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Tetragonal Tetrahedra Distortions in Cubic Sodalite Frameworks

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Abstract

A literature search for sodalite frameworks has revealed that, besides tilting, tetrahedron-edge-length distortions are an important means of releasing strains imposed by geometrical constraints. The extent of this distortion rises with the Al content in the series of framework composition $[\text{Al}_{12-n}\text{Si}_n\text{O}_{24}]^{(12-n)-}$ ($0 \leq n \leq 12$). Violations of Loewenstein's rule are connected with large tetrahedron-edge-length distortions. Geometrical relationships are given.

Introduction

The general formula for members of the sodalite family is $M_8[\text{T}_{12}\text{O}_{24}]\text{X}_2$. Tetrahedra TO_4 with $T = \text{Si}^{4+}, \text{Al}^{3+}, \text{Be}^{2+}, \text{B}^{3+}, \dots$ are connected with each other via common O atoms to form what is known as the sodalite framework. The centres of the tetrahedra occupy thereby the corners of truncated octahedra which in turn, being linked by common 4-rings and 6-rings, form a space-filling arrangement. The T cations need not be all of the same kind in a given structure. In fact, a sodalite framework with only Si has never been found (it would be a hypothetical

silica modification). Usually, part of the tetravalent Si^{4+} is replaced by other lower-charged cations (most commonly Al^{3+}) and the framework composition becomes, e.g., $[\text{Al}_6\text{Si}_6\text{O}_{24}]^{6-}$. Clearly, this framework needs charge compensation to maintain electroneutrality. This is achieved by balancing the negative charges of the framework by a combination of cations and anions being situated in the large cavities (cages) formed by the framework. Besides charge balancing, these cage cations M (typically $\text{Na}^+, \text{K}^+, \text{Ca}^{2+}, \dots$) and cage anions $X(\text{Cl}^-, \text{SO}_4^{2-}, \dots)$ have another important function as they prevent the open tetrahedra framework from collapsing. They serve as a form of spacer and when they are smaller than the size corresponding to a maximal expansion, the framework adapts itself to the size of the cage ions. Pauling (1930), who determined the structure of the natural mineral sodalite, called this volume reduction a 'partial collapse'. The mechanism by which the framework reduces its cage volume consists of cooperative rotations of the TO_4 tetrahedra about their $\bar{4}$ axes. Fig. 1 of Taylor (1972) illustrates very clearly this tilting or folding of the sodalite framework. The degree of tilting is measured by the tilt angle φ .

calculated from

$$\left(\frac{1}{2}-x\right)=\frac{d_1}{2a}. \quad (8)$$

T cations are in position 12(d) and the shortest distance between any two of them is

$$u=\frac{a}{2\sqrt{2}}. \quad (9)$$

We allow now a partial collapse of the framework, i.e. $\varphi \neq 0^\circ$, and the space group becomes $I\bar{4}3m$:

$$a'=2d_1 \cos \varphi + 2h \quad (10)$$

or

$$a'=4l\left(\sin\frac{\alpha}{2}\cos\varphi+\cos\frac{\alpha}{2}\right). \quad (11)$$

Framework O atoms are now in position 24(g) (x, x, z ; $x \sim 0.35, z \sim 0.05$) with

$$\left(\frac{1}{2}-x\right)=\frac{d_1 \cos \varphi}{2a'}; \quad z=\frac{d_1 \sin \varphi}{2a'} \quad (12)$$

and it follows that

$$\varphi=\tan^{-1}\left(\frac{z}{\frac{1}{2}-x}\right). \quad (13)$$

u can be obtained from (9) and

$$-\cos \gamma=\frac{u^2-2l^2}{2l^2} \quad (14)$$

or, after substituting and reordering,

$$-\cos \gamma=\cos \varphi \sin \alpha-\sin^2 \varphi \sin^2 \frac{\alpha}{2}. \quad (15)$$

Correspondingly, φ can be expressed in terms of α and γ :

$$\cos \varphi=\sqrt{2}\frac{\sin \frac{\gamma}{2}}{\sin \frac{\alpha}{2}}-\cot \frac{\alpha}{2}. \quad (16)$$

