Anion packing density: a universal quantity for both dense and porous crystalline inorganic phases

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To compare densities of inorganic high-pressure phases their molal volumes or specific gravities are usually employed, whereas for zeolites and other microporous materials the so-called framework density, FD, is applied. The definition of FD, which refers only to phases with three-dimensional tetrahedron frameworks, is extended to a 'generalized framework density' $\mathbf{d_f}$, which is independent of the dimensionality of the framework and the coordination number(s) of the framework cations. In this paper the anion packing density, $\mathbf{d_{ap}}$, is introduced as a new quantity which is not only applicable to any inorganic phase but, in contrast to FD and $\mathbf{d_f}$, also allows quantitative comparisons to be made for crystalline inorganic phases of any kind. The anion packing density can readily be calculated if the volume and content of the unit cell and the radii of the anions of a phase are known. From $\mathbf{d_{ap}}$ values calculated for high-pressure silica polymorphs studied under very high pressure, it is concluded that Shannon–Prewitt effective ionic radii do not sufficiently take into account the compressibility of the anions.

1. Introduction

It is a general experience that the volume of a material decreases if the pressure increases. For this reason, chemists, mineralogists and materials scientists studying an inorganic phase at high pressure determine the change of its molal volume, V_{mol}, with pressure. Often, rather than V_{mol}, the specific gravity ρ (usually but less correctly called density) is used. For a crystalline single-phase material, the specific gravity is

$$\rho = Z \cdot M / V_{uc} \cdot N_L = Z / V_{mol}, \tag{1}$$

with Z = number of formula units per unit cell, M = molecular weight, V_{uc} = volume of the crystallographic unit cell and N_L = 6.023×10^{23}, Avogadro's number. Values of specific gravity are suitable to quantitatively compare isochemical phases, *i.e.* crystalline polymorphs of a compound.

To compare densities of heterochemical oxidic phases, the volume per oxygen atom

$$V_{ox} = V_{uc} / n(O) \tag{2}$$

has been shown to be useful (Liebau, 1985), where $n(O)$ is the number of oxygen atoms per unit cell.

Scientists studying zeolites, clathrasils and related inorganic micro- and mesoporous materials, rather than applying the specific gravity or the volume per O atom, prefer to use the so-called framework density

$$FD = 1000 n(\mathbf{T}) / V_{uc} \tag{3}$$

Table 1
Values of anion packing-densities, $\mathbf{d}_{ap}$, generalized framework density, $\mathbf{d}_f$, and density ratio, $\mathbf{q}_d$, together with crystallographic data to calculate them.

$z = \sum_j n(\mathbf{X}_j^{fr})/\sum_i n(\mathbf{A}_i^{fr})$, $\mathbf{M}$ = non-framework molecule or ion, RT = room temperature. A mineral name or a chemical formula between round brackets after the chemical formula of a phase indicates its crystallographic structure type. Framework anions $\mathbf{X}_j^{fr}$ for which no coordination numbers are indicated in the chemical formula are bridging anions $\mathbf{X}_j^{fr[2]}$.

