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Reply to "Comments on 'Effects of Ultrahigh Pressures on Glass'"

by H. M. COHEN and RUSTUM ROY

WEIR and Spinner[1] recently made several comments on a note by Cohen and Roy.[2] Since it is felt that these comments may lead to a degree of confusion concerning the nature and meaning of the data reported by Cohen and Roy, a rebuttal is in order.

Weir and Spinner state that since Bridgman and Simon[3] present their results in terms of density changes, whereas Cohen and Roy present their results in terms of changes in index of refraction, a reader cannot directly compare the two sets of data until the relation between index and density has been experimentally established.

The note by Cohen and Roy clearly states (p. 523) that, on the basis of *observed* densities and refractive indices, there was a difference of only 3.5% between the respective molar refractions of the normal silica glass ($n = 1.458$) and the most dense silica glass ($n = 1.54$). Thus, the index of refraction is related to the density through the Lorentz-Lorenz equation. Although densities were measured, only the refractive indices (the more easily measured parameter) were presented because of the space limitations of the note.

The refractive index versus density plot for silica glass and a few other silicate glasses is presented in Fig. 1 to show the values of density measured and the nature of the relation between these two parameters for progressively densified silicate glasses.

Weir and Spinner also remark that the discrepancy between the results of Bridgman and Simon[3] and Cohen and Roy[2] may arise because of the relative degree to which the respective results were "...affected by plastic deformation arising from the nonhydrostatic pressures...."

There is absolutely no doubt that shear has a very pronounced effect on the rate at which the glass samples respond to the pressure-temperature environment. However, Dachille and Roy[4] have shown that shear, although it changes the kinetics of a structural transformation, *does not change the equilibrium* relations within their experimental error. The fact that shear plays an important role in the *kinetics* of densification in no way detracts from the validity of conclusions based on the observed pressure-induced compaction in glass. Further, the reference listed under footnote 2 in the note by Cohen and Roy[2] states explicitly that points falling on the same curve were obtained from samples sealed in capsules and exposed to argon pressure up to 10 kilobars.

Weir and Spinner also state that the results of Cohen and Roy are "... in interesting contrast with those of Anderson,[5] who compressed a borosilicate glass using a different experimental technique." Although the difference in experimental technique and glass composition was pointed out, it was not mentioned that the magnitude of the pressure-temperature range in Anderson's study (6.6 kilobars, 285°C) was far different from the magnitude of the pressure-temperature range used in the study by Cohen and Roy (200 kilobars, up to 600°C), and Anderson made no effort to determine whether his glass was at equilibrium with the pressure-temperature environment.

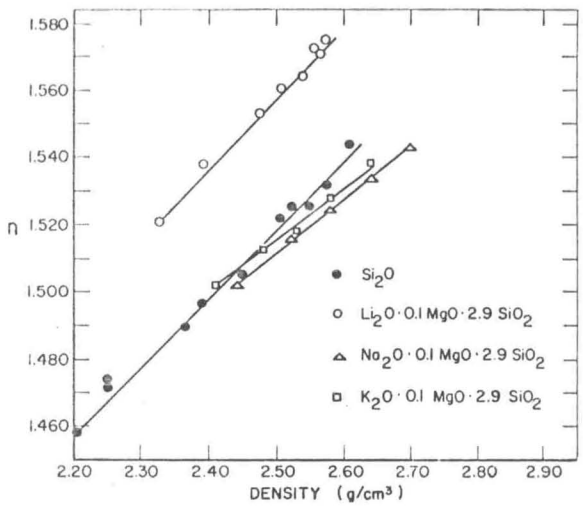

Fig. 1. The refractive indices refer to the sodium D line for silica glass and to white radiation for the other glasses. Each point represents an uncertainty of ±0.005 index of refraction units and ±0.01 g per cm³ density units. Compositions are expressed as molar ratios.

Further, Anderson's samples were exposed to gas pressure. It is quite possible that the small "reversible" density changes observed by Anderson ($\sim 8 \times 10^{-4}$ g per cm³) could arise from solution of the gaseous pressure-transmitting medium into the glass (Henry's law). The question of the equilibrium solubility of gas

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[1] C. E. Weir and S. Spinner, "Comments on 'Effects of Ultrahigh Pressures on Glass,'" *J. Am. Ceram. Soc.*, **45** [4] 196 (1962).

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

[3] 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*.

[4] F. Dachille and R. Roy, "Influence of 'Displacive-Shearing' Stresses on Kinetics of Reconstructive Transformations Effected by Pressure in the Range 0–100,000 Bars"; pp. 502–11 in Reactivity of Solids—Proceedings of 4th Symposium, Amsterdam, 1960. Edited by J. H. de Boer, W. G. Burgers, E. W. Gorter, J. P. F. Huesse, and G. C. A. Schuit. Elsevier Publishing Co., Princeton, N. J., 1961. 762 pp.; *Ceram. Abstr.*, **1962**, May, p. 131*a*.

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

in glass has never been fully investigated. Thus, it is more than understandable that the results and conclusions of Anderson are not in any way comparable with those of Cohen and Roy.

In an Addendum, Weir and Spinner state that ". . . the 40 to 80μ particles used by Cohen and Roy would be somewhat birefringent . . ." and that ". . . there were certainly deforming stresses at points of contact between particles. One wonders, then, just what the observed refractive index means."

Weir and Spinner must be aware of the possibility of determining the indices of refraction of small grains, whether they are isotropic or slightly birefringent (<0.003). Since birefringence of the order of magnitude that is relevant (i.e., 0.003) can be both recognized and easily determined under the polarizing microscope, the reported refractive indices are meaningful within the stated uncertainty.

Finally, Weir and Spinner say that "From purely theoretical considerations it would be surprising if molar refraction is not changed by densification under pressure." The note by Cohen and Roy stated that the molar refraction *was* changed by 3.5%. Its specific mention (p. 524) was ignored by Weir and Spinner. The present writers would welcome detailed treatment of such "theoretical considerations."