Relations for ideal tetrahedra can, of course, be obtained by setting $\alpha=109^\circ 28'$. Koch & Hellner (1981) have shown that the condition for the existence of a sodalite framework consisting of one type of undistorted tetrahedra is

$$8x^2-8z^2-1=0. \quad (17)$$

On the other hand, because of equations (10) and (12), a sodalite consisting of tetragonally distorted tetrahedra exists only if

$$z^2=\left(\frac{1}{4}-x\right)^2 \tan^2 \frac{\alpha}{2}-\left(\frac{1}{2}-x\right)^2 \quad (18)$$

is fulfilled.

For ordered sodalites containing two types of T cations with strict alternation of larger (primed quantities) and smaller (unprimed) TO_4 tetrahedra the following condition exists for the (still cubic) lattice parameter:

$$a=b=2(d'_1 \cos \varphi'+h)=2(d_1 \cos \varphi+h'), \quad (19)$$

which gives

$$d'_1-d_1-2d'_1 \sin^2 \frac{\varphi'}{2}+2d_1 \sin^2 \frac{\varphi}{2}=h-h'. \quad (20)$$

In practice, $d'_1 \sin^2 \varphi'/2 \sim d_1 \sin^2 \varphi/2$ and (20) can be given to a fair approximation by its solution for $\varphi'=\varphi=0^\circ$:

$$d'_1-h'=d_1-h \quad (21)$$

or

$$\frac{l'^2}{l^2}=\frac{1-\sin \alpha}{1-\sin \alpha'}. \quad (22)$$

Discussion

Equations (1)–(18) are exact only for cubic sodalites containing one type of T cation and consisting of purely tetragonally distorted TO_4 tetrahedra. These conditions are rarely perfectly fulfilled in nature. However, as Megaw (1973) pointed out, individual variations of interatomic distances and angles tend to cancel in linkage structures. Therefore, these equations are also applicable to the averaged values of actually existing sodalites, even if they contain ordered TO_4 tetrahedra of different composition or if they are not cubic. The agreement between observed and calculated values is generally very good.* For anisotropically folded sodalites (Depmeier, 1983), however, the degree of disagreement seems to increase with increasing anisotropy.

Tetragonal distortion of the TO_4 tetrahedra can mean both compression or extension, the former being the usual case for the sodalites known to date. In either case, two of the six tetrahedron edges, *viz* those designated d_1 , have lengths different from the four named d_2 . It is worth noting that the arrangement of the distorted tetrahedra in the sodalite framework is such that the edges d_1 constitute the 4-rings of the framework, whereas the 6-rings are entirely made up by d_2 edges.

Equation (5) shows that the distortion of a TO_4 tetrahedron reduces its volume; e.g. for $\alpha=120^\circ$, which corresponds to aluminate sodalites, the volume reduction is about 2.5%. In addition, it reduces the

* A list containing structural information for 17 sodalites has been deposited with the British Library Lending Division as Supplementary Publication No. SUP38981 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

volume of the unit cell [equation (11)] and also $\Delta V = V_{\text{cell}} - 12V_{\text{tetra}}$, the difference between the volume of the unit cell, V_{cell} , and the volume of the total number of tetrahedra per unit cell, $12V_{\text{tetra}}$. The ratio $Q = 12V_{\text{tetra}}/V_{\text{cell}}$ increases first quite strongly with increasing α , before it reaches a point of inflection at about $\alpha = 127^\circ$. It is interesting to note that the lattice parameter a depends more strongly on a change in α than on a change in φ [equation (11)].

