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A model for estimating the bulk modulus of polycomponent inorganic oxide glasses

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A new theory which allows the bulk modulus of polycomponent oxide glasses to be estimated to a precision of about ±7% or better, is described. It is suggested that the bulk modulus is approximately proportional to the product of the reduced Madelung constant, the mean valence charge product weighted by the relative ionicities of the various bonds, the fourth power of the reciprocal molar volume per ion pair, and a factor less than 1 which increases with the mean stiffness of bonds. The relationship can be simplified by assuming that the ionicity and stiffness factors cancel and the important result is that the product expressing the theoretical bulk modulus can be evaluated solely from a knowledge of the coordination numbers in the crystalline forms of the component oxides, and the glass composition and density. A good correlation between this simplified product and the experimental modulus of a large range of phosphate and silicate glasses is obtained, providing that the mean valence charge product does not exceed the value obtaining in the parent glass.

1. Introduction

It is useful to be able to predict the elastic properties of polycomponent oxide systems solely from a knowledge of the system composition, density and well-known tabulated physical properties. Not surprisingly, frequent exercises of this kind are to be found in published literature [1–19]. Lowenstein [1] proposed that a rough proportionality between Young's modulus and the logarithm of the "field strength" of interstitial cations, held in an extensive range of silicate-based glasses. Makishima and Mackenzie [2, 3] proposed expressions relating the elastic moduli of glasses to the dissociation energies of the constituent bonds, and the packing density of atoms expressed as a summation function of the Pauling radii. These semiempirical formulae were tested using known elastic data on silicate and borate glasses. In an extensive range of papers by Anderson and Anderson and co-workers [6, 7, 10, 11, 14, 15, 22] the bulk modulus of isostructural multicomponent crystalline oxides were related to the packing density of atoms and a summation function over the valence charge products and degree of ionic character of the various bonds. However, in contrast to the work of Makishima and Mackenzie, packing density was defined in terms of the molar volume per ion pair. Soga and Anderson [13] applied similar ideas to polycomponent glasses. More recently, Bridge and Higazy [19] proposed a model in which the elastic moduli of polycomponent oxide glasses are expressed as a summation function over the numbers of network bonds per unit volume, the cross-link densities per cation, and the stretching force constants, for each type of bond in the glass. The force constants were estimated empirically from electro-negativity data, when not otherwise known, and the model was tested on a range of phosphate glasses.

All of these models have a common feature in that elastic moduli are, in effect, related to the closeness of packing of atomic bonds, and the magnitude of their force constants (accepting that in the Makashima and Mackenzie model, bond dissociation energies are assumed to correlate with force constants – a doubtful approximation in many cases). However, the models differ substantially in the amount of calculation required and in the results that they produce. In the present paper we attempt to improve on them with a model which represents a significant development of those approaches which involve molar volume as an important variable. Only in its early stages does the treatment follow that of other workers. However, we present it in full because it contains explanatory details not available elsewhere, and would otherwise be comprehensible to the reader only by the inconvenient piecing together of accounts from multiple sources.

2. The model as developed for polycrystalline substances

2.1. Diatomic materials

If U_{ij} is the interaction energy between atom i and atom j, the total energy per molecule, given that every U_{ij} term is shared between two atoms, is

$$U_i = \sum_j U_{ij} \tag{1}$$

where the sum is taken over all atoms except $j = i$. Let us assume that U_i takes the form of the "Mie potential"

$$U_i = \frac{-a}{r^m} + \frac{b}{r^n} \tag{2}$$

The total energy per mole is

$$U = \frac{-Na}{r^m} + \frac{Nb}{r^n} \tag{3}$$

where N is Avogadro's number.

