

Refinement of the crystal structure of ramsayite (lorenzenite)

MARKKU R. SUNDBERG

Department of Inorganic Chemistry, University of Helsinki, Vuorikatu 20, SF-00100 Helsinki 10, Finland

MARTTI LEHTINEN

Department of Geology, University of Helsinki, Snellmaninkatu 5, SF-00170 Helsinki 17, Finland

RAIKKO KIVEKÄS

Department of Inorganic Chemistry, University of Helsinki, Vuorikatu 20, SF-00100 Helsinki 10, Finland

ABSTRACT

The lattice parameters and crystal structure of ramsayite, $\text{Na}_2\text{Ti}_2\text{Si}_2\text{O}_9$, have been re-determined from a specimen from the Kola Peninsula. The space group is *Pbcn* with $Z = 4$; $a = 8.7128(10)$, $b = 5.2327(5)$, and $c = 14.487(2)$ Å. The anisotropic refinement of the data using 778 reflections produced an R value of 0.026. The coordination polyhedron around Ti is a markedly distorted octahedron with no center of symmetry. Around Na there are seven oxygen atoms (Na–O distances in the range 2.307–2.602 Å); these polyhedra form dimers by sharing three oxygens. The SiO_4 tetrahedra form pyroxene-type chains in the direction of the *b* axis by sharing two oxygens with the neighboring tetrahedra. The two remaining oxygens are shared by two Ti atoms. Two vicinal TiO_6 polyhedra also share two oxygens (common edge), and the third facial oxygen is shared with the third TiO_6 polyhedron. These pairs of polyhedra lie approximately parallel to the *a-b* and *a-c* planes, respectively.

INTRODUCTION

The two mineral names ramsayite and lorenzenite refer to the same species (Kraus and Mussgnug, 1941; Sahama, 1947; Bøggild, 1953). Lorenzenite was found on an expedition to southern Greenland in 1897 (Flink, 1901), occurring in a nepheline syenite. Chemical analysis showed that it contained 11.92% ZrO_2 . Later on, in 1922, A. E. Fersman's expedition found a related mineral in the nepheline syenite of the Kola Peninsula. No Zr was found in this species (Kostyleva, 1937). Because there are very marked similarities in the crystal forms as well as in the chemical composition of the two minerals, their chemical composition was redetermined by Sahama (1947). He found less than 0.2% ZrO_2 in both minerals; moreover, ramsayite and lorenzenite specimens showed similar compositions. Because there is a wide variation in the parameters reported for the unit cell (Table 1) and because the R value (0.128) of an earlier X-ray study of ramsayite was rather poor (Ch'in-Hang et al., 1969), we undertook redeterminations of both unit-cell parameters and the crystal structure.

Besides a variation in cell parameters, there is also variation in the reported space groups (Table 1). In particular, Shurtz (1955) showed that the space group obtained by Kraus and Mussgnug is wrong. Moreover, the quality of indexing on the JCPDS card 18-1262 does not seem to be satisfactory. About half the reflections are unindexed, and the number of the space group on the card should be 60 rather than 50.

EXPERIMENTAL DETAILS

The material used for study was from the collections of the Mineralogical Museum, University of Helsinki. According to the original Russian label, the specimen (no. 4937) was collected in 1922 by the A. E. Fersman expedition and originates from the Lujavr-Urt (=Lovozero) alkali massif. Ramsayite from the same specimen was chemically analyzed by Sahama (1947).

The specimen is a coarse-grained nepheline syenite (lujavrite) and has, in addition to greenish nepheline and microcline, reddish-brown eudialite and dark brown ramsayite as its major components. The most common accessory mineral is aegirine (acmite). The subhedral ramsayite and eudialite crystals range up to 3 cm in diameter. The reader is referred to Kostyleva (1937) and Vlasov et al. (1966) for thorough descriptions of the properties of the Lovozero ramsayite.

The powder-diffraction data of Lovozero ramsayite were recorded and treated as described in detail by Lehtinen (1974). In this connection, it may be mentioned that the diffractogram of lorenzenite powder (Sahama, 1947) from Narsarsuk (Narsarsuk), Greenland, is virtually identical with that of the Lovozero ramsayite. The observed and calculated d values are given in Table 2.¹

The single-crystal study was performed with a Nicolet P3 four-circle diffractometer. The unit-cell parameters were obtained from 18 independent high-angle reflections by using least-squares methods. The details of the intensity measurements are given in Table 3. During data collection, one standard reflection was

¹ To receive copies of Tables 2 and 4, order Document AM-87-325 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Washington, D.C. 20006. Please remit \$5.00 in advance for the microfiche.

