## Free volumes in glasses and their relation to compressibilities

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Because of the disordered structure, glass has many voids in which no atoms exist. This is characterized by the structural-free volume. It is expected that the larger the structural-free volume, the larger would be the compressibility. This is verified for some alkali silicate and silver borate glasses; i.e., both the structural-free volume and the compressibility decrease monotonously with increasing alkali or silver content. Also found is that the compressibility is different for different alkali species. This implies the presence of another free volume that originates from the atoms in themselves. The atomic-free volume is defined for *s*-electron metals as alkalis and is related to the compressibility.

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## I. INTRODUCTION

Because of the disordered structure, glass has many voids in which no atoms exist. The concept of "free volume" has been used<sup>1-6</sup> as a measure of the amount of voids, although it arises originally from the treatment of diffusion of the constituents in a liquid.<sup>1</sup> It is our experience that ionic conductivity of a rapidly quenched glass from the melt is higher than that of a slowly cooled one.<sup>7</sup> This implies that the mobile ions conduct through the free volume, the space within which no atoms exist.

Doweidar<sup>8</sup> assumed that the volume of an alkali silicate  $[xR_2O(1-x)SiO_2]$  glass is filled with volume units V4, V3, and V2, where V4 (or V3 or V2) is a volume spanned by a SiO<sub>4</sub> tetrahedron having four (or three or two) bridging oxygen atoms. The difference between V4 and V3 or between V4 and V2 should be one or two volume units of  $[R^+ + (1/2)O^-]$  that is given by

$$\Delta = \mathbf{V}_R + + (1/2)\mathbf{V}_{\mathrm{O}}, \tag{1}$$

with 
$$V3 = V4 + \Delta$$
, (2)

$$V2 = V4 + 2\Delta. \tag{3}$$

From the densities at 25 °C he calculated V4, V3, and V2 as a function of x for different alkali species. He found that they are independent of x and that, although V4 is almost fixed for different alkalis, V3 and V2 increase steadily with an increase in ionic radii.

In the recent Letter,<sup>9</sup> the experimental  $\Delta$  values were reproduced theoretically by assuming that ions R<sup>+</sup> and O<sup>-</sup> are cubes, rather than spheres as Doweidar did. Therefore, the glass constituents may be represented by the cubes of volume  $(2r_i)^3$  ( $r_i$  being the atomic radius of atom *i*), the minimum volume of an atom with which the atom can escape steric interferences from its neighbors. The (structural-) free volume was then defined as the volume, within 1 cm<sup>3</sup> of a glass, which is unoccupied by the constituents, by<sup>9</sup>

$$V_f^s = 1 - \sum n_i (2r_i)^3, \tag{4}$$

where  $n_i$  is the number of atomic species *i* within 1 cm<sup>3</sup> of a glass. This is quite a rough approximation, by neglecting

ionicity of the constituents and the glass structure. Moreover, it varies, depending on the values of  $r_i$  chosen. Nevertheless, it can be a measure of the true free volume, at least in the first approximation.

When  $V_f^s$  was calculated for several alkali silicate and borate glasses,<sup>9</sup>  $V_f^s$  always decreased with an increase in alkali content. Since  $V_f^s$  reflects the volume of voids in glass, we may expect that the larger the  $V_f^s$ , the more easily would the glass be compressed when it is subjected to an external pressure. The purpose of this paper is to discuss the relationship between the free volume and the compressibility. During the course of study, we come to notice the presence of another type of free volume, inherent in the atoms themselves, besides the structural one. This is named "atomicfree volume," and is discussed for atoms of 1A and 2A atom groups.

## **II. RESULTS AND DISCUSSION**

Figure 1 shows  $V_f^s$  as a function of x for xLi<sub>2</sub>O(1 - x)SiO<sub>2</sub> (abbreviated as LS) and xNa<sub>2</sub>O(1-x)SiO<sub>2</sub>(NS) glasses using the densities from Ref. 10 and  $r_i$  values from Ref. 11. Similarly to the previous report,<sup>9</sup>  $V_f^s$  was found to decrease monotonously with an increase in alkali content. Therefore, we expect that the compressibility,



FIG. 1. Structural-free volume  $(V_f^s)$  as a function of x in  $x \text{Li}_2 O(1-x) \text{SiO}_2$  (LS) and  $x \text{Na}_2 O(1-x) \text{SiO}_2$  (NS) glasses.



