

with the 52% figure for the maximum molar volume which the ions in a glass could occupy led to the hypothesis that the densification of glass is achieved by a rearrangement of structural units which constitute the glass. The existence of structural units can be postulated on the basis of the experimental results; however, the data do not permit the delineation of specific types of structural units which might exist in a particular glass, but suggest that they may be as small as the SiO_4 tetrahedra.

The infra-red absorption patterns of progressively densified SiO_2 glass and $(2-X)\text{Na}_2\text{O} \cdot X\text{Al}_2\text{O}_3 \cdot (6-2X)\text{SiO}_2$ glasses were recorded. The major changes in the spectra are:

1. SiO_2 glass. The 9μ Si-O stretching frequency shifts to higher wavelengths. A shift of approximately 0.4μ is observed for a glass whose density increased from 2.20 to 2.60 g/cm^3 . The major absorption bands at 9 , 12 , and 21μ are noticeably broadened and weakened.
2. $(2-X)\text{Na}_2\text{O} \cdot X\text{Al}_2\text{O}_3 \cdot (6-2X)\text{SiO}_2$. The absorption band in the 9μ spectral region apparently decreases in intensity, but no new absorption bands are noticed. The absorption bands in the 13 and 22μ regions are noticeably broadened, almost disappearing in the most dense phases.

The broadening of the spectral absorption bands of silica glass and the sodium aluminosilicate glasses can be attributed to an increase in the distribution of bond angles and possibly to a more random arrangement of tetrahedral units. In other words, as these glasses are progressively densified there may be a decrease in the extent of short-range order. The anomalous decrease in the intensity of the 9μ absorption band is considered weak but admissible evidence in favour of an increase in average co-ordination of a finite fraction of the network-forming ions.

Conclusions

The data suggest that at each pressure and temperature there is a metastable equilibrium structure of the glass, and that the short-range order of the glasses studied decreases as the glass is progressively densified.

It is concluded that the densification of glass is independent of the compressibility and involves a second order structural change in the network of the glass. This structural change is brought about by a rearrangement of small structural units which constitute the

glass structure rather than a major structural rearrangement of the first co-ordination sphere of the ions. The size and type of structural unit, or units which constitute a given glass depends on the size, charge, and polarisability of the ions in the glass. The maximum density to which a glass can be densified is achieved when the structural units are irregularly closest packed.

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References

1. Tamman, G. & Jenkel, E. (1929). *Z. F. anorgan. Allgem. Chem.* **184**, 416.
- 2a. Bridgman, P. W. & Simon, I. (1953). *J. appl. Phys.* **24**, 405.
- b. Bridgman, P. W. (1924). *Amer. J. Sci.* **7**, 81.
- c. Bridgman, P. W. (1925). *Amer. J. Sci.* **10**, 359.
3. Anderson, O. L. (1956). *J. appl. Phys.* **27**, 943.
- 4a. Shishkin, N. I. (1960). *Soviet Phys., Solid State* **2**, 322.
- b. Shishkin, N. I. (1960). *Soviet Phys., Solid State* **2**, 329.
5. Cohen, H. M. & Roy, R. (1961). *J. Amer. ceram. Soc.* **44**, 523.
- 6a. Mackenzie, J. D. (1963). *J. Amer. ceram. Soc.* **46**, 461.
- b. Mackenzie, J. D. (1963). *J. Amer. ceram. Soc.* **46**, 470.
- c. Mackenzie, J. D. (1964). *J. Amer. ceram. Soc.* **47**, 76.
7. Christiansen, E. B., Kistler, S. S. & Gogarty, W. B. (1962). *J. Amer. ceram. Soc.* **45**, 172.
8. Bridgman, P. W. (1955). *Proc. Amer. Acad. Arts Sci.* **84**, 111.
9. Weir, C. E., Spinner, S., Malitson, I. & Rodney, W. (1957). *J. Res. nat. Bur. Stand.* **58**, 189.
10. Weir, C. E. & Spinner, S. (1962). *J. Amer. ceram. Soc.* **45**, 196.
11. Mackenzie, J. D. & Laforce, R. P. (1963). *Nature, Lond.* **197**, 481.
12. Aboaf, J. A. (1963). *J. Amer. ceram. Soc.* **46**, 296.
13. Ryder, R. J. & Rindone, G. E. (1960). *J. Amer. ceram. Soc.* **43**, 662.
14. Day, E. E. & Rindone, G. E. (1962). *J. Amer. ceram. Soc.* **45**, 489.
15. Kracek, F. C. (1930). *J. phys. Chem.* **34**, 2641.
16. Dache, F. & Roy, R. (1962). *High pressure technology*, p. 163. Butterworths, Washington, D.C.
17. Cohen, H. M. & Roy, R. (1962). *J. Amer. ceram. Soc.* **45**, 398.
18. Birch, F., Schairer, J. F. & Spicer, H. C. (editors) (1942). *Handbook of Physical Constants*, Geol. Soc. Amer. special papers, No. 36, p. 51.
19. Dache, F. & Roy, R. (1960). *Reactivity of solids*, p. 502. Elsevier Pub. Co., New York.
20. Douglas, R. W. & Jones, G. A. (1948). *J. Soc. glass Tech.* **32**, 309.
21. Douglas, R. W. & Isard, J. O. (1951). *J. Soc. glass Tech.* **35**, 206.
22. Dache, F. & Roy, R. (1959). *Z. Kristallogr.* **111**, 462.
23. Lacy, E. D. (1955). *The Vitreous state*, p. 23. The Glass Delegacy of the University of Sheffield.
24. Bernal, J. D. (1959). *Nature, Lond.*, **183**, 141.
25. Huggins, M. L. (1955). *J. Amer. ceram. Soc.* **38**, 172.
26. Tilton, L. W. (1957). *J. Res. nat. Bur. Stand.* **59**, 139.
27. Lippincott, E. R., Van Valkenburg, A., Weir, C. E. & Bunting, E. N. (1958). *J. Res. nat. Bur. Stand.* **61**, 61.
- 28a. Simon, I. (1957). *J. Amer. ceram. Soc.* **40**, 150.
- b. Simon, I. (1960). *Modern aspects of the vitreous state*, Vol. 1, p. 120. Butterworths Pub., Washington, D.C.