Table 1. Lattice parameters and space groups reported for ramsayite (lorenzenite)

<i>a</i>	<i>b</i>	<i>c</i>	S.g.	Ref.
14.51	8.73	5.22	<i>Pbcn</i>	Kraus and Mussnug (1941) ^a
14.51	8.76	5.23	<i>Pbcn</i>	Kraus and Mussnug (1941) ^b
14.26	8.57	5.09	<i>Pnca</i>	Belov and Belyaev (1949)
8.66	5.18	14.42	<i>Pbcn</i>	Shurtz (1955) ^c
14.518(3)	8.976(3)	5.081(5)	<i>Pnca</i>	Ch'in-Hang et al. (1969)
14.52	8.98	5.09	<i>Pnca</i>	Povarennykh (1972)
8.66	14.42	5.18	<i>Pcnb</i>	Roberts et al. (1974)
14.54	8.75	5.23	<i>Pnca</i>	JCPDS, card 18-1262 (1980)
8.707(3)	5.234(4)	14.492(3)	<i>Pbcn</i>	This work ^d
8.7128(10)	5.2327(5)	14.487(2)	<i>Pbcn</i>	This work ^e

^a Ramsayite; ^b lorenzenite; ^c synthetic lorenzenite; ^d powder-diffraction method; ^e single-crystal method.

measured after every 39 reflections. The intensities of the former showed only statistical variation. The data were corrected for Lorentz-polarization effects and also for absorption, since the ψ scans showed significant variation. The refinement of the structure was carried out using the X-RAY 76 program (Stewart, 1976) and a Univac 1108 computer. The atomic coordinates reported earlier (Ch'in-Hang et al., 1969) were transformed to space group *Pbcn* and then used as the starting parameters. After anisotropic refinement, the final *R* value was 0.026 and *R_w* was 0.035 (1/ σ^2 weights). Anomalous dispersion corrections for Ti, Na, and Si were obtained from Ibers and Hamilton (1974). The observed and calculated structure factors are given in Table 4 (see footnote 1).

RESULTS AND DISCUSSION

Lattice parameters

The lattice parameters obtained are shown in Table 1 together with values reported earlier. The precision of the parameters from the literature was, in most cases, difficult to evaluate because no standard deviations were given. However, the lattice parameters reported by Ch'in-Hang et al. (1969) deviate significantly from our values. It seems probable that the poor *R* value they obtained is due to inaccurate lattice parameters and the film method they used.

Outline of the structure

The outline of the structure obtained in this study is similar to that reported earlier (Ch'in-Hang et al., 1969).

Table 3. Crystal, intensity collection, and refinement data

Formula	Na ₂ Ti ₂ Si ₂ O ₉
Formula weight	341.95
<i>F</i> (000)	664
<i>Z</i>	4
Density (g·cm ⁻³)	
Observed	3.45(5)
Calculated	3.44
Space group	<i>Pbcn</i> (<i>D</i> _{2h} ¹⁴)
Crystal dimensions (mm)	0.11 × 0.13 × 0.20
Radiation	MoK α (λ = 0.71069 Å)
2 θ limits	5° < 2 θ < 60°
Scan rate	0.9° to 29.3°/min
Abs. coefficient (cm ⁻¹)	30.3
Number of independent reflections measured	1167
Unique data used [<i>F</i> _o \geq 6 σ (<i>F</i> _o)]	778

There is, however, one exception: The first coordinate of our O3 is 0.3336, whereas the corresponding earlier value is 0.431. The present refined atomic coordinates and temperature factors are shown in Table 5. The structure (Fig. 1) consists of pyroxene-type [Si₂O₆]_∞ chains running approximately in the direction of the *b* axis and having O5 as the bridging oxygen atom. O4 of the silicate chain is bonded to one Ti only, whereas O3 of the chain connects two neighboring Ti atoms. The TiO₆ octahedra lie in two adjacent layers, alternating in each layer with chains of NaO₇ polyhedra. This arrangement generates a close-packing system of unique type (the ramsayite type). The bond lengths and angles are shown in Table 6.