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Writing the molar volume, V, in the form

$$V = SNr^3 \tag{4}$$

where S is a constant which depends on the crystal class

$$U = \frac{-A}{V^{m/3}} + \frac{B}{V^{n/3}} \tag{5}$$

where

$$A = as^{m/3}N^{(1+m/3)}, \qquad B = bs^{n/3}N^{(1+n/3)} \tag{6}$$

For $\partial U/\partial V = 0$

$$B = (m/n)\,AV_0^{(n-m/3)} \tag{7}$$

$$U_0 = (-n + m/n)A/V_0^{m/3} \tag{8}$$

where the subscript 0 denotes equilibrium quantities. Because in equilibrium the bulk modulus

$$K = V_0\left[\frac{\partial^2 U}{\partial V^2}\right] \tag{9}$$

$$kV_0^{(m/3+1)} = (A/9)m(n-m)\ [4] \tag{10}$$

For a Coulombic potential $m = 1$ and

$$a/r = \{U_i\}_{\mathrm{a}} = (e^2/r)\sum rZ_iZ_j/r_{ij} \tag{11}$$

where the subscript a denotes the attractive component to U_i, the repulsion component does not concern us at this stage.

Defining the reduced Madelung constant

$$\alpha = \left[\sum rZ_iZ_j/r_{ij}\right]/Z_{\mathrm{a}}Z_{\mathrm{c}} \tag{12}$$

then

$$a = e^2\alpha Z_{\mathrm{a}}Z_{\mathrm{c}} \tag{13}$$

2.2. Polyatomic materials [6, 11, 13]

The interaction energy per molecule is

$$U = \tfrac{1}{2}\sum_{ij} U_{ij} \tag{14}$$

i runs from 1 to p, the number of atoms in the molecule, j runs from 1 to ∞ with $i \neq j$. The factor $\tfrac{1}{2}$ allows for the fact that all terms are shared between two atoms.

The total energy per atom pair is $U/[p/2]$, i.e.

$$U = \frac{1}{p}\sum U_{ij} \tag{15}$$

Defining a characteristic distance r^*, which is some kind of average nearest neighbour distance, by the relation

$$U = \frac{-a}{r^{*m}} + \frac{b}{r^{*n}} \tag{16}$$

where the mean molar volume per atom pair is

$$V = SNr^{*3} = 2M/\varrho p \tag{17}$$

where M is the molecular mass and ϱ is the density. Then the molar energy per atom pair is

$$U = \frac{-A}{V^{*m/3}} + \frac{B}{V^{*n/3}} \tag{18}$$

where

$$A = aS^{m/3}N^{1+m/3} \tag{19}$$

as before, in equilibrium

$$KV_0^{(m/3+1)} = (A/9)n(n-m) \tag{20}$$

For a Coulomb potential $m = 1$ and

$$a/r^* = \{U_i\}_{\mathrm{a}} = 1/p(e^2/r)\sum r^*Z_iZ_j/r_{ij} \tag{21}$$

Defining a reduced Madelung constant

$$\alpha = \left[\sum r^*Z_iZ_j/r_{ij}\right]/\sum Z_{\mathrm{a}}Z_{\mathrm{c}} \tag{22}$$

where the sum in the denominator is taken over all atoms in one molecule,

$$a = e^2\alpha/p\sum Z_{\mathrm{a}}Z_{\mathrm{c}} \tag{23}$$

Writing $(\Sigma\, Z_{\mathrm{a}}Z_{\mathrm{c}})/p = \langle Z_{\mathrm{a}}Z_{\mathrm{c}}\rangle$, the average valence product in the molecule, we have

$$a = e^2\alpha\langle Z_{\mathrm{a}}Z_{\mathrm{c}}\rangle \tag{24}$$

α varies little from structure to structure. For many diatomic and more complex solids, full calculations based on Equation 25 have shown α to follow closely the empirical relation

$$\alpha = 1.89 - 1.00/m \tag{25}$$

where m is the weighted harmonic mean of the coordination numbers in the molecule [20–24].

Combining Equations 19, 20 and 24, we find for the bulk modulus, the relation

$$K = 1/9(n-1)S^{1/3}N^{4/3}e^2\alpha\langle Z_{\mathrm{a}}Z_{\mathrm{c}}\rangle(2M/\varrho p)^{-4/3} \quad \text{(Coulomb potential)} \tag{26}$$

This equation could be used to determine the power n in the repulsive potential but this is not a very productive exercise given that there are two major approximations built into the above model, as follows.

