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Crystal Structure and Infrared Spectrum of the Cyclosilicate $Ca_2ZrSi_4O_{12}$

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The $CaO–ZrO_2–SiO_2$ phase diagram has been the subject of several investigations; two publications have pointed out the existence of $Ca_2ZrSi_4O_{12}$ whereas two other publications deny its existence. This compound has been obtained by the conventional ceramic technique at 1400°C. The cell is monoclinic, space group $P2_1/m$, with $a = 7.399(1)$, $b = 13.651(2)$, $c = 5.312(1)$ Å and $\beta = 108°9(20)$, $Z = 2$. Its structure has been determined from 880 single-crystal data and refined to $R = 0.016$ with 94 parameters; it is based on rings of Si_4O_{12} with four corner-sharing tetrahedra belonging to the type A classification of T. Zoltai and M. J. Buerger (*Z. Kristallogr.* **114**, 1–8, 1960); these rings are interconnected by ZrO_6 octahedra, outlining tunnels parallel to the c axis; calcium ions fill the 8- and 9-coordinated interstices. The low-point symmetry of the Si_4O_{12} rings precludes any detailed interpretation of the infrared spectrum, which, however, may be compared to other cyclotetrasilicate spectra, and is tentatively subdivided into groups of lines belonging to a given type of vibration.

Introduction

$Ca_2ZrSi_4O_{12}$ has been pointed out by Kordyuk and Gulko (*1*) who proceeded to triangulation of the $CaO–SiO_2–ZrO_2$ phase diagram between 1200°C and melting. They obtained this compound by heating appropriate mixtures of the binary oxides at 1400°C, for 15 hr, with an intermediate grinding. They report incongruent melting of $Ca_2ZrSi_4O_{12}$ at 1430°C into $ZrSiO_4$ and liquid. They also provide unindexed X-ray powder data (1973) along with the density (3.06) and the thermal expansion coefficient. It is worth mentioning that a tentative melting diagram has been published by Matsumoto *et al.* (*2*) from electrofused samples, but the nature of that study was such that ternary compounds would have been missed. Surprisingly, the investigation of the $CaO–ZrO_2–SiO_2$ system by Qureshi and Brett (*3*) did not find $Ca_2ZrSi_4O_{12}$; these authors claim that the presence of $ZrSiO_4$ as a primary phase in the region $SiO_2–CaSiO_3–ZrO_2$ precludes the existence of $Ca_2ZrSi_4O_{12}$. Again in their extended work on the $CaO–MgO–ZrO_2–SiO_2$ system, Sircar *et al.* (*4*) found no evidence for $Ca_2ZrSi_4O_{12}$. However, a more recent reinvestigation of the system $CaO–ZrO_2–SiO_2$ by Vetsuki *et al.* (*5*) confirms the existence of $Ca_2ZrSi_4O_{12}$ at 1400°C, and leads to the phase diagram in Fig. 1.

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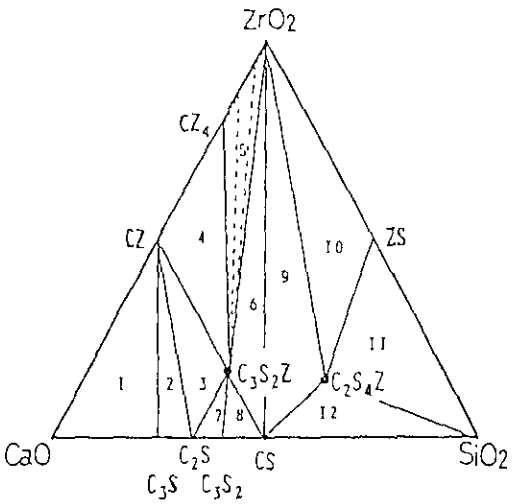

FIG. 1. $CaO–ZrO_2–SiO_2$ phase diagram.

