Silicates and Perovskites: Two Themes with Variations

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Silicates with the general formula $\mathbf{A}_m\mathrm{Si}_n\mathrm{O}_p$[**] are the third largest class of chemical compounds after the carbon compounds and the oxides. The number of silicate minerals that occur in nature is very large: At present approximately 1000 natural silicates are known and, on average, about ten new ones are discovered each year. In addition, there are also several hundred synthetic silicates. The large number of synthetic silicates can be attributed to the fact that the experimental chemist is not restricted to compositions of raw materials that appear in nature when carrying out the synthesis in the laboratory. This wide range in chemical composition, therefore, goes hand-in-hand with an exceptional diversity of different structures. Long and intensive investigations have led to a classification system of silicates on a structural chemistry basis which has contributed to a greater understanding of these important compounds.[2, 3]

Recently, silicate research has gained a strong impetus from various groups who have replaced the oxygen partially or completely by nitrogen in the $\mathbf{A}_m\mathrm{Si}_n\mathrm{O}_p$ silicates, and have thus achieved the transition from the oxosilicates to the oxonitridosilicates $\mathbf{A}_m\mathrm{Si}_n(\mathrm{O,N})_p$[4, 5] and the nitridosilicates $\mathbf{A}_m\mathrm{Si}_n\mathrm{N}_p$.[6] Here the principles governing the linkage of tetrahedra, which were relatively simple and clear for the oxosilicates, have been considerably extended. The recent discovery of an octahedrally coordinated silicon atom surrounded by six nitrogen atoms in the synthetic oxonitridosilicate $\mathrm{Ce}_{16}\mathrm{Si}_{15}\mathrm{O}_6\mathrm{N}_{32}$[5] serves as an opportunity for a comparison between these three types of silicates. The structure of this compound, which has been described as a derivative of the perovskite type by its discoverers, highlights the ability of nature to vary a simple, highly symmetrical structure type in a diversity of ways.

Oxosilicates and Silicon Oxo Salts

The exceptionally wide variety of $\mathbf{A}_m\mathrm{Si}_n\mathrm{O}_p$ compounds can be principally attributed to the central position of silicon in Group 14 of the periodic system of the elements. Silicon is therefore amphoteric; that is, its oxide acts as an acid towards oxides of metallic elements with lower electronegativity than silicon ($\chi_{\mathrm{Si}} = 1.74$[7]), but as a base towards oxides of strongly electronegative nonmetals (e.g. P_2O_5 and As_2O_5). The first of the two groups of $\mathbf{A}_m\mathrm{Si}_n\mathrm{O}_p$ compounds are the true oxosilicates. They represent the largest group by far of silicate compounds. Representatives of the second, much smaller group are more correctly described as silicon oxo salts, for example, the silicon oxophosphate, SiP_2O_7, usually abbreviated to silicon phosphate.

Oxosilicates: In the oxosilicates, every silicon atom is tetrahedrally coordinated by four oxygen atoms, so that the coordination number of silicon with respect to oxygen is $\boldsymbol{CN}(\mathrm{Si/O}) = 4$. The $[SiO_4]$ tetrahedra can be linked together through shared corners ($\boldsymbol{L} = 1$)[8] to form multiple tetrahedra, rings, chains, layers, and frameworks.[2] Linkage of the $[SiO_4]$ tetrahedra over shared edges ($\boldsymbol{L} = 2$) or even faces ($\boldsymbol{L} = 3$) is very unfavorable energetically because of the involved reduction of the distance between the silicon atoms (Figure 1) and the resulting increase in repulsive forces (Pauling's third rule), and has not yet been established with any certainty.[***] If the **A** cations are disregarded and only the silicon atoms on neighboring oxygen atoms are considered, the coordination number $\boldsymbol{CN}(\mathrm{O/Si})$ of the O atoms takes on the values 0 ($O^{[0]}$ not bound to Si), 1 (terminal $O^{[1]}$ bound to one Si atom), or 2 (bridging $O^{[2]}$ atom bound to two Si atoms). From the given restrictions for $\boldsymbol{CN}(\mathrm{Si/O})$, $\boldsymbol{CN}(\mathrm{O/Si})$, and $\boldsymbol{L}$ in Table 1, the degree of condensation of oxosilicate anions can vary between $\mathrm{Si:O} = 0.25$ for monosilicates with isolated $[SiO_4]^{4-}$ anions and $\mathrm{Si:O} = 0.5$ for silicon dioxide, SiO_2, with its three-dimensionally infinite frameworks of tetrahedra.