1. The use of equations such as 5 and 18 to obtain a bulk modulus via Equation 12 assumes that a centrally symmetric potential exists at all stages during an isotropic deformation, i.e. all atomic spacings are assumed to contract by the same fraction, or put another way, all bonds are assumed to be compressed directly rather than bent, even though ionic bonds are the least directional of all bonds. Now it takes less energy to deform a structure anisotropically (bond bending) than isotropically and so the obvious remedy is to multiply the right-hand side by a "bond bending" or "non-central force" factor s where s is <1.

2. No bond is completely ionic, i.e. there is never 100% charge transfer between positive and negative ions. A "partly covalent character" expresses the fact that a fraction of the valence change cloud envelopes both the positive and negative ions. This effect is actually quite easily allowed for without a major alteration in the model. Partial covalency reduces each valence charge e by a factor I, "the ionicity". Partial covalency may also alter the value of B but there is no strong reason to suppose that it will alter much the value of n. However, B enters into the bulk modulus relationship only implicitly through the

value of V_0 (Equation 7). So provided that we do not wish to predict the values of V_0 (experimental values being used in testing the bulk modulus relationship), covalency is completely allowed for via I (in our model).

Allowing for approximations 1 and 2, the revised bulk modulus relationship becomes

$$K = 1/9(n - 1)S^{1/3}N^{4/3}e^2\alpha s\langle I^2 Z_a Z_c\rangle(2M/\varrho p)^{-4/3} \tag{27}$$

Using Equation 8, the best fit [13] of theoretical to experimental values of molar lattice energy, U_0, of diatomic ionic crystals are obtained within $n = 9$. At the same time it is worth noting that the effect of different forms of repulsive potential other than an r^{-n} dependence, e.g. exponential forms, can be allowed for by a slight variation $\pm\varepsilon$ in the power of $(2M/\varrho p)$ appearing in Equation 27 [6, 11]. Thus more generally:

$$K \approx S^{1/3\pm\varepsilon}N^{(4/3\pm\varepsilon)}\varepsilon^2\alpha s\langle I^2 Z_a Z_c\rangle(2M/\varrho p)^{(-4/3\pm\varepsilon)} \tag{28}$$

For isostructural oxides S, α, and s may be treated as constant so that the theory can be tested using the relation:

$$K = \text{const}\langle I^2 Z_a Z_c\rangle(2M/\varrho p)^{(-4/3\pm\varepsilon)} \tag{29}$$

It is important to note that whilst the latter equation has appeared in previous literature, Equation 28 from which it has been derived is original to the author, and provides the key for subsequent extension of the model to glasses, in Section 4.

3. Review of past applications of the model (mostly crystalline oxides)

Equation 29 has been found to hold very well for a number of important classes of diatomic solids (alkalis, halides, oxides, sulphides, selenides, carbides and antimonides), both ionic and covalent with the best fit of I^2 tending to decrease (as it should do) with increasing tendency towards covalency, as measured by independent techniques such as the empirical relationships between the electronegativity scale and the fraction of ionic character [25]. The quantity ε varies from around 1/3 to zero moving from strongly ionic materials to the more covalent ones. It is noteworthy that even for covalent structures a $1/r$ dependence for the repulsive component of the lattice energy seems a reasonable assumption. Equation 29 also agreed very well with available data on several classes of polyatomic structure, for example, fluorides and complex oxides with the rutile, corundum and spinel structures [10, 11].

For the noble gas solids neon, argon, krypton, and helium experimental data are represented approximately by $K \approx (2M/\varrho p)^{-3}$ corresponding to $m = 6$ in Equation 10. Hence the above model is consistent with the Van Der Waals type of interaction supposedly responsible for the cohesion of these structures.