In view of these discrepancies, a new investigation was needed. Moreover, in the course of a study of the decalcification of calcia-stabilized zirconia by silica, we obtained a complex mixture, which, in addition to silica and $CaSiO_3$, contains a phase the composition and X-ray diffraction data of which fairly agree with the data of Kordyuk and Guiko (*1*) for $Ca_2ZrSi_4O_{12}$; however, to determine the exact X-ray powder diffraction pattern and better ascertain the composition, it was desirable to establish the crystal structure.

Experimental

To prepare $Ca_2ZrSi_4O_{12}$, we mixed, in stoichiometric proportions, zirconia, silica, and calcium carbonate. This mixture is pressed under the form of a small stick and is heated in air at 1400°C. It is heated for several days and regularly grinded. After this treatment we observed small white $Ca_2ZrSi_4O_{12}$ crystals and a phase between these crystals which seems to be a glassy phase containing Si, Zr, and Ca.

A crystal was studied by conventional X-ray techniques (oscillating crystal and Weissenberg camera). A monoclinic unit cell was found with the only condition limiting possible reflections: $0kl$ with $k = 2n$. This leads to two possible space groups $P2$ and $P2_1/m$. The cell parameters were determined by least-squares refinement of the 20 values of 25 independent reflections measured on the diffractometer: $a = 7.3990(1)$ Å, $b = 13.651(2)$ Å, $c = 5.3120(1)$ Å, $\beta = 108°9(20)$.

Structure

A nearly spherical single crystal (diameter $\sim 200\ \mu m$) was mounted on a Nonius CAD4 automatic diffractometer. The conditions for the collection of the single-crystal data and the refinement of the structure are listed in Table I. Absorption was neglected ($\mu m \sim$

TABLE I

SUMMARY OF DATA COLLECTION AND STRUCTURE REFINEMENT

Molar mass	477
Crystal size (μm)	ϕ 200
Symmetry	Monoclinic
a (Å)	7.399(1)
b (Å)	13.651(2)
c (Å)	5.312(1)
β (°)	108.9(20)
V (Å^3)	507.6
Z	2
ρ_{cal}	3.11
Space group	$P2_1/m$
Radiation	Mo$K\alpha$
Monochromator	Graphite
Scanning	$\theta, 2\theta$
Takeoff	1.7
Record limits	$\theta \leq 21$
Linear absorption coefficient μ (cm^{-1})	25
Recorded intensities	1357
Recorded intensities with $\sigma(I)/I < 0.33$	880
$F(000)$	440
Number of parameters	94
Final R value	0.016
Final R_w value	0.018
$\omega = 0.4372/(\sigma^2(F_0) + g(F_0)^2)$	$g = 0.000619$

TABLE II

ATOMIC AND THERMAL PARAMETERS ($\times 10^4$) ($Tj = \exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*))$

Atoms	Position	Symmetry	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zr	2(*a*)	1	0	0	0	41(1)[a]	39(2)	38(1)	6(1)	12(1)	5(1)
Ca(1)	2(*b*)	1	5000	0	0	101(3)	72(4)	68(3)	9(3)	22(2)	13(3)
Ca(2)	2(*c*)	*m*	1857(1)	2500	8359(2)	84(3)	84(4)	73(4)	0	20(3)	0
Si(1)	4(*f*)	1	3845(1)	1396(1)	4315(1)	50(3)	52(3)	44(3)	−5(3)	13(2)	−3(3)
Si(2)	4(*f*)	1	8176(1)	1374(1)	4330(1)	50(3)	50(4)	55(3)	−9(3)	16(3)	1(3)
O(1)	4(*f*)	1	9538(3)	1181(1)	7316(4)	71(8)	81(10)	83(9)	10(7)	2(7)	−18(7)
O(2)	2(*e*)	*m*	6864(4)	7500	6923(5)	136(14)	63(14)	60(13)	0	1(10)	0
O(3)	4(*f*)	1	1567(3)	5678(1)	7944(4)	117(9)	78(10)	95(9)	21(8)	54(7)	−5(8)
O(4)	4(*f*)	1	7446(3)	5656(2)	7889(4)	100(9)	103(11)	94(9)	44(8)	21(7)	32(7)
O(5)	2(*e*)	*m*	8632(4)	2500	3728(6)	182(14)	75(15)	113(14)	0	53(11)	0
O(6)	4(*f*)	1	3780(3)	1323(1)	7239(4)	118(9)	87(10)	71(9)	15(8)	41(7)	17(8)
O(7)	4(*f*)	1	5943(3)	1231(2)	4028(4)	64(9)	216(12)	115(10)	−32(9)	23(7)	−2(8)

