Reports

Phase Separation in Pyrex Glass

Abstract. *The contrast between phases in pyrex glass was heightened for viewing in the electron microscope by exchanging silver ions for sodium ions in the glass. The scale of phase separation is pyrex was found to be about 30 angstroms; sample of commercial soda-lime glass, prepared in the same way, showed no phase separation.*

Many borosilicate glasses separate into two amorphous phases, one rich in silica, the other in borate (*1–3*). The borate phase can often be leached out of these glasses with acid, leaving a silica matrix. There is indirect evidence from electrical conductivity (*2*), ion exchange (*4*), and gas permeation (*5*) studies that commercial pyrex borosilicate glass also separates into two amorphous phases. However, no separation in normal pyrex has been observed in the electron microscope, nor can any phase be leached from this glass, as shown by its well-known stability to chemical attack. There is some electron microscopic evidence for structural change in a pyrex-type glass after long annealing (*6*). In our work a very fine phase separation in pyrex glass was made visible in the electron microscope by exchanging silver ions for sodium ions in the glass, thus enhancing the contrast between the two phases. Samples for observation were prepared by a new technique (*7*). This "staining" and preparation technique provides a means for studying phase separation and fine structure in other glasses and perhaps even in certain crystals.

Tubes of glass closed at one end (inside diameter, about 1 cm; wall thickness, 1 mm) were placed in silver nitrate melts with silver nitrate also inside the tube. Platinum electrodes were placed in the melts, and silver was electrolyzed into the glass with 200 volts across the glass. Electrolysis was continued until the resistance of the glass no longer changed, showing that all the conducting ions (sodium) in the glass had been exchanged for silver ions. The resulting glass was highly strained; this strain could be reduced by exchanging only part of the sodium ions for silver. Results for two different glasses, a commercial pyrex (approximate composition, in percentages: SiO_2, 81; B_2O_3, 13; Na_2O, 4; and Al_2O_3, 2; by weight) and a commercial soda-lime glass (major constituents, in percentages: SiO_2, 72; Na_2O, 15; CaO, 5; MgO, 4; Al_2O_3, 2; K_2O, 1; and B_2O_3, 1) are shown here.

The samples for electron microscopy were stripped from freshly broken surfaces of the glass with cellulose acetate tape (*7*). Samples thin enough for electron transmission were found at steps on the fracture surface away from the mirror that surrounded the origin of the fracture. A thin carbon film was evaporated normally onto the tape, which was mounted on the electron microscope grid. The cellulose acetate was washed away with acetone, and the glass fragments on the carbon film could then be examined in the microscope.

In Fig. 1 are shown electron transmission photographs through lathlike fragments of pyrex and soda-lime glasses. Figure 1a shows the structure of pyrex glass in which silver ions have been exchanged for sodium ions; pyrex with no silver ions showed no structure (Fig. 1b). The latter fragment appears darker, since it was a thicker piece, even though it was narrower. The scale of the structure in Fig. 1a is about 30 Å. Thus, it is under-

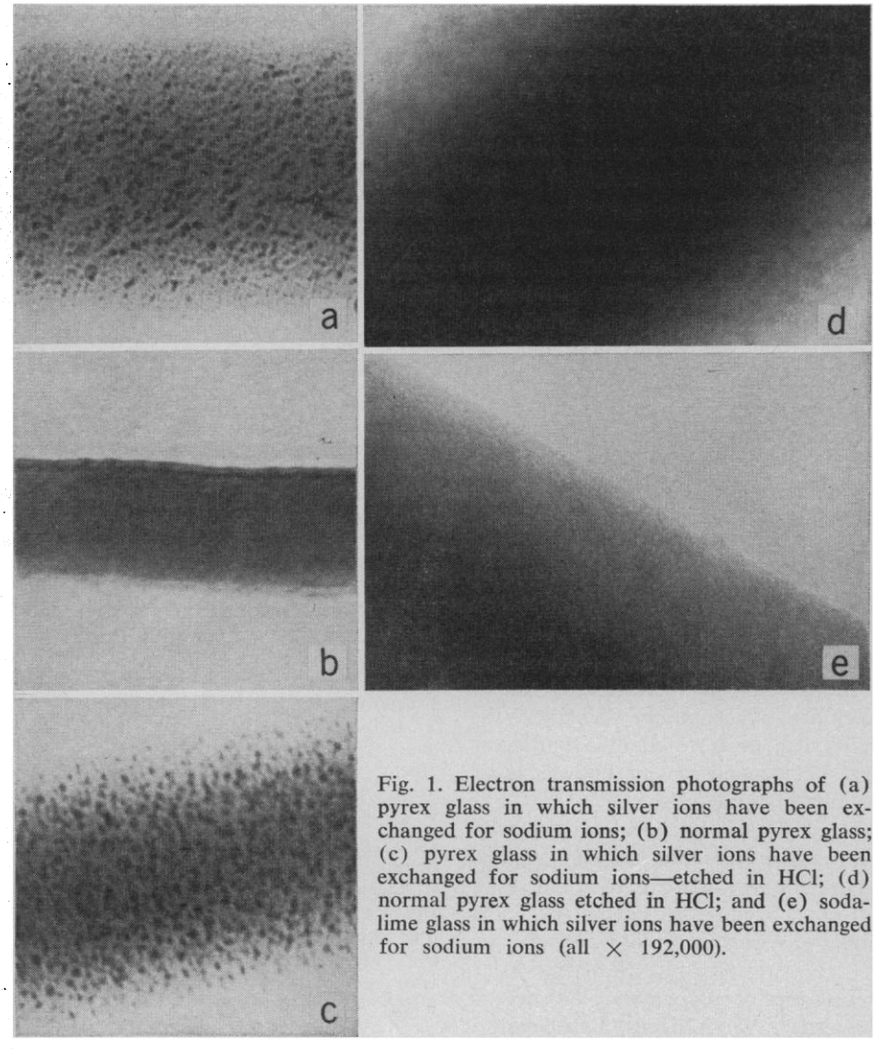

Fig. 1. Electron transmission photographs of (a) pyrex glass in which silver ions have been exchanged for sodium ions; (b) normal pyrex glass; (c) pyrex glass in which silver ions have been exchanged for sodium ions—etched in HCl; (d) normal pyrex glass etched in HCl; and (e) soda-lime glass in which silver ions have been exchanged for sodium ions (all × 192,000).