Apart from isostructural comparisons, systematic patterns in elastic constants also emerge when compounds in different structural classes are compared. Anderson [11] showed that for available data, a rule

$$K(2M/\varrho p)^x \approx \text{constant}, \quad x \approx 4; \text{ for } M/p = \text{const.} \tag{30}$$

applied. As yet the available data are too limited for this rule to have been put to a wide test. However, for the case $M/p \approx 21$, the rule is well established. Most naturally occurring minerals (complex oxides and silicates) have $M/p \approx 21$ and for existing moduli data on these, Equation 5 always holds [5, 6, 7, 14, 15]. The various references give x variously between 3 and 4 as the best fit. More extensively, Equation 8 has been shown to hold [6, 14] when volume changes are caused not just by structural changes but by any other cause (pressure, temperature or porosity changes), $M/p \approx 21$ being the only proviso. This phenomenon, i.e. the fact that the bulk modulus of oxide and silicate compounds with $M/p \approx 21$ varies as (mean molar volume per ion pair)$^{-4}$ irrespective of how volume change is caused, is called the Law of Corresponding States [7, 14, 16].

Studies of elastic constant variations at constant M/p have been performed on glasses. Anderson [13] showed that an approximate $K \propto (2M/\varrho p)^{-4}$ rule held for a representative range of 29 silicate-based glasses. These glasses encompassed a wide range of oxide constituent proportions and M/p was roughly constant in the range 21 to 25. Soga *et al.* [17] has shown that glasses and crystalline members of the As–Se system fitted a $K \approx V^{-4}$ variation. Here M/p was roughly constant between 75 and 79. Soga *et al.* [17] also showed that the same power law held for several pairs of crystalline oxides and their glassy counterparts indicating that the Law of Corresponding States seems to apply to the glass–crystal phase transformation (here $M/p \approx 21.7$ to 24.8). The simplistic systematics implied by Equation 33 is rather analogous to Birch's Law [11, 18] which purports an even simpler relationship between M/p (mean atomic weight), compressional wave velocity and density, which is satisfied by a large number of rocks and minerals.

This review would not be complete without mention of the fact that in early studies when data on relatively few oxides were available, even isostructural oxides were considered to have bulk moduli following a $(2M/\varrho p)^{-3}$ or $(2M/\varrho p)^{-4}$ law, i.e. in Equation 20 $m \approx 6$ to 9 [6]. This, in turn, led to speculation than Van Der Waals forces between close-packed oxygen spheres dominated the elastic behaviour [6, 13]. Subsequently this hypothesis was discarded on re-measurement of the bulk moduli of some oxides (CaO, Fe_2O_3 and BeO). The problem was that measurements on powdered polycrystals can easily be in gross error if imperfect compaction of the powder is present. It is safer to obtain polycrystalline values by averaging single crystal data. Then subsequently, as more oxide data became available, the fourth power law for constant M/p emerged. However, no physical meaning for this law has ever been given – why variations in S, s, I, Z_c and Z_a between different structural classes should lead to the correlations described is not obvious and to this extent the theory is rather unsatisfactory. One possibility is to suggest that the bond bending factor, s, might increase rapidly as $(2M/\varrho p)$ decreases and this, in part, begins to lend some credibility to Equation 30. The suggestion seems reasonable for the complex oxides based on silicates etc., for which Equation 30 has also been found to hold. Oxides like these have large-ringed structures compared with the simple oxides like CaO and MgO and the halides. Large-ringed structures tend to produce bond-bending effects during isotropic deformation, so reducing the bond bending factor, s. Thus it is easy to see how s could be quite strongly dependent on the atomic volume per ion pair, assuming that the latter bears some relation to ring size.

4. Extension of the model to glasses

We have just reviewed the success of Equation 29 in explaining elastic data on isostructural polycrystals. As it is difficult to see how isostructural concepts can be applied to glasses, we have to quantify s in some way, i.e. we have to use Equation 28 derived in this paper rather than Equation 29.