FIG. 2. Compressibility (*k*) as a function of structural-free volume  $(V_f^s)$  in  $x \text{Li}_2 O(1-x) \text{SiO}_2$  (LS) and  $x \text{Na}_2 O(1-x) \text{SiO}_2$  (NS) glasses.

 $k[=-(\partial V/\partial P)/V$ , where V is the glass volume and P the applied pressure], would decrease with an increase in x, or increase with an increase in  $V_f^s$ . Figure 2 shows k as a function of  $V_f^s$  for LS and NS glasses. The k values are from Ref. 10. Similar curves are obtained for  $xAg_2O(1-x)B_2O_3$  glasses using the data from Ref. 12 (Fig. 3). Although being scattered, the data fit our expectation that a glass with larger free volume would be more compressible. The curves may shift to the right or left depending on the values of  $r_i$  chosen, but the trend that NS is more compressible than LS does not change.

Why is k different for different alkali species in glasses of



FIG. 3. Structural-free volume  $(V_f^s)$  versus x and compressibility (k) versus  $V_f^s$  in  $x \operatorname{Ag_2O}(1-x) \operatorname{B_2O_3}$  glasses.

identical  $V_f^s$ ? Consider, for example, an alkali silicate glass. The SiO<sub>2</sub> glass has the highest  $V_f^s$  and the highest k. By the addition of R<sub>2</sub>O molecules,  $V_f^s$  (and k) decreases by breakage of Si-O-Si bonds into Si-O<sup>-</sup>R<sup>+</sup>R<sup>+</sup>O<sup>-</sup>-Si. Since the network former is rigid as compared to the modifiers, the difference in compressibility for different alkali species that are residing near the sites of breakage would be responsible for the observed difference in k between LS and NS. This implies that the overall free volume of a glass is given by

$$V_f = V_f^s + V_f^a \,, \tag{5}$$

where  $V_f^a$  is the atomic free volume of the atoms that constitute a glass.

Alkali metals have body-centered cubic (bcc) structures at room temperature. In a bcc structure, the fractional volume of void per unit cell is 0.320 when atoms are assumed to be spherical, or -0.299 when cubic. That is, the structural-free volume  $(V_f^s)$  is constant for different alkali metals, irrespective of the shape of atoms chosen, if  $V_f^s$  is defined as the volume, within 1 cm<sup>3</sup> of an alkali metal, in which no atoms exist. The compressibility is by definition the compression of a solid by unit pressure rise per unit volume. Therefore, on the assumption of  $k \propto V_f^s$ ,  $V_f^s$  thus defined cannot explain an increase in k with atomic numbers of alkalis.<sup>13</sup> There is even a question whether alkali metal has a structural-free volume or not. Since atoms in an alkali metal are closely packed, pressurization inevitably induces compression of atoms themselves. It is assumed hereinafter that  $V_f^s$  arises solely from the sample's structural disorder. In the following, let us discuss  $V_f^a$  for several s-electron metals.

The atomic radii tabulated in the textbooks were obtained (mainly) from x-ray diffraction of condensed matters. In the routine of research, we pay little attention to the difference between r, an atomic radius that is obtained from interatomic spacings in a condensed matter, and a, an atomic radius in free space. Since it is hard to estimate a experimentally, the estimation of a based on classical electrostatics will be made for some simple elements.

Suppose electron charge -e is homogeneously distributed on the surface of a hollow sphere of radius *a*. The calculated electric potential,  $\phi(r)$ , is illustrated in Fig. 4(A). If *a* is equal to Bohr radius,  $r_{\rm B}$ , the energy the charge -e has is

$$-e\phi(r_{\rm B}) = me^4 (4\pi\varepsilon_o\hbar)^2, \tag{6}$$

which is exactly twice the ionization energy I of the hydrogen atom, where m is the electron mass and  $\varepsilon_o$  is the permittivity of free space. This implies that the energy the charge -e on the surface of a hollow sphere of radius  $r_{\rm B}$  has would be reduced to half when the positive charge +e is placed at the center of the sphere. Figure 4(B) illustrates the corresponding potential distribution. Although the potential is zero on the surface of the sphere, the average potential of the sphere is

$$\langle \phi \rangle = \int \phi(r) d\tau / (4 \pi r_{\rm B}^3/3) = -e/8 \pi \varepsilon_o r_B, \qquad (7)$$

which is identical with I/e of the hydrogen atom.



FIG. 4. (A) The electric potential  $\phi$  as a function of distance *r* from the center of the hollow sphere of radius *a*, on the surface of which the electron charge -e is homogeneously distributed. (B) The electric potential  $\phi$  for the hollow sphere of radius *a* having -e on the surface and +e at the center.