The conformation of a cubic sodalite framework is described by either equation (16) or (18) and it is clear that either can be used for conveniently mapping sodalites according to their degree of distortion. Such a mapping is shown in Fig. 2 which is based on equation (18) and is similar to Fig. 4 of Koch & Hellner (1981). z is plotted against x and curves of constant angles α and φ are drawn. The aspect of the curves indicates that the x coordinates of the

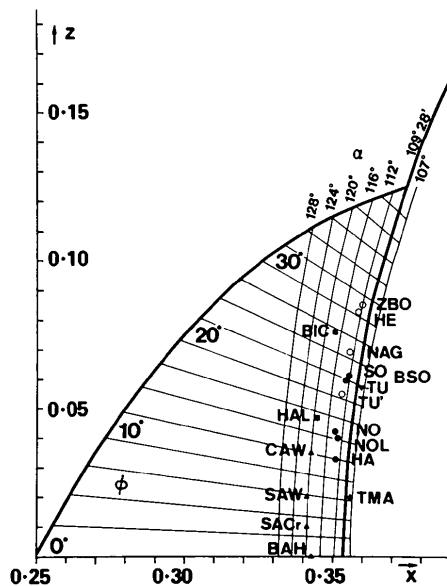


Fig. 2. z vs x fractional coordinates of the O atoms of sodalite frameworks with lines of constant tilt angles φ and curves of constant tetrahedron distortion angle α . Sodalites belonging to the series of framework composition $[\text{Al}_{12-n}\text{Si}_n\text{O}_{24}]^{(12-n)-}$ ($0 \leq n \leq 12$) are plotted with filled symbols; other framework compositions are indicated by open circles. In general, sodalites deviate from the existence line of ideal sodalites ($\alpha = 109^\circ 28'$), but the Al-rich members more than the others. Designations for the sodalites (in alphabetical order): BAH: 'barium aluminate hydrate' (Ahmed *et al.*, 1973); BIC: bicchulite (Sahl & Chatterjee, 1977); BSO: basic sodalite (Hassan & Grundy, 1983); CAW: Ca- WO_4 aluminate sodalite (Depmeier, 1984); HA: h a yne (L ohn & Schulz, 1968); HAL: synthetic h a yne No. 26.2 (L ons, 1969); HE: helvite (Holloway *et al.*, 1972); NAG: basic Na aluminogermanate sodalite (Belokoneva *et al.*, 1982); NO: nosean (Schulz, 1970); NOL: synthetic nosean (L ons, 1969); SACr: Sr- CrO_4 aluminate sodalite (Setter *et al.*, unpublished); SAW: Sr- WO_4 aluminate sodalite (Depmeier, to be published); SO: sodalite (L ons & Schulz, 1967); TMA: tetramethylammonium sodalite (Baerlocher & Meier, 1969); TU: all-Si 4-ring of tugtupite (Dan , 1966); TU': Si/Al/Be 4-ring of tugtupite (Dan , 1966); ZBO: zinc metaborate (Smith-Verdier & Garc a-Blanco, 1980).

framework O atoms depend mainly on the degree of the tetrahedron distortion, whereas the z coordinates are virtually insensitive to this distortion, but change rapidly as the tilt angle φ changes.

All filled symbols in Fig. 2 represent sodalites belonging to the series of aluminosilicate sodalites with framework composition $[\text{Al}_{12-n}\text{Si}_n\text{O}_{24}]^{(12-n)-}$; empty circles correspond to sodalites having different compositions. End members of the series are on one side ($n = 0$) the aluminate sodalites $\text{Ca}_8[\text{Al}_{12}\text{O}_{24}](\text{WO}_4)_2$ (CAW; Depmeier, 1984), $\text{Sr}_8[\text{Al}_{12}\text{O}_{24}](\text{WO}_4)_2$ (SAW; Depmeier, to be published), $\text{Sr}_8[\text{Al}_{12}\text{O}_{24}](\text{CrO}_4)_2$ (SACr; Setter & Depmeier, unpublished) and 'barium aluminate hydrate' (BAH; Ahmed, Dent Glasser & King, 1973) which are characterized by the smallest values of x of the whole series. z and φ are, in general, also small. On the other side of the series ($n = 12$) we have chosen the 4-ring of tugtupite $\{\text{Na}_8[\text{Al}_2\text{Be}_2\text{Si}_8\text{O}_{24}](\text{Cl}, \text{S})_2\}$; Dan  1966} which consists entirely of SiO_4 tetrahedra. The data point is labelled TU. This 4-ring is regarded as representing to some extent a hypothetical SiO_2 modification crystallizing in a sodalite-like framework. The value of x is the highest in the whole series. The second type of 4-ring in tugtupite is a mixed one consisting of two SiO_4 , one AlO_4 and one BeO_4 tetrahedra; it is marked TU', but will not be further considered here.