The following arguments are presented at length elsewhere [19, 25–28], and in the light of the discussion of the last paragraph of Section 3, we might write s in the form

$$s = PD \tag{31}$$

where D is a "bond directionality" or "stiffness" factor less than 1 which increases with the mean ratio of bending to stretching force constants for the bonds in glass $\langle f/f_b \rangle$, and p is another fractional quantity which increases as the tightness of packing of the glass structure increases, for constant $\langle f/f_b \rangle$. Thus both s and D are unity when isotropic deformation leads to no bending of bonds. Several measures of packing density (ring size, molar volume per ion pair, and functions involving crystal or Pauling radii) have been used in the literature on the systematics of the elastic moduli of glasses [2, 3, 19, 25–27]. The use of molar volume per ion pair has the advantage that it is easy to calculate and we shall suggest that

$$P \approx \text{const}_2 (2M/\varrho p)^{-\omega} \tag{32}$$

where $\omega \approx 4/3$. The choice of power for ω seems reasonable given the success of the ring deformation model of Bridge *et al.* [27] which proposed a fourth power dependence of compressibility on mean ring size in simple diatomic oxide glasses. Combining Equations 28, 31 and 32 we have, for polycomponent oxide glasses

$$K \approx \text{const}_3 S^{1/3} \alpha D \langle I^2 Z_a Z_c \rangle (2M/\varrho p)^x, \quad x \approx 3 \text{ or higher} \tag{33}$$

where the values of ε, m and ω are now subsumed in the index x. We have suggested that x might be somewhat higher than the sum of $(1 + m/3) + \omega$ because Van der Waals forces between different elements of a distorted three-dimensional network will make some, albeit small, contribution to the elastic properties of oxide glasses. The empirical value of $x \approx -4$ found by Anderson and Soga to fit a wide range of silicate glass compositions to a trend line $K = \text{const}\,(2M/\varrho p)^x$, now seems to have a reasonable theoretical basis. They did not estimate values of $\langle I^2 Z_a Z_c \rangle$, variations of which were presumably small compared with $(2M/\varrho p)^x$, thus showing up as a small spread of data about the trend line.

Setting aside bond bending and molar volume (or ring size) considerations, the main determinants of K in the present model (given the structural insensitivity of α) are the ionic charge numbers and the degree of ionicity. However, on a previous model of Bridge and Higazy [19] the corresponding important variables were the coordination numbers (as used in calculating the number of network bonds per unit volume) and first order stretching force constants. Whereas there is a linear dependence of bulk modulus on coordination numbers in the previous theory, the dependence of modulus on coordination number in the present model is very weak because α increases so slowly with coordination number. At first sight this seems a total contradiction; however, a closer examination shows that there is no conflict between the theories. The first term in a typical power series used to compute α is of the order of the mean coordination number (in the case of simple diatomic materials with common cation and mean coordination numbers, the final term is that coordination number). However, slowly converging oscillations in successive terms caused by the long-range nature of the Coulomb potential cause α to be only a small fraction of the first term. Now in the model of Bridge and Higazy, long-range effects, i.e. all other interactions as well as nearest neighbour interactions, are subsumed in the values of stretching force constants to be used in the model. That is, the experimental values of these constants are the net results of combined long-range and nearest neighbour interactions. Long-range effects are thus allowed for in the values of f, the values of which we anticipate will tend to become smaller with increasing coordination numbers.

The present model has the advantage of having fewer variables, the values of which are uncertain, although it remains to be seen whether discontinuities in composition gradients of modulus can be explained as successfully as the previous theory allowed. Large values of Z_a and Z_c do not lead to erroneously large values of K simply because the quantity I tends to decrease with increasing charge number.

5. Application

We shall now test Equation 33 on a broad range of silicate and phosphate glasses, the bulk moduli of which are known [2, 3, 19, 25, 29–35]. To achieve the simplest possible calculation we make an additional assumption that as I decreases the directionality of bonds, i.e. the magnitude of D, increases. Thus we assume that Equation 33 can be simplified to

$$K \approx \text{const}_4 S^{1/3} \alpha \langle Z_a Z_c \rangle (2M/\varrho p)^x, \quad x \approx -4 \tag{34}$$

In this equation only S is not readily computable. It is worth reminding ourselves that S is the ratio of the mean molar volume per ion pair to the product of the mean nearest neighbour distance and Avogadro's number. (It is, of course, constant in isostructural crystals.) Even for the extremes of bond angles occurring in inorganic structures it is difficult to imagine S to vary by more than ±30% causing K to vary by less

TABLE I Relationship between bulk modulus and the product of the reduced Madelung constant, mean volume number, and the fourth power of the reciprocal molar volume per ion (peV), for a representative range of phosphate and silicate glasses