standable that a phase cannot be leached out of pyrex glass, since an enormous pressure would be needed to force the leaching solution into such small channels. Figure 1, c and d, are photographs of pieces of pyrex glass with silver ions and without silver ions, respectively, which were etched *in situ* on the carbon film in dilute HCl. The piece shown in Fig. 1d was wider and less uniform in thickness across its width; consequently, the central portion is dark.

The dark areas in Fig. 1, a and c, result from more scattering of electrons by the phase in which silver is concentrated, which is probably the borate phase. An ion exchange study (*4*) of pyrex glass showed that 95 percent of the sodium ions were in one phase, in agreement with the concentration of the silver in one phase shown in Fig. 1.

Fragments of the soda-lime glass were examined after silver exchange in the same way as the pyrex, but no structure was seen in this glass. Figure 1e is a photograph of the edge of a large splinter of the soda-lime glass with silver ions. Indirect evidence from ionic transport measurements (*8*) indicates that this particular glass does not separate into two phases, in agreement with the microscopic observations.

After the silver was exchanged into either glass, the glass was a light yellow color. However, the absorption spec trum of the glasses showed no trace of an absorption peak near the wavelength of 0.4 μm; this peak is characteristic of silver particles (*9*). Since the reduction of only a very small fraction of the silver ions to atoms and their agglomeration to particles would show an absorption band, essentially all of the silver is in ionic form. The yellow color results from an intense absorption band related to silver ions (*10*) at a shorter wavelength (about 0.24 μm).

Two mechanisms have been proposed for phase separation in glasses. In the first, small regions of the second phase nucleate and then grow by transport of material, as is observed in many conventional phase transformations. In the second, the homogeneous phase changes continuously and uniformly into two different phases whose compositions become progressively more dissimilar. The scale or "wavelength" of this "spinodal decomposition" is usually very small and leads to two interconnected and continuous structures. However, morphology does not always provide conclusive evidence for the mechanism of separation, since the continuous structure often breaks up into discrete particles in later stages of its growth, and there is some evidence for the conversion of particles to a continuous structure (*11, 12*). In spite of these uncertainties the separation shown in Fig. 1 probably resulted from a nucleation and growth mechanism, since it seems unlikely that aging of a continuous structure would lead to such small particles. The morphology observed here for pyrex is similar to that found in thin barium silicate films by Seward *et al.* (*12*); these authors also give an extensive discussion of the relation between mechanism of separation and morphology in phase separation of glasses.

The present technique of heightening the contrast between phases should be applicable to other materials in which a heavy ion can be exchanged for a lighter one. Segregation of ions at structural features in brittle materials could also be studied by preparing samples according to the method described in this report. Since this preparation does not involve mechanical or chemical thinning, it is more likely to preserve features of interest.

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Lunar Thermal Anomalies: Infrared Observations

Abstract. *The lunar craters Tycho, Copernicus, and Aristarchus have been observed during lunar night at wavelengths between 3 and 14 microns. After an initial fast decrease to a color temperature of 220°K, the temperature remains nearly constant through the lunar night. The data suggest that these thermal anomalies (craters) contain hot and cold regions with the hot portions constituting 2 to 10 percent of the area and probably thermally connected to a subsurface temperature of about 200°K.*

Infrared observations of the moon made mostly in the 8- to 14-μ atmospheric window have delineated the macroscopic thermal behavior of the lunar surface (*1*). These observations have shown that the surface temperature drops from about 390°K at noon to about 90°K before dawn. The form of the cooling curve is determined by the thermal inertia $(\kappa\rho C)^{1/2}$, and the observed 8- to 14-μ brightness temperatures indicate that this parameter has a value of 0.001 to 0.002. Observations of the cold limb at 20 μ (*2*) have confirmed the 90°K and support the very low thermal inertia (of .001 or less). Ordinary rocks such as granite and basalt have thermal inertias near 0.05. Low inertia of the lunar surface has been taken as evidence for an insulating dust layer covering the surface.

Additional information about thermal properties of the moon's surface was gained through the discovery by Shorthill of lunar thermal anomalies. The craters Aristarchus, Copernicus, and Tycho cool much less rapidly than their surroundings during eclipse (*3*). Shorthill and Saari (*4*) observed approximately 1000 such eclipse anomalies of which the great rayed craters are the outstanding examples.

Observations of thermal anomalies

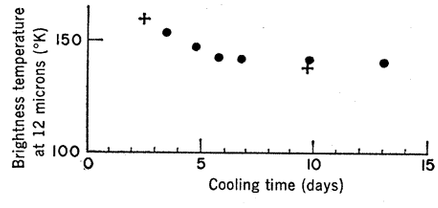

Fig. 1. Brightness temperature of Tycho at 12 μ as a function of time after sunset. (Circles) August 1968 lunation; (crosses) March 1969.