A 1:1 Si/Al ratio ($n = 6$) corresponds to the well known natural aluminosilicate sodalites, *viz* h a yne (HA; L ohn & Schulz, 1968), nosean (NO; Schulz, 1970; NOL, L ons, 1969) and sodalite (SO; L ons & Schulz, 1967) in the proper sense. The recently determined basic sodalite (BSO; Hassan & Grundy, 1983) has also been included. The values of x and α of this group are intermediate between the extreme values of the end members; z and φ are moderately high.

Only one Si-rich sodalite (Si/Al = 5:0) has been reported, *viz* tetramethylammonium sodalite (TMA; Baerlocher & Meier, 1969). Unfortunately, this material could be obtained only in the form of very tiny crystals and, therefore, the structure had to be determined from powder data. Furthermore, the space group used in the refinement was only approximately correct. Therefore, the results do not have the same level of significance as the single-crystal results of the other sodalites. In addition, there are no cage anions in the structure, which sets TMA somewhat apart from the other sodalites. Despite its particularities we have included TMA in our list as a representative of otherwise unknown Si-rich sodalite frameworks. Two aluminosilicate sodalites have an Si/Al ratio < 1:0. Bicchulite (BIC; Sahl & Chatterjee, 1977) has an Si/Al ratio of exactly 0.5, whereas L ons (1969) studied an artificial h a yne (HAL) for which he estimated a ratio of 0.4. For both types, Si- or Al-rich sodalites, the values of x and α fall between the intermediate 1:1 sodalites and the corresponding end members.

These results indicate clearly that the degree of tetrahedron distortion (measured by α) is correlated with the framework composition. This is demonstrated in Fig. 3 where angles α (averaged α for each structure) are plotted against $\bar{T}-1.35$ for the series of aluminosilicate sodalites. \bar{T} is the average bond length of the corresponding sodalite, 1.35 \AA the effective ionic radius of O^{2-} for coordination number (CN) II (Shannon & Prewitt, 1969) and $\bar{T}-1.35$ is, thus, the average T cation radius. The linear-regression line drawn has a correlation coefficient of 0.965. The conspicuous linear relationship between α and the average cation radius is interesting and needs an explanation.

Equation (7) shows that a sodalite framework consisting of ideal tetrahedra and being in its fully expanded state would have an angle $\angle(T-O-T)$ of 160.5° . This value is unfavourable because in silicate linkage structures the preferred angle is about 145° (Megaw, 1973). Therefore, a strain is created and two possibilities exist for the structure to reduce this angle and, thereby, to release the strain, *viz* (i) by increasing the tilt angle φ or, (ii) by increasing the angle α . The first is the favourite mechanism for the Si-rich side of the series, whereas the second prevails for Al-rich members. The tilt angle φ is mainly determined by the cage content, whereas α depends on the framework composition, or, to be more precise, on the Al content.

Clearly, the strain in the 4-rings of the sodalite framework is higher than in the 6-rings and, consequently, the gain in energy is higher if the strain is reduced here. That is why for sodalites usually a simultaneous opening of α and narrowing of γ_0 occurs in the 4-rings. The amount of opening of α is limited by $\text{O}\cdots\text{O}$ repulsions in the 6-rings. This is demonstrated by the nearly constant d_2 values within a group of given framework composition. Hence, the longer Al-O bonds allow smaller α' angles and larger α angles than the shorter Si-O bonds. The observed slight increase of d_2 with increasing Al content can be attributed to the higher ionic character of the Al-O

bond as compared with the more covalent Si-O bond. The increased ionic character leads, together with the increasing negative charge of the framework, to increased repulsion of the framework O atoms and, thus, to a longer equilibrium distance.