[a] Estimated standard deviations are given in parentheses.

TABLE III

INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Zr(1)	2 × O(3)	2.053(2)	Ca(2)	2 × O(6)			2.347(2)
CN = 6	2 × O(4)	2.064(2)	CN = 9	O(2)			2.375(3)
	2 × O(1)	2.105(2)		2 × O(1)			2.424(2)
				O(5)			2.818(3)
				2 × O(4)			3.147(2)
				O(2)			3.238(3)
Ca(1)	2 × O(6)	2.317(2)	Si(1)	O(2)		Si(1)	130.4(2)
CN = 8	2 × O(4)	2.579(2)	Si(2)	O(5)		Si(2)	141.6(2)
	2 × O(3)	2.589(2)	Si(2)	O(7)		Si(1)	161.7(1)
	2 × O(7)	2.631(2)					
Si(1)	O(6)	1.572(2)	O(6)	Si(1)		O(4)	118.6(1)
	O(4)	1.606(2)	O(6)	Si(1)		O(7)	114.8(1)
	O(7)	1.623(2)	O(6)	Si(1)		O(2)	110.0(1)
	O(2)	1.660(1)	O(4)	Si(1)		O(7)	101.8(1)
			O(4)	Si(1)		O(2)	104.2(1)
			O(7)	Si(1)		O(2)	106.1(1)
Si(2)	O(3)	1.596(2)	O(3)	Si(2)		O(1)	117.4(1)
	O(1)	1.602(2)	O(3)	Si(2)		O(7)	102.8(1)
	O(7)	1.620(2)	O(3)	Si(2)		O(5)	109.3(1)
	O(5)	1.627(1)	O(1)	Si(2)		O(7)	111.9(1)
			O(1)	Si(2)		O(5)	104.2(1)
			O(7)	Si(2)		O(5)	111.4(1)

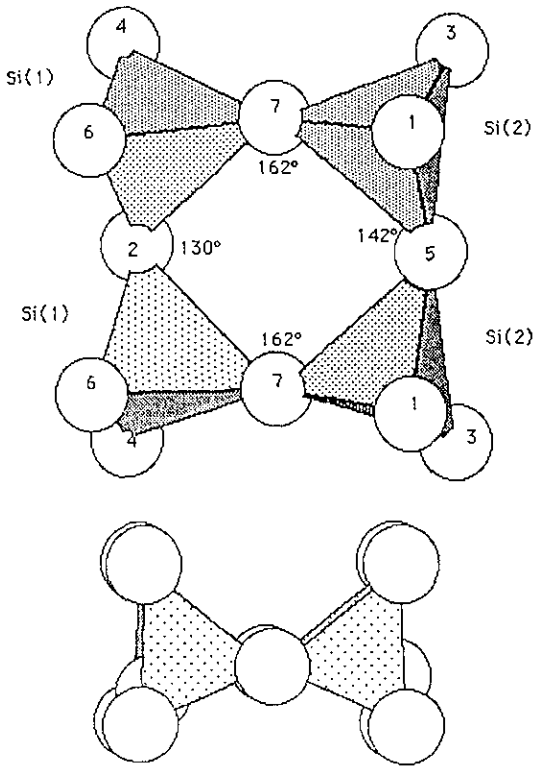

FIG. 2. (Top) Arrangement of the four-tetrahedra rings. (Bottom) Profile view of the arrangement of the four-tetrahedra rings.