TiO₆ polyhedron

The TiO₆ polyhedron is a considerably distorted octahedron, with six nonequivalent Ti–O bond lengths (in the range 1.820 to 2.181 Å) and with Ti lying off-center. Although one of the coordinates for O3 differs significantly from the value reported by Ch'in-Hang et al. (1969), the average of the bond lengths (1.99 Å) is identical to the corresponding average of the earlier determination. The average value falls halfway between the two values corresponding to the Ti⁴⁺–O and Ti³⁺–O bond lengths, calculated from the sum of the effective ionic radii, 1.96 and 2.02 Å, respectively (Shannon, 1976). However, it seems that even when Ti has the oxidation number +4, there is considerable variation in the bond lengths. In Ba₆Ti₁₇O₄₀, among 11 TiO₆ polyhedra, the Ti–O distances tend to have greater values when Ti does not lie at the center of symmetry (Hofmeister and Tillmanns, 1984). Moreover, the chemical analysis (Sahama, 1947) leads us to assume that the valence state of Ti is Ti⁴⁺.

The off-center distortion is well known in the polymorphs of TiO₂, where variations in temperature and pressure produce significant changes both in symmetry around Ti(IV) and in the bonding parameters (Simons and Dachille, 1967; Horn et al., 1972; Meagher and Lager, 1979). It has been proposed that the ferroelectricity and the accompanying distortion of the TiO₆ coordination polyhedron in perovskite-type crystals may have their origin in a second-order Jahn-Teller effect (Bersuker, 1966).

In one direction the TiO₆ pseudo-octahedra form a di-

Table 5. The atomic coordinates and temperature factors ($\times 100$) for ramsayite with their standard deviations

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti	0.1513(1)	0.1322(1)	0.3309(1)	0.32(2)	0.33(2)	0.65(2)	0.013(12)	0.023(13)	0.061(12)
Na	0.0643(1)	0.6450(2)	0.1537(1)	1.31(5)	1.23(5)	1.42(5)	0.38(4)	0.11(4)	-0.01(4)
Si	0.3421(1)	0.2961(1)	0.5267(1)	0.49(3)	0.41(3)	0.76(3)	-0.02(2)	-0.04(2)	0.01(2)
O1	0.0000	0.0060(5)	0.2500	0.84(11)	0.69(9)	1.03(10)	0	-0.24(9)	0
O2	0.1817(2)	0.4407(3)	0.2758(1)	0.79(8)	0.76(7)	0.97(7)	-0.17(5)	-0.23(6)	0.13(6)
O3	0.3336(2)	0.2967(3)	0.4152(1)	0.67(8)	0.69(7)	0.78(7)	-0.07(5)	-0.05(6)	0.09(6)
O4	0.0089(2)	0.2428(3)	0.4280(1)	0.58(8)	0.94(7)	1.30(8)	-0.06(5)	0.23(6)	-0.01(6)
O5	0.2357(2)	0.0598(3)	0.5670(1)	0.77(8)	0.54(7)	0.99(7)	-0.23(5)	0.10(6)	0.03(6)

Note: The temperature factors are of the form $\exp[-2\pi^2(h^2a^2U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$.

meric unit by sharing O1, which is a nonsilicate oxygen. In a second direction there is a four-membered unit, but here two oxygens, O2 and O3, are shared. The other non-silicate oxygen, O2, also has the shortest bond to Na⁺. These four-membered rings form polymeric chains running parallel to the [Si₂O₆]_∞ chains. In a third direction there is a unit consisting of an eight-membered ring, Ti^b-O3-Si-O4^g-Ti^g-O3ⁱ-Si-O4^h. (The superscripts refer to the symmetry operators given in Table 6 and Fig. 1.)

Surroundings of the Na ion

There are seven oxygen atoms around Na in the range of 2.306 to 2.604 Å. The polyhedra form dimers by sharing O1, O2, and O2* (Fig. 2). The shortest distance between two Na ions is 3.008 Å. The coordination number seven is rather uncommon; a similar coordination polyhedron is found in Na₄Ti₅O₁₂, but in that compound the Na polyhedra form infinite linear chains, and the shortest Na-Na distance in the chain is 3.443 Å (Werthmann and Hoppe, 1984).

In pyroxenes the usual coordination number for Na is eight, with six shorter and two longer Na-O distances. The average values are 2.414 Å for the former and 2.514 Å for the latter (Clark et al., 1969), whereas the average

value in ramsayite (2.43 Å) lies in between. It is also near the sum of the effective ionic radii of Na and O, which is 2.47 Å (Shannon, 1976).