The higher ionic character of the Al-O bonds as compared with the Si-O bonds also has the consequence that the angle $\angle(\text{O}-\text{Al}-\text{O})$ is more easily deformable than $\angle(\text{O}-\text{Si}-\text{O})$. This makes it just feasible that the Al-rich sodalites can profit from the possibility of strain reduction by increasing α , as offered by the long T -O distance. This is clearly demonstrated by the aluminogermanate sodalite NAG $\{\text{Na}_8[\text{Al}_6\text{Ge}_6\text{O}_{24}](\text{OH})_2\}$; Belokoneva, Dem'yanets, Uvarova & Belov, 1982}. With respect to size, Ge is comparable with Al, but its electronegativity is equal to that of Si. The more covalent character of the Ge-O bond prevails and the value of α for NAG is comparable with those of 1:1 aluminosilicates and not with aluminate sodalites, as one would assume taking into account the ionic radii only.

This leads to the argument that Si-rich members of the aluminosilicate series have only a small possibility of reducing strain by opening α ; they must rather change φ in order to obtain favourable γ values. They have, therefore, generally higher values of φ than Al-rich members. Higher values of φ mean smaller cage ions and *vice versa*. Therefore, it seems plausible to assume that Si-rich sodalites containing cage ions whose sizes would imply very low or even zero values of φ are unlikely to exist. This argument is supported by an observation of Henderson & Taylor (1978). For aluminosilicate sodalites containing large anions like SO_4^{2-} or I^- , they observed kinks in the thermal-expansion curve, separating two temperature ranges of high and low thermal expansion, respectively. They proposed two possible causes, *viz* either the framework had reached its fully expanded state or the cage cations had reached the position $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$. They favoured the second explanation. We propose a third possibility, *viz* that a certain lower limit of φ , φ_{\min} , exists which depends only on the framework composition and which increases as the Si content increases. This lower limit of φ is thought to be given by the requirements of γ to have a maximal value, γ_{\max} , of about 150° . Equation (16) gives the relation between α , φ and γ and it is shown graphically in Fig. 4 with φ as a function of α and with γ as a parameter. Curves of constant γ are plotted and the data points for the different sodalites are shown with the same symbols as in Fig. 2. In fact, we observe that all sodalites (with the exception of TMA, whose particularities have been mentioned) plot on one side of a limiting zone (hatched) which is regarded as representing γ_{\max} and $\varphi_{\min} = f(\text{Si}/\text{Al})$. φ_{\min} increases with the Si content of the groups of aluminosilicate sodalites. These groups are indicated by their Si/Al ratio at the top of the vertical lines which give the

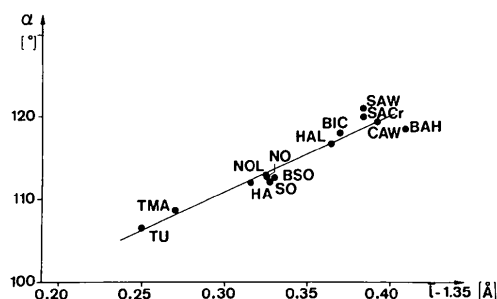


Fig. 3. The tetrahedron distortion angle α vs the observed bond length $T-O$ minus the effective ionic radius of O for the sodalites of the aluminosilicate series. The correlation coefficient of the linear-regression line is 0.965. Designations are explained in the legend of Fig. 2.

average values of α for all members of the respective group.

The sodalites which are not part of the aluminosilicate series can be explained using the same arguments as above. $\text{Na}_8[\text{Al}_6\text{Ge}_6\text{O}_{24}](\text{OH})_2$ (NAG; Belokoneva, Dem'yanets, Uvarova & Belov, 1982) and helvite (HE; Holloway, Giordano & Peacor, 1972) are very similar to 1:1 aluminosilicates, only in NAG Ge takes the role of Si and Be takes that of Al in HE. The B-O bond in $\text{Zn}_8[\text{B}_{12}\text{O}_{24}]\text{O}_2$ (ZBO; Smith-Verdier & García-Blanco, 1980) is even more covalent than the Si-O bond and a deformation of the tetrahedron angle is, therefore, even less probable.