Name	Chemical formula	V_{uc} (Å³)	$\sum_j n(\mathbf{X}_j^{fr})/\sum_i n(\mathbf{A}_i^{fr})$	z	$r(\mathbf{X}_j^{fr[CN]})$ (Å)	$\mathbf{d}_{ap}$	$\mathbf{d}_f$	$\mathbf{q}_d \times 10^2$	Reference
Densest sphere packings		–	–	–		0.7405	–	–	
Phases with $CN(\mathbf{A}_i^{fr}) = 4$									
Coesite	SiO_2	546.60	32/16	2	1.35	0.603	29.27	2.061	Geisinger et al. (1987)
Quartz (RT)	SiO_2	113.59	6/3	2	1.35	0.544	26.41	2.061	Glinnemann et al. (1992)
Cristobalite (RT)	SiO_2	171.03	8/4	2	1.35	0.482	23.39	2.061	Schmahl et al. (1992)
Tridymite (RT)	SiO_2	2110.15	96/48	2	1.35	0.469	22.75	2.061	Graetsch & Flörke (1991)
Silica-ZSM-22	$\|\mathbf{M}_m\|[Si_nO_{2n}]$	1214.89	48/24	2	1.35	0.407	19.76	2.061	Papiz et al. (1990)
Dodecasil-1H	$\|\mathbf{M}_m\|[Si_nO_{2n}]$	1840.98	68/34	2	1.35	0.381	18.47	2.061	Gerke & Gies (1984)
H-ZSM-5	$\|\mathbf{M}_m\|[Si_nO_{2n}]$	5343.32	192/96	2	1.35	0.370	17.97	2.061	Koningsveld et al. (1990)
Silica-ferrierite	$\|\mathbf{M}_m\|[Si_nO_{2n}]$	1868.34	72/36	2	1.35	0.397	19.27	2.061	Gies & Gunawardane (1987)
Ferrierite-Mg	$\|(Mg_{0.5},K,Na,Ca_{0.5})_7(H_2O)_{18}\|$-$[Al_7Si_{29}O_{72}]$	2039.90	72/36	2	1.35	0.364	17.65	2.061	Alberti & Sabelli (1987)
RUB-23	$\|Cs_{10}(Li,H)_{14}(H_2O)_{12}\|$-$[Li_8Si_{40}O_{96}]$	2708.89	96/48	2	1.35	0.365	17.72	2.061	Park et al. (2000)
Tschörtnerite	$\|Ca_4(K,Ca_{0.5},Sr_{0.5},Ba_{0.5})_6$-$Cu_3(OH)_B(H_2O)_n\|$ $[Al_{12}Si_{12}O_{48}]$	31 614.0	768/384	2	1.35	0.250	12.15	2.061	Effenberger et al. (1998)
	GeO_2 (quartz)	121.51	6/3	2	1.35	0.509	24.69	2.061	Glinnemann et al. (1992)
Berlinite	$[AlPO_4]$(quartz)	231.30	12/6	2	1.35	0.535	25.94	2.061	Sowa et al. (1990)
Alarsite	$[AlAsO_4]$(quartz)	245.82	12/6	2	1.35	0.503	24.41	2.061	Sowa (1991)
	$[BeP_2O_6]$ III	860.35	48/24	2	1.35	0.575	27.90	2.061	Schultz & Liebau (1981)
	$\|H_2\mathbf{M}(H_2O)_2\|$-$[HZn_6P_5O^{[2]}_{16}O^{[3]}_4]$	1993.31	80/44	1.818	1.35,1.36	0.415	22.07	1.882	Chidambaram & Natarajan (1998)
	$\|Cs_3(H_2O)_4\|$-$[Zn_4As_3O^{[2]}_{12}O^{[4]}]$	1013.28	26/14	1.857	1.35,1.38	0.265	13.82	1.924	Harrison et al. (2000)
Parthéite	$\|Ca_2(H_2O)_4\|$-$[H_2Al_4Si_4O^{[1]}_2O^{[2]}_{15}]$	1756.36	68/32	2.125	1.34,1.35	0.398	18.22	2.184	Engel & Yvon (1984)
Ussingite	$\|Na_2\|[HAlSi_3O^{[1]}O^{[2]}_8]$	399.44	18/8	2.25	1.34,1.35	0.463	20.03	2.313	Rossi et al. (1974)
	$\|K_2Ce\|[Si_6O^{[1]}_6O^{[2]}_9]$	1346.46	60/24	2.50	1.34,1.35	0.455	17.83	2.554	Karpov et al. (1977)
	$Be^{[4]}F^{[2]}_2$ (quartz RT)	100.46	6/3	2	1.285	0.531	29.86	1.778	Wright et al. (1988)
	$\|Ca\|[P^{[4]}_2N^{[2]}_4]$	643.17	32/16	2	1.43	0.609	24.88	2.450	Schmid et al. (2001)
	$P^{[4]}O^{[2]}N^{[2]}$ (quartz)	102.81	6/3	2	1.35,1.43	0.658	29.18	2.256	Léger et al. (2001)
	$P^{[4]}O^{[2]}N^{[2]}$ (cristobalite)	148.87	8/4	2	1.35,1.43	0.606	26.87	2.256	Léger et al. (2001)
	$P^{[4]}_4O^{[2]}N^{[2]}_4N^{[3]}_2$	283.22	14/8	1.75	1.35,1.43, 1.44	0.595	28.25	2.108	Ronis et al. (1995)
Phases with $CN(\mathbf{A})^{fr} \neq 4$									
Stishovite	$Si^{[6]}O^{[3]}_2$ (rutile)								
	at 10^{-4} GPa	46.62	4/2	2	1.36	0.904	42.91	2.107	Andrault et al. (1998)
	at 54.8 GPa	40.70	4/2	2	1.36	1.036	49.15	2.107	Andrault et al. (1998)
	$Ge^{[6]}O^{[3]}_2$ (rutile)	55.57	4/2	2	1.36	0.758	35.99	2.107	Bolzan et al. (1997)
Cassiterite	$Sn^{[6]}O^{[3]}_2$ (rutile)	71.51	4/2	2	1.36	0.589	27.97	2.107	Bolzan et al. (1997)
Plattnerite	$Pb^{[6]}O^{[3]}_2$ (rutile)	83.31	4/2	2	1.36	0.506	24.01	2.107	Harada et al. (1981)
	$Si^{[6]}O^{[3]}_2$ ($CaCl_2$)								
	at 63.0 GPa	40.00	4/2	2	1.36	1.054	49.99	2.107	Andrault et al. (1998)
	at 120 GPa	36.54	4/2	2	1.36	1.153	54.74	2.107	Andrault et al. (1998)
	$Si^{[7]}O^{[3]}O^{[4]}$(baddeleyite)								
	at ca 10^{-4} GPa	92.99	8/4	2	1.36,1.38	0.927	43.01	2.155	El Goresy et al. (2000)
	$Zn^{[6]}F^{[3]}_2$ (rutile)	69.37	4/2	2	1.30	0.531	28.83	1.840	Baur & Khan (1971)
Fluorite	$Ca^{[8]}F^{[4]}_2$	163.78	8/4	2	1.31	0.460	24.42	1.883	Zhurova et al. (1996)