It is difficult to describe the coordination polyhedron. We may say that it is a capped, distorted trigonal prism or a capped, distorted trigonal antiprism, or even a capped, distorted octahedron (Fig. 2).

The SiO₄ tetrahedra

The lengths of the bridging bonds in the pyroxene-type [Si₂O₆]_∞ chain are clearly longer than the other two bonds (Table 6). The nonequivalence of the Si-O bond lengths is consistent with Cruickshank's (1961) model for *d-p* π-bond formation in silicates, i.e., the Si-O bonds to non-bridging oxygens (higher π-bond order) are shorter than those to the bridging oxygens (lower π-bond order). The angle O3-Si-O4^g (116.82° e.s.d. 0.11°) deviates approximately 7° from the ideal value in a tetrahedron, which is 109.47°. This must be considered a highly significant deviation in light of the standard deviation. This anomaly is also seen in the silicate chains of pyroxenes, where the angle has been found to be in the range 115.1 to 118.3° (Clark et al., 1969; Morimoto and Güven, 1970).

Table 6. The bond lengths (Å) and angles (°) with their standard deviations

TiO ₆ polyhedron							
Ti-O1	1.884(1)	O1-Ti-O2	98.0(1)	O2-Ti-O4	98.33(8)	O4-Ti-O2*	157.30(9)
-O2	1.820(2)	O1-Ti-O3	175.33(9)	O2-Ti-O2 ^a	99.71(9)	O4-Ti-O3*	82.68(8)
-O3	2.181(2)	O1-Ti-O4	95.96(7)	O2-Ti-O3 ^a	165.39(9)	O2 ^a -Ti-O3*	76.41(7)
-O4	1.968(2)	O1-Ti-O2 ^a	95.04(8)	O3-Ti-O4	86.89(8)		
-O2 ^a	1.939(2)	O1-Ti-O3 ^a	96.34(9)	O3-Ti-O2 ^a	83.57(7)		
-O3 ^a	2.143(2)	O2-Ti-O3 ^a	77.85(7)	O3-Ti-O3 ^a	87.68(8)		
Avg. Ti-O	1.99(13)						
NaO ₇ polyhedron							
Na-O2	2.306(2)	O2-Na-O1 ^b	91.29(7)	O1 ^b -Na-O4 ^c	151.10(6)	O2 ^c -Na-O3 ^f	66.82(6)
-O1 ^b	2.414(2)	O2-Na-O2 ^c	82.76(7)	O1 ^b -Na-O5 ^d	86.86(6)	O4 ^c -Na-O5 ^e	115.82(7)
-O2 ^c	2.604(2)	O2-Na-O4 ^c	94.86(7)	O1 ^b -Na-O5 ^e	145.10(6)	O4 ^c -Na-O5 ^e	63.80(6)
-O5 ^d	2.489(2)	O2-Na-O5 ^d	114.12(7)	O1 ^b -Na-O3 ^f	77.61(5)	O4 ^c -Na-O3 ^f	82.49(7)
-O5 ^e	2.401(2)	O2-Na-O5 ^e	82.67(6)	O2 ^c -Na-O4 ^c	68.41(6)	O5 ^d -Na-O3 ^f	95.05(7)
-O3 ^f	2.381(2)	O2-Na-O3 ^f	148.29(8)	O2 ^c -Na-O5 ^d	161.21(7)	O5 ^d -Na-O5 ^e	65.01(6)
Avg. Na-O	2.43(9)	O1 ^b -Na-O2 ^c	84.47(6)	O2 ^c -Na-O5 ^e	128.28(7)	O5 ^e -Na-O3 ^f	122.85(8)
SiO ₄ tetrahedron							
Si-O3	1.617(2)	O3-Si-O5	109.2(1)	O5-Si-O4 ^g	105.5(1)		
-O5	1.652(2)	O3-Si-O4 ^g	116.8(1)	O5-Si-O5 ^h	105.7(1)		
-O4 ^g	1.601(2)	O3-Si-O5 ^h	109.52(9)	O4 ^g -Si-O5 ^h	109.5(1)		
-O5 ^h	1.645(2)	Si-O5-Si ^h	137.2(1)				
Avg. Si-O	1.63(2)						

^a 1/2 - x, -1/2 + y, z;

^b x, 1 + y, z;

^c -x, y, 1/2 - z;

^d x, 1 - y, -1/2 + z;

^e 1/2 - x, 1/2 - y, -1/2 + z;

^f -1/2 + x, 1/2 + y, 1/2 - z;

^g 1/2 + x, 1/2 - y, 1 - z;

^h 1/2 - x, 1/2 + y, z.