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[**] In accordance with a proposal from Smith, Roberts, Bayliss, and Liebau,[1] a differentiation is made in the structure formula between the usual symbols for the chemical elements B, C, F, H, I, K, N, O, P, S, U, V, W, and Y and the symbols accentuated in bold type for mono- or polyatomic species which occupy specific crystallographic positions (structure sites). These structure-site symbols are for cations: **A** (independent of coordination), **D** (coordination number $\boldsymbol{CN} \geq 9$), **E** ($\boldsymbol{CN} = 8, 7$), **G** ($\boldsymbol{CN} = 6$), **J** ($\boldsymbol{CN} = 5$), **Q** ($\boldsymbol{CN} = 4$, planar, or 2, linear), **T** ($\boldsymbol{CN} = 4$, tetrahedral), ***L*** (cations with a lone electron pair), and **M** (for molecules), **X** (for monatomic anions), and **Z** (polyatomic anions). Structural parameters such as ***CN*** for coordination number, ***L*** for linkedness (linkage type), and others are written in italic and bold type.[2]

[***] The structure of fibrous SiO_2 described in 1954, said to contain chains of edge-sharing $[SiO_4]$ tetrahedra,[9] has not been verified up to now.

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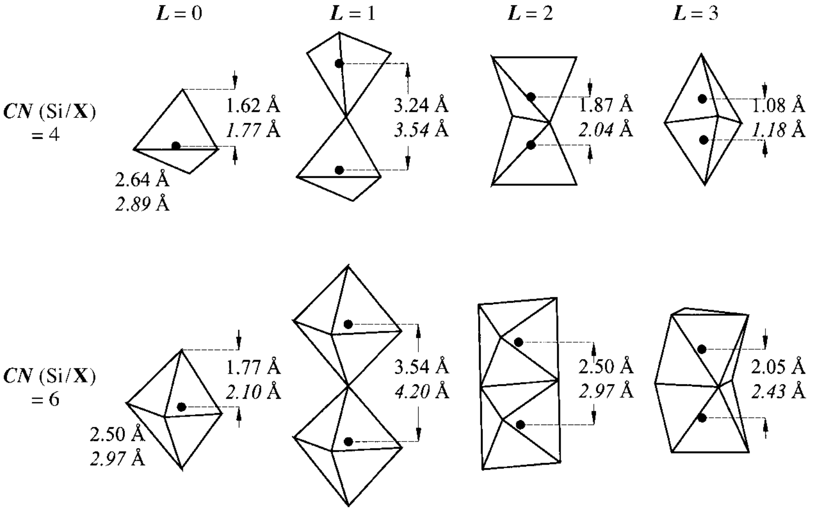


Figure 1. Mean atomic distances $d(\mathrm{Si{-}X})$ and $d(\mathrm{X \cdots X})$ of $[\mathrm{SiX_4}]$ tetrahedra and $[\mathrm{SiX_6}]$ octahedra and maximum distances $d(\mathrm{Si \cdots Si})$ for corner-, edge-, and face-sharing polyhedra of these types. Normal type: **X** = O; italic type: **X** = N.