A seemingly paradoxical behaviour has to be mentioned. Whereas for the *average* TO_4 tetrahedron in the series $[\text{Al}_{12-n}\text{Si}_n\text{O}_{24}]^{(12-n)-}$ the values describing the distortion (e.g. α) rise monotonically as n decreases, we find for *individual* TO_4 tetrahedra in ordered (1:1) aluminosilicate sodalites that the AlO_4 tetrahedron is always more regular than the SiO_4 tetrahedron. This concerns the species h aüyne (L ohn & Schulz, 1968), nosean (L ons, 1969), sodalite (L ons & Schulz, 1967) and basic sodalite (Hassan & Grundy, 1983). The straightforward explanation results from equation (22), because it indicates an inverse relationship between l' and α' (l and α) for α' and $\alpha > 90^\circ$. The fact that the AlO_4 tetrahedron can adopt high values of α in aluminate sodalites as well as small values in ordered aluminosilicate sodalites proves again the more ionic character of the Al-O bond. The conformation of the aluminosilicate sodalites is thus mainly determined by the SiO_4 tetrahedra, whereas the AlO_4 tetrahedra adapt themselves to the given

situation. For helvite (Holloway, Giordano & Peacor, 1972) and $\text{Na}_8[\text{Al}_6\text{Ge}_6\text{O}_{24}](\text{OH})_2$ (Belokoneva, Dem'yanets, Uvarova & Belov, 1982), which are also ordered sodalites, the differences in the radii of the two T cations are so small that the distortions of the two tetrahedra are not significantly different [cf. equation (22)].

The fact that the tetrahedron distortion in sodalites increases with the Al content has a parallel in at least two more all-Al analogues of aluminosilicate structures. The first is that of alkaline-earth aluminates with the stuffed tridymite structure (e.g. CaAl_2O_4 ; H orkner & M uller-Buschbaum, 1976); the second is pentacalcium trialuminate (Vincent & Jeffery, 1978) which is similar to gehlenite (Lounisnathan, 1970). Both contain all-corner Al-connected AlO_4 tetrahedra (the latter only one type out of four) and in both cases the tetrahedron distortion (which is no longer tetragonal, however) is significantly larger in the case of the Al analogues. Furthermore, the tetrahedra of the Al_6O_{18} rings in the structures of $\text{Ca}_{8.5}\text{NaAl}_6\text{O}_{18}$ (Nishi & Tak uchi, 1975) and of $\text{Ca}_3\text{Al}_2\text{O}_6$ (Mondal & Jeffery, 1975) show distortion parameters which are comparable to those of aluminate sodalites. In all these cases $\text{Si}/\text{Al} < 1.0$ and, consequently, at least some, if not all, AlO_4 tetrahedra are connected with other AlO_4 tetrahedra. They represent, therefore, examples of violations of Loewenstein's (1954) aluminium avoidance rule. The examples shown suggest that this rule should be completed by the statement that, if a structure cannot avoid to link AlO_4 tetrahedra with each other, it tends to reduce the imposed structural strain by increasing the edge-length distortion of the AlO_4 tetrahedra.

Other examples of the relation between framework composition and tetrahedron distortion are under study.

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Note added in proof: When this paper was in the press we were informed of another study which, almost simultaneously, dealt with a similar topic (Hassan & Grundy, 1984). It seems that the geometrical model proposed in that paper could advantageously be completed by our considerations. This would concern particularly the sodalites having a framework composition different from the 1:1 aluminosilicates.

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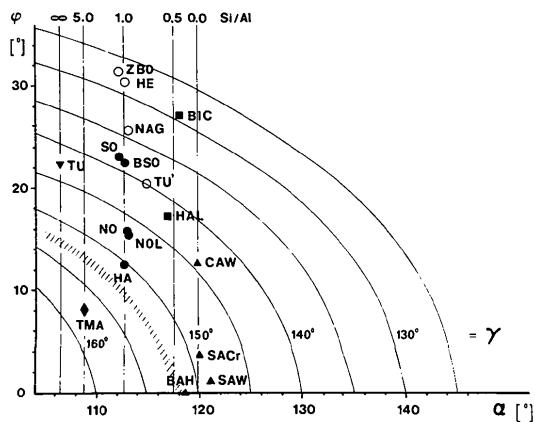