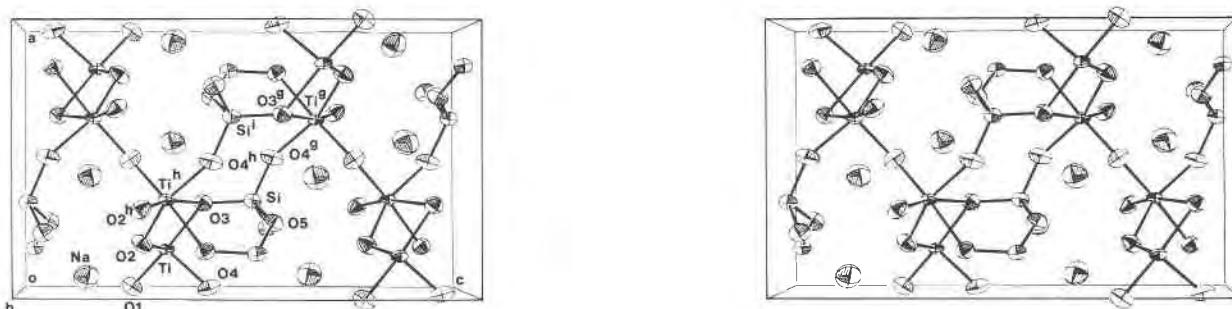


Fig. 1. Stereoscopic view of the unit-cell contents in ramsayite. The thermal ellipsoids are drawn at the 90% probability level. The superscripts of the atoms refer to the symmetry operators given in Table 6, except $1-x$; $1-y$; $1-z$.

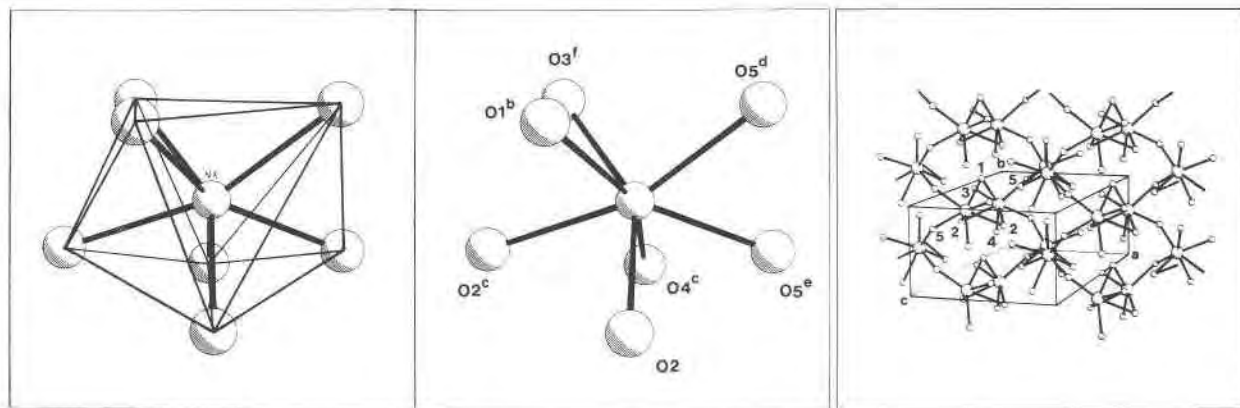


Fig. 2. On the left: a stereoscopic view of a NaO_7 polyhedron. On the right: layer structure of the NaO_7 polyhedra. The numbers refer to oxygen atoms only. The atom symbols and superscripts are omitted for clarity.