Table 1. Comparison of the coordination relationshiops in oxo- and nitridosilicates and the resulting theoretically possible molar Si:**X** ratios of their $[\mathrm{Si_rX_s}]$ polyhedral structures.[a]

		X = O	**X** = N
***CN*(Si/X) = 4**	***L***	0,[b] 1, (2)	(0),[b] 1, 2
	***CN*(X/Si)**	0,[b] 1, 2	(0),[b] 1, 2, 3, 4
	$(\mathrm{Si{:}X})_{\mathrm{theor.}}$	0.25 to 0.5	0.25 to 0.75
	$(\mathrm{Si{:}X})_{\mathrm{obs.}}$	0.25 to 0.5	0.333 to 0.75
***CN*(Si/X) = 6**	***L***	0,[b] 1, 2, (3)	(0),[b] (1), (2), (3)
	***CN*(X/Si)**	0,[b] 1, 2, 3	(0),[b] (1), (2), (3), (4)
	$(\mathrm{Si{:}X})_{\mathrm{theor.}}$	0.1667 to 0.5	0.1667 to 0.75
	$(\mathrm{Si{:}X})_{\mathrm{obs.}}$	0.1667 to 0.5	–

[a] The values in parentheses are theoretically possible but have not yet been definitely established. [b] Oxygen atom ("free") not bound to silicon ($\mathrm{O^{[0]}}$).

Silicon oxo salts: Typical compounds of this group, such as $\mathrm{SiP_2O_7}$,[10] contain silicon in octahedral coordination. The tendency of silicon to form $[\mathrm{SiO_6}]$ octahedra instead of $[\mathrm{SiO_4}]$ tetrahedra is stronger with increasing electronegativity of the **A** atoms.[11] Since the O–O bond distance of about 2.50 Å in $[\mathrm{SiO_6}]$ octahedra is considerably smaller than the corresponding distance of about 2.64 Å in $[\mathrm{SiO_4}]$ tetrahedra, the transition of the coordination number, ***CN***(Si/O), from 4 to 6 is associated with a decrease in volume and can therefore be initiated by an increase in pressure. In fact, the majority of currently known phases that contain $[\mathrm{SiO_6}]$ octahedra have been formed at pressures greater than 8 GPa.

Since the Si–O bond distances in the $[\mathrm{SiO_6}]$ octahedra are longer than those in the $[\mathrm{SiO_4}]$ tetrahedra, it follows that the distances between the Si atoms of linked $[\mathrm{SiO_6}]$ octahedra are also longer, and so the repulsive forces between them are weaker than those between linked tetrahedra (Figure 1). In agreement with this, edge sharing (***L*** = 2) between $[\mathrm{SiO_6}]$ octahedra is not uncommon, and even a linkage over the common faces of two $[\mathrm{SiO_6}]$ groups appears to be energetically somewhat more favorable than the linkage of two $[\mathrm{SiO_4}]$ tetrahedra over a common edge.

An increase in the coordination number ***CN***(Si/O) from 4 to 6 involves an increase in the mean ***CN***(O/Si) coordination number. In fact, $\mathrm{O^{[3]}}$ atoms occur in structures with linked $[\mathrm{SiO_6}]$ octahedra—in addition to the oxygen species $\mathrm{O^{[0]}}$, $\mathrm{O^{[1]}}$ and $\mathrm{O^{[2]}}$—that have not been observed so far in structures with linked $[\mathrm{SiO_4}]$ tetrahedra (Table 1). The molar atomic ratio Si:O of polyhedral structures which consist exclusively of $[\mathrm{SiO_6}]$ octahedra can therefore range between 0.1667 (e.g. in $\mathrm{SiP_2O_7}$) and 0.5 (in stishovite, a high-pressure phase of $\mathrm{SiO_2}$).

In addition to the pure oxosilicates and the pure silicon oxo salts, there is a range of compounds that contain both $[\mathrm{SiO_4}]$ tetrahedra and $[\mathrm{SiO_6}]$ octahedra.[12] After spectroscopic investigations indicated the existence of fivefold-coordinated silicon in glasses made by quenching silicate melts previously held at a few GPa of pressure,[13a,b] $[\mathrm{SiO_5}]$ polyhedra, together with $[\mathrm{SiO_6}]$ octahedra, have been established by a crystal structure determination of high-pressure $\mathrm{CaSi_2O_5}$.[13c] Such $[\mathrm{SiO_5}]$ polyhedra have long been assumed to exist as the transition state in condensation and hydrolysis reactions in aqueous solution and in rheological and diffusion processes in silicate melts.[14] Compounds containing $[\mathrm{SiO_5}]$ polyhedra and compounds with mixed ***CN***(Si/O) coordination numbers that are stable at intermediate pressures occupy an intermediate position between the oxosilicates and the silicon oxo salts.