when comparing densities or porosities of such phases (Bärlocher *et al.*, 2001). Here FD is defined as the number of $[\mathbf{TO_4}]^1$ tetrahedra of the host framework per 1000 Å³ (not taking into account the guests occupying pores within the host; McCusker *et al.*, 2001) and $n(\mathbf{T})$ is the number of host $\mathbf{T}$ atoms per unit cell. To the best of our knowledge, the framework-density concept has up to now only been applied to inorganic oxidic phases with three-dimensional host frameworks of corner-sharing $[\mathbf{TO_4}]$ tetrahedra.

In the present paper it is shown that the framework density FD allows quantitative comparisons to be made only for phases with three-dimensional frameworks of $[\mathbf{TO_4}]$ tetrahedra that have an atomic ratio $n(\mathrm{O})/n(\mathbf{T}) = 2$. To extend the applicability to inorganic materials of any kind, *i.e.* to dense and porous ones independent of the chemical characters and coordination numbers of their cations $\mathbf{A}$ and their anions $\mathbf{X}$ and of their atomic ratios $z = n(\mathbf{X})/n(\mathbf{A})$,

(i) the definition of FD is extended into a generalized framework density and

(ii) the anion packing density is introduced.

2. Anion packing density

An inorganic compound of the general formula

$$(\mathbf{A_1})_{a_1}(\mathbf{A_i})_{a_i}(\mathbf{A_p})_{a_p}(\mathbf{X_1})_{x_1}(\mathbf{X_j})_{x_j}(\mathbf{X_q})_{x_q}$$
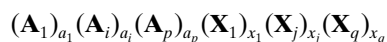
can be considered to be composed of monatomic cations $\mathbf{A_i}$ and anions $\mathbf{X_j}$, where a_i and x_j are the stoichiometric numbers of the corresponding ions. Not taking into consideration the degree of ionicity or covalency of the $\mathbf{A_i} - \mathbf{X_j}$ bonds, ions in inorganic phases are usually approximated as more or less rigid spheres of radii $r(\mathbf{A_i})$ and $r(\mathbf{X_j})$. Of the various sets of ionic radii, that published by Shannon & Prewitt (1969, 1970) and Shannon (1976) is the most comprehensive one. This set of effective ionic radii has been derived from a very large crystal structure database and has widely and very successfully been applied to crystal chemical problems of any kind. In this set of radii the large majority of anions are larger than the cations so that inorganic crystal structures are often described as more or less dense packings of anions, the cations occupying voids between the anions. Under this assumption, an inorganic structure is the more dense and the less porous, the higher the fraction of its total volume that is occupied by the anions.