Component proportions (mol %)																			Density, ϱ (g cm^{-3})	Mean molecular mass, M	No. of atoms in formula, p	Mean vol. per ion pair, $2M/\varrho p$ (cm^3)	Bulk modulus, (GPa)	Mean coordination number, m	Reduced Madelung constant, α	Mean valence product, $\langle Z_aZ_c\rangle$	$\alpha\langle Z_aZ_c\rangle / \{M/\varrho p\}^4$ (10^{-5} cm^{12})	Reference for bulk modulus
SiO_2	CoO	CaO	Cu_2O	BaO	TiO_2	MgO	BeO	PbO	Li_2O	Na_2O	ZnO	Al_2O_3	Fe_2O_3	CuO	MoO_3	WO_3	V_2O_5	P_2O_5										
70									30										2.33	51.0	3.00	14.57	50.9	3.46	1.6	6.2	22.0	
70								30											4.36	109	2.70	18.5	25.6	3.07	1.56	6.8	9.1	
																		100	2.52	141.8	7.00	16.10	25.3	2.47	1.47	10	22	
										24.15		1.70						74.15	2.328	122.0	6.00	17.46	27.9*	3.07	1.56	7.31	12.3	[32]
										27.61		0.22						72.17	2.338	120.6	5.89	17.50	20.1*	3.2	1.58	7.29	12.3	[32]
										27.35		3.14						69.51	2.361	118.8	5.84	17.23	22.3*	3.28	1.58	7.19	12.9	[32]
										33.74		1.62						64.64	2.377	114.3	5.62	17.12	22.0*	2.98	1.55	6.69	12.1	[32]
										42.49		1.41						56.10	2.435	107.4	5.27	16.74	24.3*	3.69	1.62	5.98	12.3	[32]
										56.22		3.31						40.47	2.520	95.7	4.68	16.22	26.5*	4.23	1.65	5.02	12	[32]
											36.90	2.32						60.78	2.705	118.7	5.10	17.20	30.9*	3.05	1.56	7.26	12.9	[32]
											41.65	2.61						55.74	2.793	115.7	4.86	17.04	29.9*	3.12	1.57	6.96	13.0	[32]
											48.49	1.81						49.70	2.897	111.9	4.54	17.00	25.8*	3.13	1.58	6.63	12.5	[32]
											50.75	1.25						47.96	2.960	110.6	4.43	16.90	28.4*	3.26	1.58	6.48	12.6	[32]
											53.90	1.17						44.93	3.033	108.9	4.28	16.76	30.3*	3.29	1.59	6.3	12.7	[32]
											60.12	0.82						39.06	3.258	105.2	3.98	16.23	34.1*	3.38	1.59	6.02	13.8	[34]
													38					62	3.01	148.7	6.24	15.83	43.0	3.3	1.59	7.8	19.7	[34]
														54				46	3.29	108.2	4.30	15.30	39.7	3.2	1.58	6.3	18	[34]
															60			40	3.11	143.1	5.20	17.70	24.2	3.2	1.58	11.5	18.5	[34]
															66			34	3.22	143.3	5.02	17.73	24.1	3.3	1.59	11.6	18.7	[34]
															76			24	3.55	143.5	4.72	17.13	29.7	3.4	1.60	11.7	21.7	[34]
															85			15	3.71	143.6	4.45	17.40	32.8	3.53	1.61	11.8	21.0	[34]
																67		33	4.92	202.1	4.99	16.47	45.8	2.8	1.53	11.6	24	[34]
																68.5	1.5	30	4.88	204.1	4.95	16.90	40.5	2.85	1.54	11.53	21.8	[34]
															2.3	69.7		28	5.02	204.7	4.84	16.84	45.9	2.85	1.54	11.7	22.4	[34]
																	45	55	2.81	169.4	7	16.26	38.4	3.0	1.56	10	22.3	[33, 34]
																	60	40	2.82	165.9	7	16.80	34.5	3.2	1.58	10	19.8	[33, 34]
																	70	30	2.88	169.9	7	16.85	32.1	3.3	1.59	10	19.7	[33, 34]
																	80	20	2.92	173.9	7	17.01	30.3	3.5	1.6	10	19.1	[33, 34]
85									15										2.258	55.6	3	16.42	40.9	3.07	1.56	7.1	15.2	[30]
	59.2																	40.8	3.26	102.2	4.04	15.54	52.9	4.53	1.67	5.53	15.8	[25]
	37.6																	62.4	2.865		5.12	16.56	37.2	3.75	1.62	6.72	14.5	[25]
		45																55	2.656	103.3	4.75	16.95	34.1	4.02	1.64	6.27	12.5	[28]
		11.6	16.1											8.43				55	3.074	126.1	5.35	15.42	39.5	2.789	1.53	6.58	17.8	[28]
															53			47	3.058	142.9	5.41	17.27	30.3	3.11	1.57	11.38	20.0	[26]
		21.0	5.0											16.28				57.74	2.911	113.8	4.94	15.82	38.3	3.36	1.59	6.64	16.9	[28]
37.2						24.4	31.8					6.6							2.785	46.87	2.57	13.1	100.5	4.12	1.65	5.45	30.5	[3]
52.8						21.2	20.3					5.7							2.629	51.17	2.70	14.4	74.2	3.56	1.61	6.00	22.5	[3]
48.0		10.3				8.7	27.0					5.7							2.723	50.92	2.63	14.22	82.4	3.73	1.62	5.87	23.3	[3]
52.7					25					22.5									2.80	63.9	3	15.27	53.0	3.73	1.62	6.65	19.8	[3]
				50														50	3.8	147.6	4.5	17.26	38.0	4.2	1.65	6.00	11.2	[36]
						60.5												39.5	2.655	80.4	3.975	15.24	43.22	4.58	1.67	5.47	16.9	[35]
						32.0												68.0	2.545	109.4	5.4	15.92	33.3	3.52	1.61	6.56	16.4	[35]
					20					30								50	2.749	62.5	3	15.15	50.0	3.73	1.62	6.36	19.6	[3]