Fig. 4. The tilt angle φ vs the tetrahedron distortion angle α with curves of constant γ . Sodalites are plotted with the same point symbols and designations as in Fig. 2. Members of the aluminosilicate series are grouped together corresponding to their Si/Al ratio. This is given at the top of the vertical lines, which correspond to the average α values of that group. With the exception of TMA, all sodalites plot on one side of a hatched zone which is regarded as representing minimal values of φ . This is a function of the framework composition (or α) and is thought to be determined by a constant maximal value of γ .

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Crystallographic Studies of the Farringtonite-type Phases $\gamma\text{-Zn}_2\text{Co}(\text{PO}_4)_2$ and $\gamma\text{-(Zn}_{0.50}\text{Co}_{0.50})_3(\text{PO}_4)_2$

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Abstract

The two solid solutions $\gamma\text{-Zn}_2\text{Co}(\text{PO}_4)_2$ and $\gamma\text{-(Zn}_{0.50}\text{Co}_{0.50})_3(\text{PO}_4)_2$ have been prepared and equilibrated at 1070 K. The structures ($P2_1/n$, $Z=2$) are isomorphous with ' $\gamma\text{-Zn}_3(\text{PO}_4)_2$ ' and with the mineral *farringtonite*, $(\text{Mg, Fe, Mn, Ca})_3(\text{PO}_4)_2$, with $M_r = 379.61$, $a = 7.536$ (1), $b = 8.413$ (1), $c = 5.049$ (1) Å, $\beta = 94.74$ (1)°, $V = 319.0$ (1) Å³, $D_x = 3.952$ Mg m⁻³, and $M_r = 376.40$, $a = 7.545$ (2), $b = 8.406$ (2), $c = 5.054$ (2) Å, $\beta = 94.56$ (2)°, $V = 319.4$ (2) Å³, $D_x = 3.914$ Mg m⁻³, respectively. The crystal structures have been refined on the basis of neutron powder diffraction data ($\lambda = 1.55$ Å, $T = 295$ K) with the Rietveld full-profile refinement technique, to $R_p = 0.078$ and 0.066 ($R_f = 0.052$ and 0.036). The metal cations are strongly ordered, with Zn^{2+} dominating at the five- and Co^{2+} at the six-coordinated sites; $K_D(\text{Zn, Co}) \approx 9$. The MO_5 polyhedra are distorted trigonal bipyramids, while the MO_6 octahedra are almost regular. Some thermodynamical calculations are included. The JCPDS Diffraction File No. for $\gamma\text{-Zn}_2\text{Co}(\text{PO}_4)_2$ is 34-1491.

Introduction

As part of a project concerning the crystal chemistry of metal phosphates (*cf.* Nord & Kierkegaard, 1980), investigations with the aim of determining cation distributions between five- and six-coordinated sites have been undertaken. Many suitable reference structures are found among divalent-metal phosphate minerals, such as the *farringtonite*, $(\text{Mg, Fe, Mn, Ca})_3(\text{PO}_4)_2$, structure, isomorphous with ' $\gamma\text{-Zn}_3(\text{PO}_4)_2$ ' (Calvo, 1963), and the *graftonite*, $(\text{Fe, Mn, Ca})_3(\text{PO}_4)_2$, structure (Calvo, 1968; Kostiner & Rea, 1974).

Numerous farringtonite-type $\gamma\text{-(Zn}_{1-x}\text{M}_x)_3(\text{PO}_4)_2$ solid solutions may be prepared (Sarver, Katnack & Hummel, 1959; Brown & Hummel, 1963; Nord & Stefanidis, 1981), and some cation distribution studies have now been completed constituting the first systematic study of partitioning among five- and six-coordinated sites for M^{2+} ions. Various techniques have been used, such as X-ray diffraction (*e.g.* Nord, 1977), ⁵⁷Fe Mössbauer spectroscopy (Annersten, Ericsson & Nord, 1980), or Rietveld (1969) refinements