In analogy to common practice in zeolite chemistry, the structure of any crystalline inorganic single phase material can be considered to consist of a framework of monatomic so-called framework cations and anions $\mathbf{A}^{\mathrm{fr}}$ and $\mathbf{X}^{\mathrm{fr}}$, respectively, and possibly of non-framework cations, anions and perhaps molecules $\mathbf{A}^{\mathrm{nfr}}$, $\mathbf{X}^{\mathrm{nfr}}$ and $\mathbf{M}^{\mathrm{nfr}}$, respectively, which occupy voids

within the framework. According to IUPAC recommendations (McCusker *et al.*, 2001), the chemical formulae of such inorganic phases are given in the form

$$|\mathbf{A}^{\mathrm{nfr}}_{a^{\mathrm{nfr}}} \mathbf{X}^{\mathrm{nfr}}_{x^{\mathrm{nfr}}} \mathbf{M}^{\mathrm{nfr}}_{m^{\mathrm{nfr}}}|[(\mathbf{A}^{\mathrm{fr}}_i)_{a_i}(\mathbf{X}^{\mathrm{fr}}_j)_{x_j}],$$

where a^{nfr}, x^{nfr}, m^{nfr}, a_i and x_j are the stoichiometric numbers of the various atoms (see second column of Table 1).

The unit-cell volume of such material can be divided into the volume occupied by the framework anions and the volume of the voids between these anions, $V_{\mathrm{uc}}^{\mathrm{vba}}$,

$$V_{\mathrm{uc}} = \sum_j [n(\mathbf{X}_j^{\mathrm{fr}}) \cdot V(\mathbf{X}_j^{\mathrm{fr}})] + V_{\mathrm{uc}}^{\mathrm{vba}}, \tag{4}$$

which can be written as

$$V_{\mathrm{uc}} = \mathbf{d}_{\mathrm{ap}} \cdot V_{\mathrm{uc}} + V_{\mathrm{uc}}^{\mathrm{vba}}$$

with

$$\mathbf{d}_{\mathrm{ap}} = \sum_j [n(\mathbf{X}_j^{\mathrm{fr}}) \cdot V(\mathbf{X}_j^{\mathrm{fr}})]/V_{\mathrm{uc}}, \tag{5}$$

$$\mathbf{d}_{\mathrm{ap}} = \sum_j [n(\mathbf{X}_j^{\mathrm{fr}}) \cdot (4/3)\pi r(\mathbf{X}_j^{\mathrm{fr}})^3]/V_{\mathrm{uc}}. \tag{6}$$

Here $n(\mathbf{X}_j^{\mathrm{fr}})$ is the number of anions of type $\mathbf{X}_j^{\mathrm{fr}}$ per unit cell, $V(\mathbf{X}_j^{\mathrm{fr}})$ is the volume occupied by an anion $\mathbf{X}_j^{\mathrm{fr}}$ and $r(\mathbf{X}_j^{\mathrm{fr}})$ is the radius of $\mathbf{X}_j^{\mathrm{fr}}$.

$\mathbf{d}_{\mathrm{ap}}$, as defined by (5) and 6, is called the 'anion packing density'. It can readily be calculated using only the Shannon–Prewitt radii and the volume and content of the unit cell. If the unit cell contains only one type of anion, these equations reduce to

$$\mathbf{d}_{\mathrm{ap}} = n(\mathbf{X}^{\mathrm{fr}}) \cdot V(\mathbf{X}^{\mathrm{fr}})/V_{\mathrm{uc}}, \tag{7}$$

$$\mathbf{d}_{\mathrm{ap}} = n(\mathbf{X}^{\mathrm{fr}}) \cdot (4/3)\pi r(\mathbf{X}^{\mathrm{fr}})^3/V_{\mathrm{uc}}. \tag{8}$$

Since no further assumptions with regard to the crystal structure and composition have been made to derive (5) and (6), the anion packing density $\mathbf{d}_{\mathrm{ap}}$ is defined for inorganic phases of any structure, in contrast to the framework-density FD which, according to (3), is defined only for phases with three-dimensional oxidic tetrahedron frameworks.