Nitridosilicates and Oxonitridosilicates

Although, up to now, the structures of only a couple of dozen $\mathbf{A}_m\mathrm{Si}_n\mathrm{N}_p$ nitridosilicates and four $\mathbf{A}_m\mathrm{Si}_n\mathrm{O}_p\mathrm{N}_q$ oxonitridosilicates have been sufficiently well established, it is possible to derive principles for crystal chemical analysis. These principles are compared in Table 1 with those of the $\mathbf{A}_m\mathrm{Si}_n\mathrm{O}_p$ oxo compounds. Table 2 contains values of several parameters of the elements silicon, oxygen, and nitrogen that are useful for a rough interpretation.

Table 2. Several parameters that are useful for the interpretation of silicate structures.

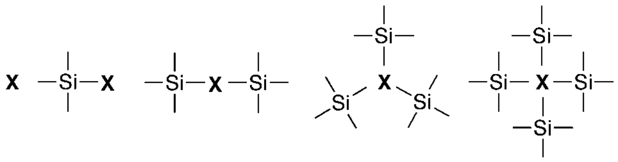
	Si	**X** = O	**X** = N
$r^{[4]}$ [Å][a]	0.26	1.38	1.46
χ[b]	1.74	3.50	3.07
$\Delta\chi$[c]	–	1.76	1.33
$I_{\mathrm{Si-X}}$ [%][d]	–	53	36

[a] Effective radius of the fourfold coordinated ions.[15] [b] Electronegativity.[7] [c] $\Delta\chi = \chi_{\mathbf{X}} - \chi_{\mathrm{Si}}$. [d] $I_{\mathrm{Si-X}} = 1 - \exp[-0.25(\chi_{\mathbf{X}} - \chi_{\mathrm{Si}})^2]$ (ionicity).[16]

Nitridosilicates: In all the $\mathbf{A}_m\mathrm{Si}_n\mathrm{N}_p$ structures known so far, silicon is, without exception, tetrahedrally coordinated; these compounds are therefore true nitridosilicates. No indications were found for $[\mathrm{SiN_6}]$ octahedra, even in phases that were synthesized at high pressures. This means that silicon nitrido salts corresponding to the silicon oxo salts are, until now, not known. This reflects the predicted lower tendency of silicon to sixfold coordination with the larger nitride ion $\mathrm{N^{3-}}$ than with the smaller oxide ion $\mathrm{O^{2-}}$, in accordance with the radius–ratio rule (Pauling's first rule). The low tendency to form $[SiN_6]$ octahedra is decreased further by the fact that, owing to the lower electronegativity of nitrogen, the Si–N bond is considerably more covalent than the Si–O bond, whereby the nonmetallic character of silicon and therefore its sp^3 character are strengthened.

Since $[SiN_4]$ tetrahedra are larger than $[SiO_4]$ tetrahedra, $r(N^{3-}) > r(O^{2-})$, and the stronger covalent character of the Si–N bond means that the effective charge of the Si atoms in $[SiN_4]$ is lower than in $[SiO_4]$ tetrahedra, the repulsive forces between the Si atoms of linked $[SiN_4]$ tetrahedra in nitridosilicates are lower than the equivalent forces in oxosilicates. Despite the low number of known nitridosilicate structures, the above statement is supported by the finding that both corner-sharing ($\boldsymbol{L} = 1$) and edge-sharing ($\boldsymbol{L} = 2$) tetrahedra exist in $BaSi_7N_{10}$,[6i] whereas edge-sharing of $[SiO_4]$ tetrahedra has never been satisfactorily established in the much more numerous oxosilicates (see footnote[***] on p. 1733).