0.25). Atomic scattering factors for Zr^{4+}, Ca^{2+}, Si^{4+}, and O^- and anomalous dispersion correction where taken from Ibers and Hamilton (*6*). All computer programs used were taken from Sheldricks (*7*). A list of the structure factors can be obtained from the authors on request.

The structure refined satisfactorily in the centrosymmetric space group $P2_1/m$. Zirconium and calcium atom positions were obtained using the direct method procedure of the Shelx 76 program. Silicon and oxygen atoms positions were determined, step by step, by difference Fourier synthesis. Final refinement with individual and anisotropic temperature factors leads to the residual factor $R = 0.016$ ($R_w = 0.018$). The atomic and thermal parameters are listed in Table II, and the main interatomic distances and angles (*8*) are given in Table III.

Discussion

The Structure

$Ca_2ZrSi_4O_{12}$ belongs to the cyclosilicate class, with isolated rings of four tetrahedra, connected by ZrO_6 octahedra (Figs. 2 and 3). The sharing coefficient (SC), as proposed by Zoltai (*9*), is

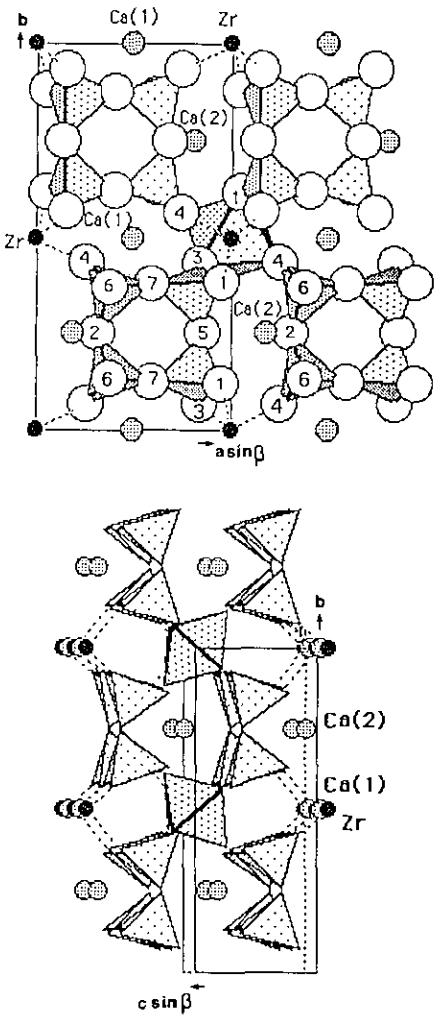

FIG. 3. Overall structure: (top) tunnels inside the Si_4O_{12} rings parallel to the c axis and interstices filled by calcium (projection along the c axis); (bottom) connection of the rings by the ZrO_6 octahedra and interstices filled by calcium (projection along a direction at ~5° of the a axis).

TABLE IV

CALCULATED BOND STRENGTHS

Ca(1)	1.86	O(1)	1.97
Ca(2)	1.84	O(2)	2.15
Si(1)	4.11	O(3)	1.98
Si(2)	4.16	O(4)	1.93
Zr	4.05	O(5)	1.98
		O(6)	1.89
		O(7)	2.01

$$SC = 2n + 1 - (n^2 + n)A/4T = 1.5$$

where n = integer of $4T/A$ (*9*), T = tetrahedrally coordinated cation subscript (*3*), and A = anion subscript (*10*). This value of the sharing coefficient is in the range 1.25–1.5 expected for large isolated groups of tetrahedra.