If the crystal structure of a phase and, therefore, the coordination number(s) of its framework anions with regard to their surrounding framework cations, $CN' = CN(\mathbf{X}^{\mathrm{fr}}/\mathbf{A}^{\mathrm{fr}})$, are known, their corresponding anion radii, $r(\mathbf{X}_j^{\mathrm{fr}[CN]})$, given in the literature should be used. This seems to be preferable over the use of the usual coordination number(s) $CN(\mathbf{X}^{\mathrm{fr}})$, which takes into account all cations and molecules surrounding a framework anion, because usually the $\mathbf{A}^{\mathrm{fr}}-\mathbf{X}^{\mathrm{fr}}$ bonds are considerably stronger than the bonds between the framework anions and the non-framework species. If only lattice constants of the phase are known, the radius corresponding to the most likely coordination number CN' will give a good approximation.

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3. Generalized framework density

In order to study the relation between anion packing density d_{ap} and the framework density of an arbitrary inorganic compound, independent of the dimensionality of its framework and the coordination number(s) of its cations, the definition of the framework density FD of (3), which applies only to phases with three-dimensional tetrahedron frameworks, has to be extended. The corresponding quantity

$$\mathbf{d}_f = 1000 \sum_i n(\mathbf{A}_i^{fr}) / V_{uc} \qquad (9)$$

which is generally applicable, is called 'generalized framework density'.

4. Anion packing density *versus* generalized framework density

4.1. The density ratio $q_d = d_{ap}/d_f$

From (5), (6) and (9) it follows that the density ratio $\mathbf{q_d}$ amounts to

$$\mathbf{q_d} = \mathbf{d}_{ap}/\mathbf{d}_f = \sum_j [n(\mathbf{X}_j^{fr}) \cdot V(\mathbf{X}_j^{fr})]/1000 \sum_i n(\mathbf{A}_i^{fr}),$$

$$= \langle V(\mathbf{X}_j^{fr}) \rangle \cdot \sum_j n(\mathbf{X}_j^{fr})/1000 \sum_i n(\mathbf{A}_i^{fr}),$$

$$\mathbf{q_d} = z \langle V(\mathbf{X}_j^{fr}) \rangle / 1000, \qquad (10)$$

$$\mathbf{q_d} = z \langle (4/3)\pi r(\mathbf{X}^{fr})^3 \rangle / 1000. \qquad (11)$$

Here $z = \sum_j n(\mathbf{X}_j^{fr}) / \sum_i n(\mathbf{A}_i^{fr})$ is the atomic ratio between the sums of the anions and cations considered to form the structural framework, and

$$\langle V(\mathbf{X}_j^{fr}) \rangle = \sum_j [n(\mathbf{X}_j^{fr}) \cdot V(\mathbf{X}_j^{fr})] / \sum_j n(\mathbf{X}_j^{fr}) \qquad (12)$$

is the average of the volumes of all framework anions in the unit cell.

If the framework contains only one kind of anion $\mathbf{X}^{fr}$, (10) and (11) reduce to

$$\mathbf{q_d} = z \cdot V(\mathbf{X}^{fr})/1000, \qquad (13)$$

$$\mathbf{q_d} = z \cdot (4/3)\pi r(\mathbf{X}^{fr})^3/1000. \qquad (14)$$

In Table 1 calculated values of d_{ap}, d_f and q_d are given for a wide variety of phases, together with information which is necessary to calculate them.