REFERENCES

- Belov, N.V., and Belyaev, L.M. (1949) Crystal structure of ramsayite $\text{Na}_2\text{Ti}_2\text{Si}_2\text{O}_{10}$. *Doklady Akademii Nauk SSSR*, 69, 805–808 (in Russian).
- Bersuker, I.B. (1966) On the origin of ferroelectricity in perovskite-type crystals. *Physics Letters*, 20, 589–590.
- Bøggild, O.B. (1953) The mineralogy of Greenland. *Meddelelser om Grønland*, 149, 442 p.
- Ch'in-Hang, Simonov, M.A., and Belov, N.V. (1969) Crystal structure of ramsayite. *Doklady Akademii Nauk SSSR*, 186, 820 (in Russian).
- Clark, J.R., Appleman, D.E., and Papike, J.J. (1969) Crystal-chemical characterization of clinopyroxenes based on eight new structure refinements. *Mineralogical Society of America Special Paper 2*, 31–50.
- Cruickshank, D.W. (1961) The role of $3d$ orbitals in π -bonds between (a) silicon, phosphorus, sulfur, or chlorine and (b) oxygen or nitrogen. *Journal of the Chemical Society*, 5486–5505.
- Flink, Gustav. (1899, 1901) On the minerals from Narsarsuk on the Firth of Tunugdliarfik in Southern Greenland. *Meddelelser om Grønland*, 24, 9–180.
- Hofmeister, Wolfgang, and Tillmanns, Ekkehart. (1984) Refinement of barium tetratitanate, BaTi_4O_9 , and hexabarium 17-titanate, $\text{Ba}_6\text{Ti}_7\text{O}_{40}$. *Acta Crystallographica*, C40, 1510–1512.
- Horn, Manfred, Schwerdtfeger, C.F., and Meagher, E.P. (1972) Refinement of the structure of anatase at several temperatures. *Zeitschrift für Kristallographie*, 136, 273–281.
- Ibers, J.A., and Hamilton, W.C., Eds. (1974) *International tables for X-ray crystallography*, vol. IV. Kynoch Press, Birmingham, England.
- Joint Committee of Powder Diffraction Standards (JCPDS) (1980) Mineral powder diffraction file. Data book. JCPDS—International Centre for Diffraction Data, Swarthmore, Pennsylvania.
- Kostyleva, E. (1937) Ramsayite. In A.E. Fersman and E.M. Bohnstedt, Eds. *Minerals of the Khibina and Lovozero tundras*, p. 132–135. Lomonosov Institute of the Academy of Sciences of USSR, Moscow.
- Kraus, O., and Musgnug, F. (1941) Identität von Lorenzenit und Ramsayit. *Naturwissenschaften*, 29, 182.
- Lehtinen, Martti. (1974) Degree of Al/Si order in potassium feldspars. A combination of X-ray and infrared data. *Contributions to Mineralogy and Petrology*, 47, 223–230.
- Meagher, E.P., and Lager, G.A. (1979) Polyhedral thermal expansion in the TiO_2 polymorphs: Refinement of the crystal structures of rutile and brookite at high temperature. *Canadian Mineralogist*, 17, 77–85.
- Morimoto, Nobuo, and Güven, Necip. (1970) Refinement of the crystal structure of pigeonite. *American Mineralogist*, 55, 1195–1209.
- Povarennykh, A.S. (1972) *Crystal chemical classification of minerals*, vol. 1. Plenum Press, New York.
- Roberts, W.L., Rapp, G.R., and Weber, Julius. (1974) *Encyclopedia of minerals*. Van Nostrand-Reinhold, New York.
- Sahama, Th.G. (1947) Analysis of ramsayite and lorenzenite. *American Mineralogist*, 32, 59–63.
- Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, A32, 751–767.
- Shurtz, R.F. (1955) Synthesis and atomic structure of lorenzenite. *American Mineralogist*, 40, 335.

- Simons, P.Y., and Dache, Frank. (1967) The structure of TiO_2 II, a high-pressure phase of TiO_2 . *Acta Crystallographica*, 23, 334–336.
- Stewart, J.M., Ed. (1976) The X-ray system, version of March 1976. Technical Report TR-446, Computer Science Center, University of Maryland.
- Vlasov, K.A., Kuz'menko, M.Z., and Es'kova, E.M. (1966) The Lovozero alkali massif. Oliver & Boyd, Edinburgh.
- Werthmann, R., and Hoppe, Rudolf. (1984) Zur Kenntniss von $\text{Na}_4\text{Ti}_5\text{O}_{12}$. *Zeitschrift für Anorganische und Allgemeine Chemie*, 519, 117–133.

MANUSCRIPT RECEIVED JANUARY 15, 1986
MANUSCRIPT ACCEPTED SEPTEMBER 2, 1986