While oxosilicates only contain oxygen atoms which are either bound to none, one, or two silicon atoms ($O^{[0]}$, $O^{[1]}$, $O^{[2]}$), nitrogen atoms have been found in nitridosilicates that are bound to three or four silicon atoms ($N^{[3]}$, $N^{[4]}$), in addition to the species $N^{[1]}$ and $N^{[2]}$ (Scheme 1, Table 1). The histogram in Figure 2 shows the frequency distribution of known nitridosilicates relative to the occurrence of the different $\mathbf{X}^{[CN(\mathbf{X}/Si)]}$ species.



$\boldsymbol{CN}(\mathbf{X}/Si)$	0	1	2	3	4
$O^{[CN(O/Si)]}$	$O^{[0]}$	$O^{[1]}$	$O^{[2]}$	(–)	(–)
$N^{[CN(N/Si)]}$	(–)	$N^{[1]}$	$N^{[2]}$	$N^{[3]}$	$N^{[4]}$

Scheme 1. Linkages of the **X** anions with silicon in oxosilicates (**X** = O) and nitridosilicates (**X** = N); (–): not observed.

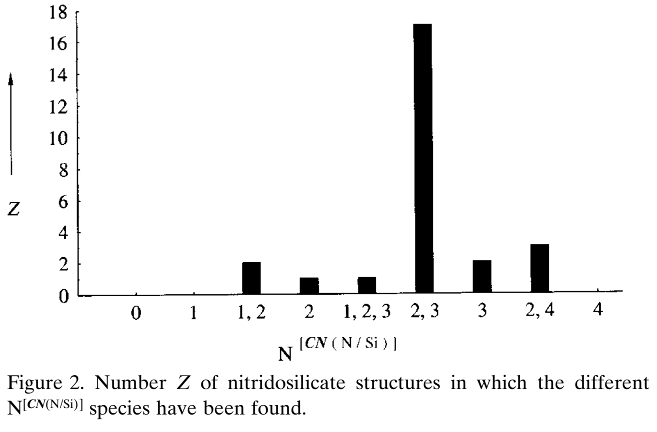


Figure 2. Number Z of nitridosilicate structures in which the different $N^{[CN(N/Si)]}$ species have been found.

From the restrictions given for $\boldsymbol{CN}$(Si/N), $\boldsymbol{CN}$(N/Si) and $\boldsymbol{L}$ in Table 1, it follows that the degree of condensation of the $[SiN_4]$ tetrahedra in nitridosilicates can range from 0.25 for isolated single tetrahedra (not observed up to now, probably because of its high formal charge of –8) and 0.75 (realized in the tetrahedral frameworks of α- and β-Si_3N_4).

Oxonitridosilicates: It would be expected that the oxonitridosilicates are structurally intermediate between the oxo- and the nitridosilicates. This is true for the few representatives of this group of compounds for which exact structure determinations are available,[4, 5] and for a range of further examples for which isotypy with known oxosilicates, such as Ca_2SiO_4, åkermanite ($Ca_2MgSi_2O_7$), and pseudowollastonite ($Ca_3Si_3O_9$), could be established from powder X-ray diffraction data.[17] They contain $[Si\mathbf{X}_4]$ tetrahedra with O:N ratios ranging from 3:1 in $LaEu^{II}[SiO_3N]$[17a] to 1:3 in Si_2N_2O.[4b]

$Ce_{16}Si_{15}O_6N_{32}$

This extraordinary phase was recently synthesized by Köllisch and Schnick[5] at about 1500 °C and normal pressure and structurally investigated by single-crystal X-ray diffraction. It contains both tetrahedrally and octahedrally coordinated silicon atoms, and is not formally a pure oxonitridosilicate, but comes very close with a molar atomic ratio of $Si^{[4]}:Si^{[6]} = 14:1$.