*Estimated from the approximate relationships for glasses: $G \approx 0.4E$, $K \approx 2E/3$, [4] p. 90.

TABLE II Coordination numbers for component oxides, used for calculating the reduced Madelung constant of multicomponent oxide glasses

Oxide	Coordination numbers for M and O	Arithmetic mean coordination number	Reference
P_2O_5	3.2	2.4	[38] p. 473
SiO_2	4.2	2.67	[38] p. 803
CoO	6.6	6	[38] p. 441
CaO	6.6	6	[38] p. 441
MgO	6.6	6	[38] p. 441
BaO	6.6	6	[38] p. 441
PbO	4.4	4	[38] p. 481
ZnO	4.4	4	[38] p. 441
CuO	4.4	4	[38] pp. 102, 445
BeO	4.4	4	[38] p. 441
Na_2O	4.8	5.33	[38] p. 441
Li_2O	4.8	5.33	[38] p. 441
TiO_2	6.3	4	[38] p. 441
Cu_2O	2.4	2.67	[38] p. 441
Al_2O_3	6.4	4.8	[38] p. 441
Fe_2O_3	6.4	4.8	[38] p. 441
WO_3	6.2	3	[38] p. 441
MoO_3	6.3(3) 6.2(2) 1 dangling 0	3.73	[38] p. 473
V_2O_5	ditto	3.73	[38] pp. 470, 471