4.2. Materials with three-dimensional tetrahedron frameworks

The first part of Table 1 [phases with $CN(\mathbf{A}_i^{fr}) = 4$] contains data on a number of phases with both dense and porous inorganic three-dimensional tetrahedron frameworks. For the vast majority of such phases, including the zeolites, z is equal to 2. Their host frameworks are, at least on average, fully linked, *i.e.* each $\mathbf{X}^{fr}$ anion is shared between two [$\mathbf{TX}_4$] tetrahedra. There are, however, several phases with, at least on

average, underlinked (or often, less correctly, called interrupted) and a few with, at least on average, overlinked tetrahedron frameworks with $z > 2$ and $z < 2$, respectively (Liebau, 2001, 2002).

From the last but one column of the first part of Table 1 the following conclusions can be drawn.

(i) All oxidic ($\mathbf{X}^{fr}$ = O) phases with fully linked tetrahedron frameworks (*i.e.* with two-coordinated O atoms, O2 only) have the same value $\mathbf{q_d} = 2V(\mathrm{O}^{[2]})/1000 = 0.02061$. Consequently, d_{ap} and d_f, which for $z = 2$ is identical with FD, are proportional to each other.

(ii) Oxidic phases with, at least on-average, underlinked or overlinked ($z \simeq 2$) tetrahedron frameworks have $\mathbf{q_d}$ values > 0.0206 and < 0.0206, respectively. This indicates that for these phases d_{ap} and d_f (and of course FD) are no longer proportional.

(iii) According to (11) and (14), the density ratio $\mathbf{q_d}$ depends not only on z, but also on the radii $r(\mathbf{X}_j^{fr})$ of the framework anions. In particular, $\mathbf{q_d}$ values are the higher the larger the anions $\mathbf{X}_j^{fr}$. For example, because BeF_2 and CaP_2N_4 both have fully linked non-oxidic tetrahedron frameworks [$z = 2$ and $CN(\mathbf{X}_j^{fr}/\mathbf{A}^{fr}) = 2$], the $\mathbf{q_d}$ values 0.01778 and 0.02450 deviate considerably from the value of 0.02061 for corresponding oxidic phases. Consequently, even for phases with $z = 2$ and $CN' = 4$, but different framework cations, $\mathbf{X}^{fr}$, d_{ap} and d_f are not proportional to each other.

4.3. Materials with other than tetrahedron frameworks

In the second part of Table 1, values of d_{ap}, d_f and $\mathbf{q_d}$ are given for a number of phases with $CN(\mathbf{A}_i^{fr}) \neq 4$, in fact with $CN(\mathbf{A}_i^{fr}) > 4$. From the calculated values it can be seen that since the radius of a given ion increases slightly as its coordination number CN increases (see Table 1 of Shannon & Prewitt, 1969, and Table 1 of Shannon, 1976), the density ratio $\mathbf{q_d}$ is somewhat different even for polymorphs of equal composition but different coordination numbers. For example, $\mathbf{q_d}$ increases from 0.02061 for $Si^{[4]}O^{[2]}_2$ *via* 0.02107 for $Si^{[6]}O^{[3]}_2$ to 0.02155 for $Si^{[7]}O^{[3]}O^{[4]}$. This shows that, even for such polymorphs, d_{ap} and d_f are not proportional to each other.

5. Conclusions

5.1. Suitability of d_{ap} and d_f for quantitative comparisons of densities and porosities

Table 1 contains two groups of phases for which $\mathbf{q_d}$ is constant (0.02061 and 0.02107, respectively), because all phases within each group have the same value of both z and $r(\mathbf{X}^{fr})$. This means that within each of these groups d_{ap} and d_f are proportional to each other and, therefore, equally suited to quantitatively compare densities and porosities of these phases. In contrast, for phases which differ either in the chemical nature (and, therefore, radius) of their framework anions or their z values or both, $\mathbf{q_d}$ is not constant and the densities d_{ap} and d_f are no longer proportional. Nevertheless, a general tendency of the two densities is obvious from the

table: an increase of $\mathbf{d}_{ap}$ goes roughly along with an increase of $\mathbf{d}_f$. A few examples, however, reveal that there is no strong correlation between the two. For instance, $\mathbf{d}_{ap}$ of BeF_2 (0.531) is considerably lower than that of CaP_2N_4 (0.609), whereas $\mathbf{d}_f$ of BeF_2 (29.86) is higher than that of CaP_2N_4 (24.88).