At first sight, the existence of $Si^{[6]}$ in this phase is surprising since it does not contain strongly electronegative cations ($\chi_{Ce} = 1.08$) and was not synthesized under high pressure. Even more interesting is the fact that, although the tendency to form $[Si\mathbf{X}_6]$ octahedra is lower for $\mathbf{X} = N^{3-}$ than for $\mathbf{X} = O^{2-}$, the structure determination reveals that the 14 $Si^{[4]}$ atoms per formula unit are probably statistically surrounded by oxygen and nitrogen atoms, whereas the $Si^{[6]}$ atom is, with high probability, only coordinated by nitrogen atoms. Therefore, there must be a particular reason that a few of the silicon atoms in $Ce_{16}Si_{15}O_6N_{32}$ are, against all expectations, octahedrally coordinated.

A possible reason, given by the authors, is that the structure of this cerium oxonitridosilicate bears certain similarities with the perovskite type $\mathbf{A}^{[12]}\mathbf{G}^{[6]}\mathbf{X}_3$ (see footnote[**] on p. 1733). Therefore, the structure can be described as a cubic $4 \times 4 \times 4$ superstructure of the ideal cubic perovskite type, in which four of the 64 $\mathbf{G}^{[6]}$ positions per superstructure unit cell are occupied with $Si^{[6]}$, 56 with $Si^{[4]}$, and four are unoccupied, whereas the 64 $\mathbf{A}^{[12]}$ positions are all occupied by Ce^{3+} ions. The valence is compensated for by 24 O^{2-} and 128 N^{3-} ions, so that 40 **X** positions of the perovskite superstructure cell are unoccupied. The cerium oxonitridosilicate phase is therefore a perovskite variant with an ordered distribution of vacancies, both in the sublattice of the octahedrally coordinated **G** cations and in the anion sublattice, and with a very extensive substitution of the $\mathbf{G}^{[6]}$ cations by $Si^{[4]}$ cations. It can therefore be described by the formula $Ce_{16}(Si^{[6]}Si^{[4]}_{14}\square)(O_6N_{32}\square_{10})$, where the coordination number of the Ce^{3+} ions is considerably lower than 12 as a consequence of the vacancies (□) in the anion sublattice. In addition, the change in coordination of $\mathbf{G}^{[6]}$ to $Si^{[4]}$ requires that the positions of the O^{2-} and N^{3-} ions deviate considerably from the **X** positions in ideal perovskite.

Such a large difference between the structure of the cerium compound and that of the ideal perovskite type clearly provokes the question whether this structure relationship is crystal chemically and energetically relevant or whether it is coincidence, imagination, or unrealistic. To answer this question, the various modifications of the ideal perovskite type are discussed below.

Stoichiometric Perovskites

The starting point is the ideal perovskite structure with a cubic unit cell ($a \approx 3.93$ Å), the space group $Pm\bar{3}m$, and one formula unit of $\mathbf{A}^{[12]}\mathbf{G}^{[6]}\mathbf{X}_3$. The structure is usually represented as a three-dimensional framework of corner-shared, regular octahedra with centers occupied by the **G** cations, while the large **A** cations occupy the dodecahedral sites between eight octahedra.

This aristotype structure can, while maintaining the topology of the bonds, be deformed to hettotype structures[*] with lower symmetries, in the sense of Megaw,[18] by one of three mechanisms: a) distortion of the $[\mathbf{X}_6]$ octahedra, b) shifting of the $\mathbf{G}^{[6]}$ cations from the octahedra centers, and c) cooperative tilting of the $[\mathbf{X}_6]$ octahedra around two-, three-, or fourfold rotation axes.

Two or all three of these mechanisms can occur simultaneously, and the resulting structures can be either ordered, or statically or dynamically disordered. The symmetry of such a distorted perovskite structure can be cubic, tetragonal, rhombohedral, or octahedral, down to triclinic subgroups of $Pm\bar{3}m$.[19]