The geometry of the four-tetrahedron rings may be compared to the four typical arrangements depicted by Zoltai and Buerger (*9*). The present ring arrangement, shown in Fig. 2, is close to type A of Zoltai and Buerger, despite the lack of a four-order rotation axis and a horizontal mirror; it is actually a pseudo-type A, because it would be sufficient to slightly move the oxygen atoms [especially O(2) upward] to recover these symmetry elements.

With respect to the stability of these four-tetrahedron rings, Zoltai and Buerger (*9*) have calculated the sum of the interionic potential energies, from elementary coulombic interactions, for the different tetrahedral ring arrangements, plotted as a function of n (number of ring members). They found for loop A (with full symmetry n/m) that the minimum energy occurs for $n = 5$, and this does not change much with the loss of symmetry elements. Accordingly the present four-tetrahedron arrangement, which is not far from the minimum, should be rather stable, which is an agreement with its melting temperature.

There is little to say about the six-coordination of zirconium, which is rather com-

TABLE V

CALCULATED DISTANCES AND INTENSITIES FOR $Ca_2ZrSi_4O_{12}$

khl			*D*(Å)	$I_{calc.}$
1	0	0	7.000	119
0	2	0	6.825	394
1	1	0	6.228	98
1	0	−1	4.903	51
1	2	0	4.886	112
0	1	−1	4.716	27
1	1	−1	4.615	251
0	2	1	4.046	888
1	2	−1	3.982	207
1	3	0	3.815	89
1	0	1	3.571	286
2	0	0	3.500	31
2	0	−1	3.442	59
2	1	0	3.390	258
0	3	1	3.373	87
2	1	−1	3.337	302
2	2	0	3.114	411
2	2	−1	3.073	460.1
1	4	0	3.067	184.1
0	4	1	2.823	1000.0
2	3	0	2.774	121.7
2	3	−1	2.745	64.8
1	1	−2	2.605	45.4
1	5	0	2.543	33.7
2	0	1	2.515	159.9
0	0	2	2.512	22.0
1	2	−2	2.473	47.2
2	1	1	2.473	29.8
0	1	2	2.471	147.6
2	0	−2	2.451	119.9
2	4	0	2.443	62.2
2	2	1	2.360	74.0
0	2	2	2.358	108.1
2	2	−2	2.307	104.4
3	2	0	2.207	32.2
2	3	1	2.201	44.4
2	3	−2	2.158	41.9
2	5	0	2.152	46.9
3	3	−1	2.150	34.0
0	6	1	2.072	23.2
1	6	−1	2.063	25.7
2	4	1	2.024	157.9
0	4	2	2.023	34.8
2	4	−2	1.991	121.3
2	6	0	1.907	145.9
2	6	−1	1.898	193.0
3	3	−2	1.890	23.0
4	0	−1	1.849	239.5
3	2	1	1.825	25.8
1	4	2	1.821	65.7
1	7	−1	1.812	21.9