The question then arises which of these two quantities reflects the degree of space filling by the framework ions better and is more suitable for quantitative comparisons of densities and porosities.

The answer to this question is not immediately evident from (5), (6), (9) and (12). However, since in the great majority of inorganic coordination compounds the framework anions are, often considerably, larger than the framework cations, they contribute most to the space filling. This implies that as long as $r(\mathbf{X}^{fr}) \geq r(\mathbf{A}^{fr})$, the porosity is mainly determined by the anions so that the anion packing density $\mathbf{d}_{ap}$ is to be preferred over the generalized framework density $\mathbf{d}_f$; and this even the more because $\mathbf{d}_{ap}$ takes into account the numbers *and* sizes of *all* kinds of framework anions in the unit cell, $\sum_j [n(\mathbf{X}_j^{fr}) \cdot V(\mathbf{X}_j^{fr})]$, whereas $\mathbf{d}_f$ considers only the overall number of framework cations per unit cell, $\sum_i n(\mathbf{A}_i^{fr})$, without regard for their sizes and chemical nature.

5.2. Ionic radii

Both the anion packing-density concept and the Shannon–Prewitt radius concept presume that the shape of the anions can be approximated by spheres, corresponding to the ionic character of the $\mathbf{A}_i$—$\mathbf{X}_j$ bonds. The highest theoretical value of rigid-sphere packings is $\mathbf{d}_{ap} = \pi/(18)^{1/2} = 0.7405$. Values higher than that, if not due to error in the determination of the unit cell size, have so far only been found for high-pressure phases (see column 7 of Table 1). This suggests two explanations.

(i) The $\mathbf{X}_j$ anions have been deformed by pressure and can no longer be considered as spherical.

(ii) Until approximately 1975 the number of accurately determined crystal structures at high pressure was rather small. Therefore, the dependence of ionic radii on pressure has not been taken into account by Shannon and Prewitt in deriving the effective ionic radii in their tables. Consequently, the reduction of anion size under high pressure has not been taken into account sufficiently.

Probably, both these effects contribute if anion packing-density values higher than 0.8 are calculated as, for example, in the case of the SiO_2 polymorphs with $CN(\mathbf{A}_i^{fr}) > 4$. The fact that $\mathbf{d}_{ap}$ of stishovite increases steadily from 0.904 at ambient pressure to 1.036 at 54.8 GPa, and that of SiO_2 ($CaCl_2$) from 1.054 at 63.0 GPa to 1.153 at 120 GPa (Andrault *et al.*, 1998) suggests that the latter of the two effects predominates because packing densities higher than 1.00 are physically impossible. Therefore, derivation of ionic radii as a function of pressure, based on high-pressure structure studies, is required.

5.3. Cation and atom packing densities

Although the anion packing density has been defined for any inorganic phase that can be considered to be composed of anions and cations, it will be the more useful the higher the

radius ratio $r(\mathbf{X}_j^{fr})/r(\mathbf{A}_i^{fr})$. Since for the great majority of inorganic compounds with relatively high ionic character of their $\mathbf{A}_i$—$\mathbf{X}_j$ bonds the radius ratio $r(\mathbf{X}_j^{fr})/r(\mathbf{A}_i^{fr}) > 1$, the anion packing-density concept will be widely applicable. For the much smaller portion of inorganic compounds for which $r(\mathbf{X}_j^{fr})/r(\mathbf{A}_i^{fr}) < 1$, the 'cation packing density'

$$\mathbf{d}_{cp} = \sum_i \left[n(\mathbf{A}_i^{fr}) \cdot (V(\mathbf{A}_i^{fr}) \right] / V_{uc} \tag{15}$$

may describe the situation better.

Similarly, for metals and metallic alloys the 'atom packing density'

$$\mathbf{d}_{atp} = \sum_{uc} V(\text{atom}) / V_{uc} \tag{16}$$

should be adequate, in which $V(\text{atom}) = (4/3)\pi r(\text{atom})^3$ and for the $r(\text{atom})$ the metallic radii of the elements tabulated by Laves (1956) can be used.

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