Such distortions can be caused by changes in temperature or pressure, or by the choice of the chemical species in the sites $\mathbf{A}^{[12]}$, $\mathbf{G}^{[6]}$, and **X**. Stoichiometric perovskites of the general formula $\mathbf{A}^{\mathrm{I}}\mathbf{G}^{\mathrm{II}}\mathbf{X}_3^{-\mathrm{I}}$, $\mathbf{A}^{\mathrm{II}}\mathbf{G}^{\mathrm{I}}\mathbf{X}_3^{-\mathrm{I}}$, $\mathbf{A}^{\mathrm{I}}\mathbf{G}^{\mathrm{V}}\mathbf{X}_3^{-\mathrm{II}}$, $\mathbf{A}^{\mathrm{II}}\mathbf{G}^{\mathrm{IV}}\mathbf{X}_3^{-\mathrm{II}}$, and $\mathbf{A}^{\mathrm{III}}\mathbf{G}^{\mathrm{III}}\mathbf{X}_3^{-\mathrm{II}}$ are known, in which the **A** and **G** cations and the **X** anions can vary over a wide range in relation to their size. $ThTaN_3$,[20] a nitridoperovskite with the general formula $\mathbf{A}^{\mathrm{IV}}\mathbf{G}^{\mathrm{V}}\mathbf{X}_3^{-\mathrm{III}}$, and the oxonitridoperovskites $LaWO_{0.6}N_{2.4}$ and $BaTaO_2N$[21] have also been synthesized. The ordered distribution of two different cations **A** and **A′** or/and **G** and **G′** on the **A** or **G** sites often leads to a multiplication of the volume of the unit cell of the ideal perovskite structure, for example to a tetragonal or cubic $2 \times 2 \times 2$ superstructure cell in $(CaFe)Ti_2O_6$ or $(CaCu_3)Ge_4O_{12}$.[22] In connection with the cerium oxonitridosilicate[5] described by Köllisch and Schnick, it is worth mentioning that stoichiometric perovskites with the composition $CaSiO_3$[23] and $MgSiO_3$[24] have been synthesized under high pressure and structurally analyzed.

Nonstoichiometric Perovskites (Defect Perovskites)

If the **A** or **G** site, or even both, are each occupied by cations of different valence, the valence balance is achieved by the vacancies in the **A** and/or **X** sublattice, and more rarely in the **G** sublattice. Many $\mathbf{AG}O_3$ phases are known in which the element in the **G** position, such as Nb, Ta, Ti, Fe, Mn, Cr, or W, can take on different oxidation states relatively easily. In some cases, it can be extremely difficult or even impossible to synthesize stoichiometric $\mathbf{AG}O_3$ perovskite phases with such cations. In the ceramic and geosciences literature, compositions are very often given as $\mathbf{AG}O_x$ or $\mathbf{A}_x\mathbf{G}O_3$, since it is not always known how the valence balance has been achieved. With the cubic tungsten bronzes $\mathbf{A}_xWO_3$, for example, x can be as low as $x = 0$, so that WO_3 and the isotypic ReO_3 can be considered as defect perovskites with a maximum concentration of vacancies in the **A** sublattice. The **G** position can also be occupied by atoms of different chemical elements with differing valencies, such as in $Ca_2AlSiO_{2.5}$.[25]

If the **G** positions are occupied by smaller cations, such as Si, which have a strong preference for tetrahedral coordination, then the perovskite type can even "cope" with the substitution of $[\mathbf{G}O_6]$ octahedra with $[\mathbf{T}O_4]$ tetrahedra. This is accompanied by the appearance of vacancies in the anion sublattice. In this way, the calcium sodium and europium sodium silicates $Na_2Ca_2(SiO_3)_3$, $Na_2Ca(SiO_3)_2$, $Na_2Eu(SiO_3)_2$, and $Na_4Ca(SiO_3)_3$, which have been described as cyclosilicates with rings of six and twelve $[SiO_4]$ tetrahedra, respectively,[26] can be considered as defect perovskites $[(Na,Ca)_6\square_2]_{\mathbf{A}}$ $[(Na,Ca)_2^{[6]}Si_6^{[4]}]_{\mathbf{G}}$ $[O_{18}\square_6]_{\mathbf{X}}$, $[(Na,Ca)_7\square]_{\mathbf{A}}$ $[(Na,Ca)_2^{[6]}Si_6^{[4]}]_{\mathbf{G}}$ $[O_{18}\square_6]_{\mathbf{X}}$, and $[(Na,Eu)_7\square]_{\mathbf{A}}$ $[(Na,Eu)_2^{[6]}Si_6^{[4]}]_{\mathbf{G}}$ $[O_{18}\square_6]_{\mathbf{X}}$ with a rhombohedral $2 \times 2 \times 2$ superstructure or $[(Na,Ca)_8]_{\mathbf{A}}$ $[(Na,Ca)_{1.92}^{[6]}Si_6^{[4]}\square_{0.08}]_{\mathbf{G}}$ $[O_{18}\square_6]_{\mathbf{X}}$ with a cubic $4 \times 4 \times 4$ superstructure. The many minerals of the lovozerite group[27] also belong to this homeotypic group of silicates. It is apparent that the phase described by Köllisch and Schnick,[5] $[Ce_{16}]_{\mathbf{A}}$ $[Si^{[6]}Si_{14}^{[4]}\square]_{\mathbf{G}}$ $[O_6N_{32}\square_{10}]_{\mathbf{X}}$, also belongs to this group of defect perovskites.