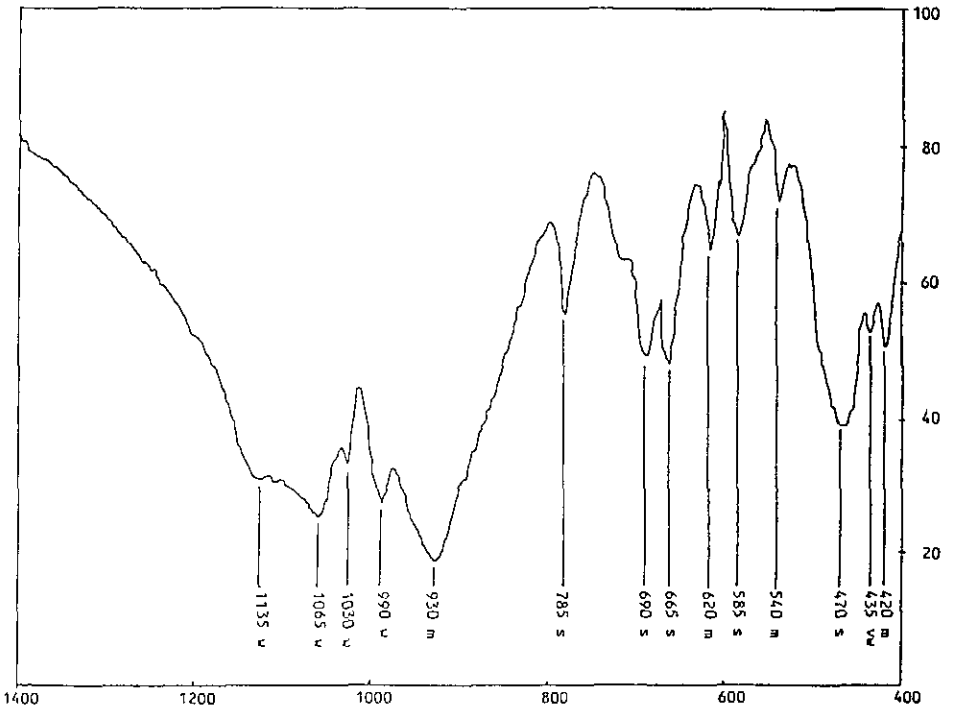

FIG. 4. Infrared spectrum of $Ca_2ZrSi_4O_{12}$.

mon, as for instance in the perovskite $CaZrO_3$ (*11*). The overall structure is depicted in Fig. 3; the framework, based on SiO_4 and ZrO_6 polyhedra, includes six-ring channels, running along the *a* and *c* axes, populated by Ca^{2+}, where it has 8- and 9-coordination (Table III).

Bond strengths have been calculated using the Brown and Altermatt data (*12*). The results are displayed in Table IV; there is rough agreement with the expected values, within a $\pm 10\%$ uncertainty range.

At last it is worth noting that the tunnels, inside the Si_4O_{12} rings, have inner dimensions that would allow intercalation and diffusion of small ions or molecules, whereas the six-ring channels are occupied by Ca.

On the other hand, in view of its interest in the field of phase diagram research, the calculated powder diagram is also given in Table V.

The Infrared Spectrum

The infrared spectrum is presented in Fig. 4. Full assignment of the observed lines is difficult, because the Si_4O_{12} ring has a low-point symmetry; however, we can try to distinguish several groups of lines which may be separated and ascribed to a given type of vibration.

We have presented, in Fig. 5, several experimental or calculated infrared data. We can start with the four infrared active vibrations of isolated SiO_4 tetrahedra, with the values calculated by Saksena *et al.* (*10*) and later by Griffith (*13*). They may be divided into two groups at frequencies lower than 600 cm^{-1} (ν_2, ν_3) and higher than ~800 cm^{-1} (ν_1, ν_3); accordingly there is a gap, from 600 to 800 cm^{-1} where other vibrations (non tetrahedral cations) occur.

But the polymerization of SiO_4 groups has important effects. The degeneracy of ν_2, ν_3,