The above discussion allows us to derive atomic radii of atoms in free space as follows: Consider an atom that has one or two electrons in the outermost s orbital whose interactions with other electron(s) are assumed to be small. Then the atomic radius in free space a may be related to the first ionization energy of the atom I by

$$e^2/4\pi\varepsilon_o a = 2l,\tag{8}$$

or by

$$a(A) = 7.1999/I (eV).$$
 (9)

The atomic radii thus obtained *a* would expand to *r* when atoms are gathered together to a condensed matter, by repulsive interactions of the valence electrons with electrons of nearby atoms. From the difference in *r* and *a*,  $V_f^a$  may be defined by

$$V_f^a = c(r^3 - a^3), (10)$$

where *c* is a parameter characteristic of an atom group. We assume that an atom in the condensed state can be compressed from *r* to *a* under conventional pressures. For example, the Cs metal has larger  $V_f^a$  than the Li metal, so it would have larger compressibility than the Li metal. Figure 5 shows *k* as a function of  $V_f^a$  for two atom groups (1A and 2A). The *k* values are from Ref. 13. Although being scattered a little, the data lie around the straight lines that pass through the origin, to give

$$k = c' V_f^a = c''(r^3 - a^3), \tag{11}$$

where c' and c'' are the parameters. One of the reasons of small k values for the 2A atom group as compared to 1A may be that the number of free-electrons per atom that contribute to the bulk modulus (the reciprocal of the compress-



FIG. 5. Compressibility (k) as a function of  $V_f^a/c$  [Eq. (10)] in solid elements of 1A and 2A atom groups.

ibility) is plural in the former as compared to single in the latter. It is to be noted that the correlations are poorer for other atom groups.

The difference in k between NS and LS glasses (Fig. 2) may be related to the difference in  $V_f^a$  between Na and Li metals. Since the atomic (and ionic) radius of Li is smaller than that of Na, the nuclear attraction on the valence electron of Li is not so much screened by inner-shell electrons. Therefore, the valence electron is more strongly bound to the nucleus so that interactions with electrons of nearby atoms would be less favorable, whence we obtain smaller  $V_f^a$  and smaller k. It is to be noted that the Li metal is eight times more compressible than Si. This may be the reason why k in alkali silicate glass depends strongly on the alkali species.

Finally, let us consider alkali metals a little further. Figure 6 shows k as a function of  $l^3$ , the volume of a unit cell. That the data points lie around the straight line crossing the origin and that the lattice constant l is equal to  $(4/\sqrt{3})r$  for a bcc lattice mean that k satisfies the relation

$$k = c''' r^3, \tag{12}$$

where c''' is a parameter. From Eqs. (11) and (12) it is ex-



FIG. 6. Compressibility (k) as a function of  $l^3$ , the volume of a unit cell for alkali metals.



FIG. 7. The ratio r/a (r and a being the atomic radii of atoms in a condensed matter and in free space, respectively) as a function of r for alkali metals.

pected that the ratio r/a is constant for different alkali metals. Contrary to our expectation, the ratio increases steadily from 1.14 (Li) to 1.44 (Cs) (Fig. 7). This increase may be caused by an increase in atom-atom repulsions with an increase in atomic number.

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## **III. CONCLUSION**

Suppose the free volume  $V_f$  characterizes a space in a condensed matter in which no atoms exist.  $V_f$  is defined [Eq. (5)] as the sum of the structural-free volume  $V_f^s$  due to the sample's structural disorder, and the atomic-free volume  $V_f^a$  due to the difference in atomic radii of the atoms in a condensed state and in free space. We expect that a sample having larger  $V_f$  is more compressible when it is subjected to an external pressure.

For several ion-conducting glasses, the relations between  $V_f^s$  and the concentration x of network modifying cations and between the compressibility k and  $V_f^s$  were tested. It is found that, as x increases,  $V_f^s$  decreases and concomitantly k decreases, as expected. Also found is that k is dependent not only on  $V_f^s$  but also on alkali species, or on  $V_f^a$ .

When atoms are gathered together, the atomic radii expand by atom-atom interactions. This expansion defines  $V_f^a$  by Eq. (10). For simple atoms as alkalis, the atomic radii in free space are estimated using classical electrostatics. The *k* values as a function of  $V_f^a$  for 1A and 2A solid elements lie near the straight lines passing through the origin.

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