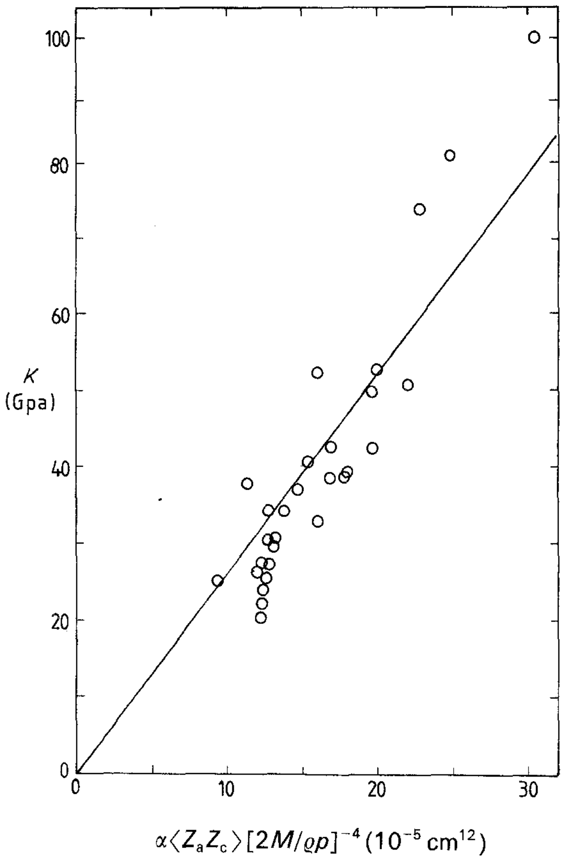

Figure 1 Test of relationship between bulk modulus and the product of the reduced Madelung constant, mean valence number and the fourth power of the reciprocal molar volume per ion pair, in phosphate and silicate glasses. For identification of data points with specific glasses, see Table I. The choice of glasses is constrained only by the condition that the mean valence number does not exceed the value of this number on the parent glass.

than ±10%, all other factors remaining the same. Because the K values of the glasses specified in Table I span a range of 500%, a reasonable test of Equation 1 ought to be provided by these glasses. To compute α and $\langle Z_aZ_c\rangle$ the coordination numbers of the various atoms are assumed to be the same as obtaining in the component oxides [36] (Table II). Assuming that the double bond P=O in P_2O_5 gives but a minor contribution to the compressibility of P_2O_5, the coordination of the P atom is assumed to be three-fold. For simplicity, arithmetical and not weighted harmonic means of the cation and anion coordination numbers have been computed from the glass compositions. In Table I it will be seen that α varies by less than 10% over the entire range of glasses, thus amply justifying the approximation. The value of $\langle Z_aZ_c\rangle$ was computed from the glass compositions and the number of network bonds per formula unit (i.e. the cation coordination numbers) for each glass component.

6. Results and discussion

In Fig. 1, the product $\alpha\langle Z_aZ_c\rangle(M/\varrho p)^{-4}$ is plotted against experimental bulk modulus, for some 27 glasses involving 20 different oxide components. The only constraint used to select the glasses is that $\langle Z_aZ_c\rangle$ was less than the value obtaining in the basic glass former. It will be noted that a reasonably linear relationship exists. The gradient of a least squares fit curve, treating the origin as a certain point, is determined to ±7%, consistent with the expected tolerance of $S^{1/3}$. Many other glass compositions [2, 3, 19, 25–36] subject to the same constraint on $\langle Z_aZ_c\rangle$ fit the same pattern, but are not tabulated on grounds of space. However, glasses with $\langle Z_aZ_c\rangle$ higher than found in the basic glass former, representative examples of which are shown in Table I, reduce the linear correlation substantially. Furthermore, from the limited data available, borate glasses do not fit the curve of Fig. 1.

7. Conclusion

The bulk modulus of a range of phosphate and silicate glasses containing many different oxides can be predicted to a precision of ±7% from a knowledge of the glass composition, density, and the anion, cation coordination and valencies of the component oxide. The range is defined by the constraint that $\langle Z_aZ_c\rangle$ should be less than the value occurring in the basic glass former. Quite possibly the application of Equation 34 has not yet been optimized. It could be that the assumption that D increases as I decreases is not the best one to make and that a wider range of glasses can be accommodated by the model by assuming D to be constant, and thus by retaining I in Equation 33. In other words, it could be that glasses with very high $\langle Z_aZ_c\rangle$ values did not fit our model simply because by eliminating I from Equation 33, the effect of $\langle Z_aZ_c\rangle$ was exaggerated. Values of I could be estimated from cation and anion electronegativity, for example, by means of Pauling's expression for fractional ionic character. This approach involves considerably more calculation than has been adopted at present, and if fruitful will be presented in a future publication.

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