as amorphous or microcrystalline structures [5-7]. It is interesting to note that the method has been very rarely applied to ultra-fast quenching of oxides or mixtures of oxides, e.g. [8, 9].

This letter describes splat-cooling of binary mixtures of oxides based mainly on Fe₂O₃, Al₂O₃ and Ga₂O₃ which has led to the formation

of new glasses.

The technique which has been used is the "gun" technique [1, 2], which consists of accelerating a liquid globule to a very high speed and spreading it on to a heat conductive surface. A small quantity of a mixture of oxides is melted in an induction heated platinum crucible which has an orifice of about 1 mm at the bottom. A shockwave generated by the bursting of a thin polyethylene diaphragm forces the liquid through the orifice and drives it against a copper substrate placed 4 cm below the crucible.

Experiments have been carried out in the following binary systems: Fe_2O_3 -BaO, Fe_2O_3 -CaO, Fe_2O_3 -PbO, Al_2O_3 -PbO and Ga_2O_3 -PbO. In the latter two systems non-crystallinity had been noticed in our laboratory in the course of other experiments in which water quenching was used [10, 11].

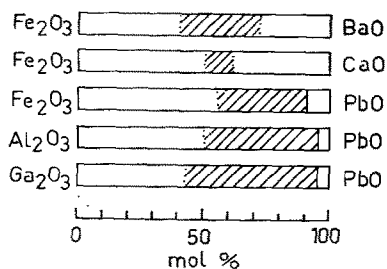


Figure 1. Composition ranges in which glasses were obtained by ultra-fast quenching.

Glasses have been obtained in the composition ranges shown in Fig. 1 (solid lines represent well-defined limits whereas dotted lines indicate the present boundaries imposed by the temperature limitations of our experimental device). Samples were in the form of transparent flakes and/or thin films. The thickness was uneven and varied from one to a few microns. Some areas were thin enough to enable electron microscopy studies without prior thinning. X-ray and electron diffraction patterns revealed diffuse rings characteristic of non-crystalline structures.

Upon heating during DTA experiments, the Fe_2O_3 glasses exhibited behaviour different from the Al_2O_3 and Ga_2O_3 glasses. The Fe_2O_3 glasses crystallized very rapidly within a few degrees whereas Al_2O_3 and Ga_2O_3 glasses showed exothermic effects spread over a much wider

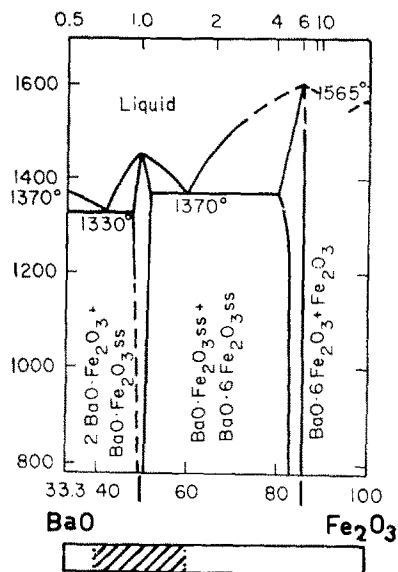


Figure 2. Glass-forming region (mol %) in relation to the phase diagram for the system BaO- Fe_2O_3 .

temperature range extending sometimes over 100°C . A slight endothermic effect was noticed in several glasses just before crystallization.

Whereas some glasses based on aluminium and gallium oxides have been previously found [12] this letter reports the first glasses based on Fe_2O_3 and not including any of the usual glass formers SiO_2 , GeO_2 , B_2O_3 , P_2O_5 , etc. It is interesting to note that the composition ranges for which glasses have been obtained almost invariably include eutectic compositions (Fig. 2).

Our results seem to show that the observations of Stanworth [13] concerning the glass forming ability of oxides of the elements of groups III to VI as a function of the electronegativity and atomic radius of the corresponding cation, can be extended to iron sesquioxide. In the graph proposed by Stanworth, trivalent iron would fall in a region where glasses can be expected. The structure and properties of these glasses are under investigation.

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Phase transformations in molecular crystals

In recent studies of polymorphic transformations in molecular solids Mnyukh *et al* [1, 2] have shown that, in general, no definite orientational relationship can exist between the crystal lattices of two polymorphs. Their morphological and X-ray evidence covers a wide range of

molecular solids including aromatic and non-aromatic structures, structures involving hydrogen bonds and the "rotator phase" solids and shows that a plurality of indefinite orientations is invariably observed.

In this communication attention is drawn to certain observations made during our studies of the photochemistry of aromatic solids [3] which is strongly at variance with the above generaliz-

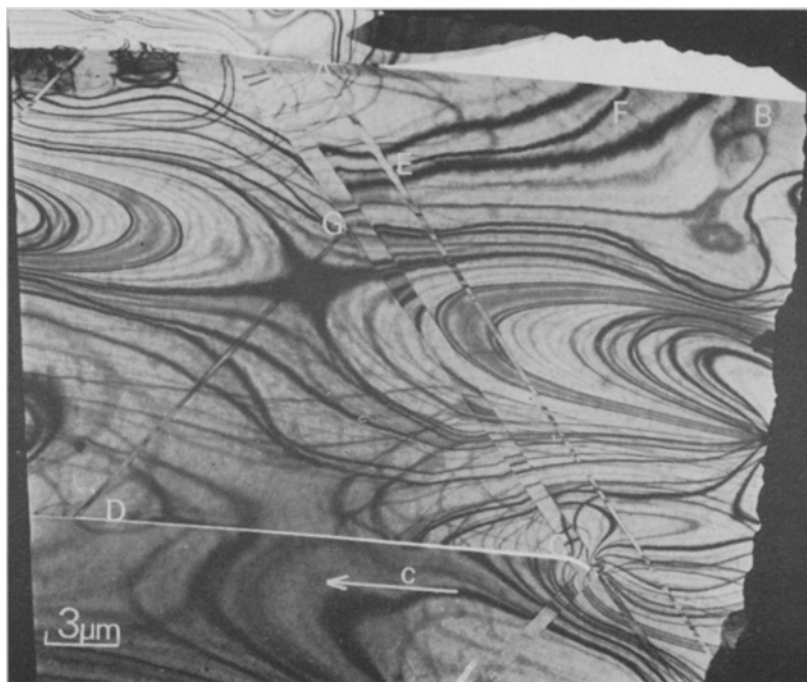


Figure 1 An electron micrograph of a crystallite of 1:8 dichloro-10-methyl anthracene showing plates of a new structure within the parent matrix. The habit planes are approximately parallel to crystallographically equivalent {301} planes.