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Comments on "Effects of Ultrahigh Pressures on Glass"

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In a recent note[1] on the effects of ultrahigh pressures on glass, the writers, Cohen and Roy, compare their results with those of Bridgman and Simon,[2] who made similar measurements. Cohen and Roy point out that their results concerning threshold pressures and amounts of densification obtained for silica glass differ from those of Bridgman and Simon. Bridgman and Simon, however, give all their results in terms of density changes directly, whereas Cohen and Roy present all their results in terms of index of refraction of the sodium D line (although they state that density measurements were also made). Consequently, the published results of the two groups of experiments cannot be compared by a reader until a relation between index and density has been established under these experimental conditions. One is not justified in assuming that the well-established relation between these two properties which accompanies heat treatment alone also applies to compression. This may be particularly pertinent when the temperature is an added variable. It has been found, for instance,[3] that on compression at a constant temperature the index does not vary as it does on heat treatment alone. The index depends on both the density and the absorption spectrum. On heat treatment, the change in index (in the visible region) may be accounted for by changes in density alone with no concomitant change in absorption. The effect of changes of density on the absorption spectrum is currently a subject of great interest and activity,[4] and it is known that both changes of temperature and pressure produce shifts in the absorption bands. In fact, it also appears that shifts may result at constant density achieved by differing pressure and temperature combinations.[4] Indeed, it seems that since Cohen and Roy have both density and index data, a comparison of these properties would cast further light on these basic problems.

A question also arises concerning the relative degree to which both Bridgman and Simon's and Cohen and Roy's results may have been affected by plastic deformation arising from the nonhydrostatic pressures involved in both these experiments. In a subsequent paper[5] Bridgman attempted to resolve this question by using a "very approximately hydrostatic pressure" achieved by enclosing his glass specimens in lead. Under those circumstances he reported no change in thickness of his specimens after applying 100 kb. He states that "we may conclude that the plastic shearing deformation plays an essential role in the increase of density." This conclusion suggests that any possible actual increased densification achieved by Cohen and Roy (over that obtained by Bridgman and Simon) arose from the fact that their powdered silica specimens were subject to greater plastic deformation than the thin disks used by Bridgman and Simon.

A final observation concerns the effect of time on the results. Cohen and Roy state that "the effect of time, at any given temperature and pressure, on the final density of silica glass becomes negligibly small after the first $^1/_2$ to 1 minute." These results are in interesting contrast with those of Anderson,[6] who compressed a borosilicate glass using a different experimental technique. He reported that the density change at a constant pressure consisted of an initial reversible increase that approached a constant value after 5 hours plus a subsequent irreversible increase that continued unabated for periods as long as 5 days. In view of these differences in results (with different glasses), it is not surprising perhaps that Cohen and Roy presented an entirely different theory (involving a second-order transition) for the nature of the processes involved in compression than the earlier one given by Anderson.

ADDENDUM: It has been pointed out to the writers that one should certainly expect that the 40 to 80μ particles used by Cohen and Roy would be somewhat birefringent, although this might be difficult to show on such sizes. There were certainly deforming stresses at points of contact between particles. One wonders, then, just what the observed refractive index means. From purely theoretical considerations it would be surprising if molar refraction is not changed by densification under pressure. Thus, no simple direct correspondence between refractive index and density should be assumed.

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[1] H. M. Cohen and Rustum Roy, "Effects of Ultrahigh Pressures on Glass," *J. Am. Ceram. Soc.*, **44** [10] 523–24 (1961).

[2] P. W. Bridgman and I. Simon, "Effect of Very High Pressures on Glass," *J. Appl. Phys.*, **24** [4] 405–13 (1953); *Ceram. Abstr.*, **1953**, September, p. 168*g*.

[3] C. Weir, S. Spinner, I. Malitson, and W. Rodney, "Optical and Volumetric Relaxation Effects in Glass Following Removal of High Hydrostatic Pressures," *J. Research Natl. Bur. Standards*, **58** [4] 189–94 (1957); RP 2751.

[4] Propriétés Optiques et Acoustiques des Fluides Comprimés et Actions Intermoléculaires, Colloques Internationaux du Centre National de la Recherche Scientifique. Centre de la Recherche Scientifique, Paris, 1959.

[5] P. W. Bridgman, "Miscellaneous Effects of Pressure on Miscellaneous Substances," *Proc. Am. Acad. Arts Sci.*, **84** [1] 111–29 (1955).

[6] O. L. Anderson, "Effect of Pressure on Glass Structure," *J. Appl. Phys.*, **27** [8] 943–49 (1956); *Ceram. Abstr.*, **1957**, January, p. 6*c*.

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