The decreasing degree of structural similarity to the ideal perovskite type of the derivatives described here confirms that the description of the cerium compound as a defect perovskite[5] is justified. The large variability of the perovskite type can also be seen as an expression of its strong stability. This stability does decrease with decreasing degree of structural similarity, but still provides a contribution to the stability of such complicated structures that should not be overlooked. This contribution could be the reason that $Ce_{16}Si_{15}O_6N_{32}$, against all expectations, contains $[SiN_6]$ octahedra, even if they are only few in number (see above).

What significance does this stabilizing influence have to such a variable structure type as perovskite? A comparison of different perovskite derivatives shows that the cations on the **A** positions do not deviate (or at the most very slightly) from the highly symmetrical special positions of the ideal perovskite structure. The deviations of the cation positions of the **G** substructure are also very slight, even when the coordination number is reduced from six to four. Only the anion positions of the **X** substructure deviate, at times extensively, from the ideal, highly symmetrical positions. Therefore, one interpretation could be that the stability of the structure is primarily determined by the highly symmetrical potential distribution of the cations. The anions take over the function of shielding the cations from each other, so that their contribution to the stabilization is also considerable, even when the arrangement deviates strongly from the special positions in ideal perovskite.

One indication that this very simplified interpretation is reasonable is given by the investigations by Vegas et al.[28] They established, with the help of statistical analysis, that the topology of the cations in the spinels $\mathbf{G}_2^{[6]}\mathbf{T}^{[4]}O_4$, the delafossites $\mathbf{Q}^{[2]}\mathbf{G}^{[6]}O_2$, and the bixbyites $\mathbf{G}_2^{[6]}O_3$ resembles the

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[*] The aristotype of a structure type has the highest possible space group symmetry. Structure-type variants that are derived from the aristotype by reduction of its symmetry to a subgroup symmetry are designated hettotypes.

topology of the corresponding metal, and even that the distances between the cations are very similar to the distances in the relevant metal structures. Borides of the types $\mathbf{AB}_2$, $\mathbf{AB}_4$, and $\mathbf{AB}_6$ show similar behavior.[29]

Outlook

The cerium compound $Ce_{16}Si_{15}O_6N_{32}$ described by Köllisch and Schnick[5] is no unimportant exotic from the rarities collection of chemical fundamental research. On the contrary, it encourages conclusions to be drawn of wide-ranging crystal chemical significance. Its high concentration of vacancies in the anion sublattice leads to the expectation of high ionic conductivity. The close relationship to other defect perovskites encourages the targeted synthesis of new materials with interesting electrical, magnetic, and optical properties.

It is unlikely that oxonitrido- or nitridosilicates will occur as minerals in the crust and in the upper mantel of the earth owing to the high oxygen fugacity. However, they could possibly exist in further depths of the earth, on planets and planetlike bodies with low oxygen but high nitrogen fugacity, or in interstellar space. The discovery of the mineral sinoite (Si_2N_2O) in meteorites and in cosmic dust[30] could serve as the first example.

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Keywords: cerium · nonstoichiometric compounds · perovskite phases · silicates · solid-state structures

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