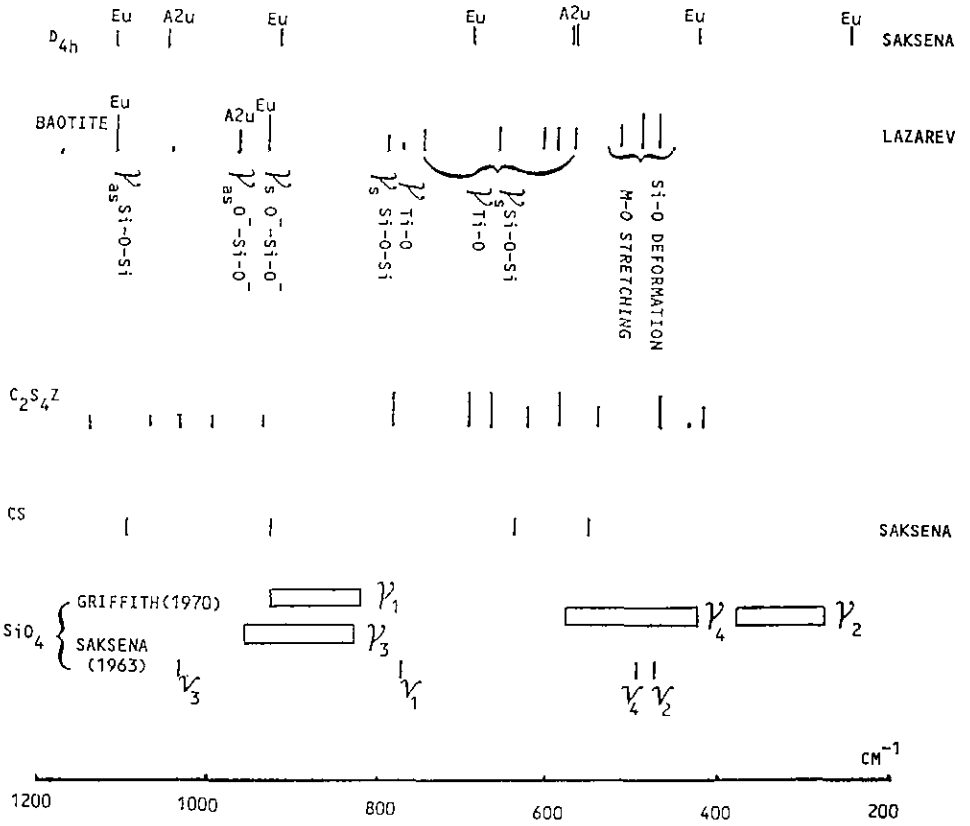

FIG. 5. Experimental or calculated infrared data.

and ν_4 is lifted, and there are now different force constants for the Si–O (bridging) and Si–O (terminal) bonds; second, a new type of band attributable to deformation of the Si–O–Si linkage appears in the region 550–750 cm^{-1}, at a position that depends on the Si–O–Si angle, and we recall here that there are three different such angles (cf. Table III) from 130° to 141° and 162°. In practice (*14*), Si–O_t stretching bands appear in the region 950–1200 cm^{-1}, and Si–O–Si bending bands between 550 and 750 cm^{-1}, on the high- and low-frequency sides of the orthosilicate bands at 800 and 950 cm^{-1}; it must be noted that polymerization to form ring anions, such as Si_4O_{12}, has an effect similar to that of chain formation (*14*).

Beyond these general considerations, Saksena *et al.* (*10*) made an additional step by calculating the infrared spectrum of an Si_4O_{12} ring with the highest symmetry D_{4h} (*10*), as shown in Fig. 5. They used the force constants

$$K(\text{Si–O}_t) = 5 \times 10^5$$

$$K_1(\text{Si–O}_b) = 4 \times 10^5$$

$$K_2'(\text{Si–O–Si}) = 0.7 \times 10^5 \text{ dyn/cm}.$$

In D_{4h} symmetry, there are nine infrared active vibrations, six belonging to the E_u and three to the A_{2u} representations. They conclude that cyclosilicates possess a distinctive band in the range 800–900 cm^{-1}.

These results may be compared to the experimental spectrum of baotite, given by Lazarev (*15*), which is a cyclotetrasilicate $Ba_4Ti_6ClO_{16}(Si_4O_{12})$. There is partial agreement with the calculated spectra: it

may be separated into three regions, as proposed above, and this conclusion may be extended to $Ca_2ZrSi_4O_{12}$, where clearly there is a group of five lines at or above 900 cm^{-1}, which may be ascribed to the Si–O_t stretching vibrations, and one strong line at 785 cm^{-1}, which could be ascribed to the Si–O–Si bending band. The low-frequency region at and below 700 cm^{-1} is highly complex; encompasses the Si–O_b, Zr–O, and Ca–O bands; and is difficult to unravel.

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